



Solvatochromism, optical and electronic properties of thiosemicarbazone derivatives in solution phase

Yunus Emre Kara¹ · Yadigar Gülseven Sıdır² · İsa Sıdır² · Fatma Kandemirli³

Received: 25 April 2023 / Accepted: 4 January 2024 / Published online: 12 February 2024
© The Author(s) 2024

Abstract

The electronic structure, solvatochromic and some optoelectronic properties of five different thiosemicarbazone (TSCs) derivatives with different substituents consisted from indole ring, benzyl ring and conjugated thiosemicarbazide have been investigated in detail. UV–vis. absorption spectra of TSC compounds have been analyzed in solvent media with different polarity. The spectral changes are observed to forming of solvent effects and substituents. Spectral behaviors and electronic transitions are interpreted based on the UV-Vis. spectra. Solvatochromic behaviors were defined by linear solvation energy relationships via multiple linear regression analysis by using Kamlet-Abboud-Taft and Catalán parameters. In addition, the correlations of electronic absorption transition energy with Marcus optical dielectric parameter and Reichardt-Dimroth parameter were also determined. Some optoelectronic parameters such as forbidden band gap energy and refractive index have been determined in different solvent medium. Thiosemicarbazone derivatives have a global electronic absorption transition energy of about 3.351 eV. According to LSER calculations, polarizability-induction of electronic transitions of the investigated molecules is effective. The (E)-4-(4-nitrobenzyl)-1-(2-oxo-2H-indol-3(3aH)-ylidene)thiosemicarbazide (TSC-B) compound that does not a methoxy group and contain nitro group substituent and has the highest forbidden energy range.

Keywords Solvatochromism · Optoelectronic properties · Thiosemicarbazones · UV–vis absorption · Refractive index · LSER · Solution phase

✉ Yadigar Gülseven Sıdır
yadigar.gulseven@gmail.com; ygsidir@beu.edu.tr

Yunus Emre Kara
yemrekara13@gmail.com

İsa Sıdır
isa.sidir@gmail.com

Fatma Kandemirli
fkandemirli@yahoo.com

¹ Graduate Education Institute, Department of Physics, Bitlis Eren University, Bitlis, Türkiye

² Faculty of Arts & Science, Department of Physics, Bitlis Eren University, Bitlis, Türkiye

³ Faculty of Engineering and Architecture, Department of Biomedical Engineering, Kastamonu University, Kastamonu, Türkiye

1 Introduction

Thiosemicarbazones are organic compounds that can be synthesized by the condensation reaction of semicarbazidine with some suitable aldehydes or ketones (Ateş et al. 2018). This group of compounds, whose general structure is $R_1=N-NH-(=S=)-NH-R_2$, has been studied in recent years for its use in the treatment of many diseases due to its biological and pharmacological properties.

TSCs have been used in the treatment of many diseases since their use in the treatment of smallpox in 1960 (Pelosi et al. 2010). Since then, many studies have been carried out on the spectroscopic properties of thiosemicarbazones, their synthesis with metal complexes, crystal structure and biological applications (Lobana et al. 2009). Many types of TSCs have been used to design drugs because of their biological and pharmacological properties (Jiménez-Pulido et al. 2008). The reason why they are used in the treatment against various diseases is that they exhibit antibacterial, antifungal, antidiabetic, antitumor, anti-proliferative, anticancer, herbicidal, anticorrosion and anti-inflammatory activities. Therefore, many syntheses of TSCs are a valuable compound group in pharmaceutical field (Prajapati and Patel 2009).

Many studies have been carried out on the metal complexes of TSCs in researches to develop more effective drugs due to the ineffectiveness of platinum-based drugs, which are widely used in the treatment of cancer diseases, and many harmful side effects (Gatti et al. 2018). Metal complexes of TSCs have attracted attention due to their different bonding styles and structural diversity. The reason for this interest was intramolecular hydrogen bonding, steric majority at the azomethine carbon atom, more voluminous coligand and π - π stacking interactions (Netalkar et al. 2015).

Solvatochromism is a phenomenon used to help us understand the molecule in its surroundings. This phenomenon involves many different intermolecular forces and are influenced by the dynamic processes of solvents. The absorption spectrum affects both the energy of the excited state under the influence of the environment and also determines the state with the lowest energy. For this reason, solvatochromism is more prominent in the absorption spectra (Marini et al. 2010). When a molecule is excited by a photon, its dipole moment changes. The change in this solvation energy is the solvatochromic shift, which is defined as the difference in absorption energy. Shifts occur as the absorption band changes in position, shape, and optical density. It is defined as bathochromic (red) shift and hypsochromic (blue) shift with increasing solvent polarity. The bathochromic shift is named, positive solvatochromism and the hypsochromic shift, negative solvatochromism. An increase in solvent polarity change from bathochromic to hypsochromic or vice versa is called reverse solvatochromism. If the polarity of the medium increases during charge transfer transitions, then, a bathochromic shift occurs in the solvatochromic bands. If the polarity of the medium decreases during charge transfer transitions, then, a hypsochromic shifts occur in the solvatochromic bands (Reichardt 2008; Reichardt and Welton 2011; Sidir et al. 2023).

Some parameters of optoelectronic materials can be found such as capacity to absorb to incident light, interaction to electric field of the light, the forbidden energy gap of the materials, refractive index. Optoelectronics have the ability to detect light. Optoelectronics can be thought of as a subfield photonics. Refractive index as optoelectronic property depends on the forbidden energy gap which is the energy difference between HOMO and LUMO for the molecules. (Sidir et al. 2023, 2019, 2021;

Benosmane et al. 2023; Tauc and Menth 1972; Tauc 2000; Moss 1985, 1950; Ravindra et al. 1979).

In this study, the electronic structures, solvatochromic and some optoelectronic properties of five different thiosemicarbazone derivatives were investigated. The electronic absorption transitions, solvatochromic and optoelectronic parameters of the studied compounds have been reported for the first time. The absorption spectra were investigated in solvents with different polarities. While performing multiple linear regression analysis using Kamlet-Abboud-Taft and Catalán parameters in solvatochromic studies (Kamlet and Taft 1976; Abboud et al. 1981; Catalán 2009), their relationship with the maximum electronic transition energies was found using Marcus optical dielectric function (Marcus 1963, 1965) and Reichardt-Dimroth parameter (Reichardt 1994; Dimroth et al. 1963). For the optoelectronic properties, the forbidden energy gap was calculated by Tauc method (Tauc and Menth 1972; Tauc 2000), and the experimental refractive index was found using the Moss (Moss 1985, 1950), Ravindra (Ravindra et al. 1979), Hervé-Vandamme (Herve and Vandamme 1994), Kumar-Singh (Kumar and Singh 2010) and Reddy (Reddy and Anjaneyulu 1992) relations.

2 Materials and methods

2.1 Materials

The synthesis steps, purification and characterization of thiosemicarbazone compounds (see Fig. 1) were performed as given in the literature (Ganim et al. 2019; Kandemirli et al. 2012, 2015). Cyclohexane, benzene, o-xylene, diethyl ether, 1-octanol, 1-heptanol, 1-hexanol, ethanol, methanol and DMSO solvents with different properties such as non-polar, polar protic and polar aprotic were purchased from Sigma-Aldrich company with spectroscopic grade and HPLC properties.

2.2 Spectroscopic measurements

The molecular structure and IUPAC nomenclature of new TSCs are shown in Fig. 1. All the solutions were prepared at approximately 2×10^{-5} M. Using the Perkin Elmer Lambda-35 UV-Vis spectrophotometer (200–700 nm), the UV-vis absorption spectra of the TSCs were recorded in a standard quartz cuvette at room temperature and in solvent medium.

2.3 LSERs

Linear solvation energy relationships (LSERs), proposed by Kamlet et al., were developed for the correlation of physicochemical and biochemical events. On the other hand, developed the linear solvation energy relationship (LSER) with the correlation of some thermodynamic properties to measure intermolecular solute ionic liquid interactions (Padaszynski and Domanska 2011). The multiple parameter equations derived with using the solvatochromic parameters are given as follows. Kamlet-Abboud-Taft solvatochromism model is constituted by the four parameters presented in Eq. (1) (Kamlet et al. 1983; Kamlet and Taft 1976; Abboud et al. 1981).

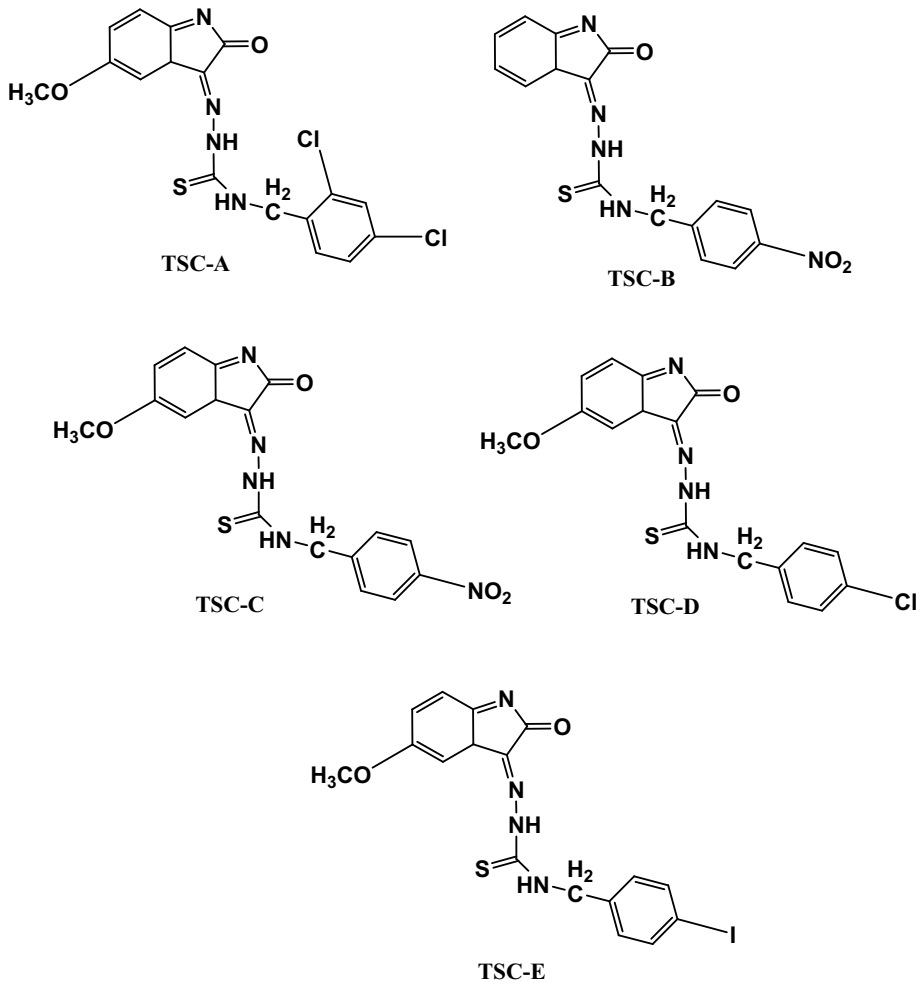


Fig. 1 The molecular structure of TSC derivatives. (E)-4-(2,4-dichlorobenzyl)-1-(5-methoxy-2-oxo-2H-indol-3(3aH)-ylidene) thiosemicarbazide (TSC-A); (E)-4-(4-nitrobenzyl)-1-(2-oxo-2H-indol-3(3aH)-ylidene)thiosemicarbazide (TSC-B); (E)-4-(4-nitrobenzyl)-1-(5-methoxy-2-oxo-2H-indol-3(3aH)-ylidene) thiosemicarbazide (TSC-C); (E)-4-(4-chlorobenzyl)-1-(5-methoxy-2-oxo-2H-indol-3(3aH)-ylidene) thiosemicarbazide (TSC-D); (E)-4-(4-iodobenzyl)-1-(5-methoxy-2-oxo-2H-indol-3(3aH)-ylidene) thiosemicarbazide (TSC-E)

$$\vartheta_{max} = C_0 + C_1 f(n) + C_2 f(\epsilon) + C_3 \beta + C_4 \alpha \quad (1)$$

In here, ϑ_{max} is the maximum absorption wavenumber changing depend on the solvent structure.

The β and α describe hydrogen bond acceptor and hydrogen bond donor capacities of solvent, respectively. Polarizability-orientation function and Polarity-induction function are defined to be $f(n) = (n^2 - 1)/(n^2 + 2)$ and $f(\epsilon) = (\epsilon - 1)/(\epsilon + 2)$, respectively (Reichardt 2008).

The equation of the Catalán model with four parameters is given in Eq. (2) (Catalán 2009).

$$\vartheta_{max} = C_5 + C_6SP + C_7SdP + C_8SA + C_9SB \quad (2)$$

In this model, multiple parameters are deployed in order to gather information about solute–solvent interactions. Where ϑ_{max} is the maximum absorption wavenumber depending on SP solvent polarizability, SdP solvent dipolarity, SA solvent acidity and SB represents solvent basicity. The all parameters used in LSER studies have been listed in Table 1S.

2.4 Optoelectronic calculations

The optical and electronic behaviors of semiconductors are understood based on two fundamental parameters. These are inferred by the energy band gap and the refractive index. The light absorbance threshold of semiconductors determines the energy band gap, and the refractive index is a measure of transparency to incident light. The relationship between these two optoelectronic parameters of semiconductors is still a subject of research due to its role in semiconductor band structures. In addition, the electronic structure properties of materials such as polarizability and dielectric constant are determined based on the refractive index and can be calculated using the energy band gap. These parameters are important descriptors for the design of optoelectronic devices (Sıdır et al. 2023; Benosmane et al. 2023).

The mass excitation coefficient ($\alpha_{mass}(\text{Lg}^{-1} \text{cm}^{-1})$) describes the light absorbed by a molecule at a specific wavelength per mass density for optoelectronic applications.

$$\alpha_{mass} = \varepsilon/MA$$

where $\varepsilon (\text{Lmol}^{-1} \text{cm}^{-1})$ is the molar excitation coefficient and MA is the molar weight. The band width or band gap of the optical transition (E_g) depends on the absorbance coefficient $\alpha_{mass} (\text{cm}^{-1})$ and the energy of the photon ($h\nu$ (eV)) (Tauc and Menth 1972; Tauc 2000).

Refractive index and energy gap, which are the main elements of optoelectronic properties, are physical properties of molecules. These two physical elements allow the band gap structures of materials to vary for continuous and optimal absorption of broadband spectral sources. Optical energy range and refractive index are interesting properties of materials. The refractive index is a key element for any material as it relates to the electronic polarizability of the ions and the local field within the materials. Researchers have done model studies for the relationships between band gaps, electronegativity and refractive indices (Sıdır et al. 2023, 2019, 2021; Benosmane et al. 2023).

Different materials have different energy band gaps and different models have been proposed accordingly when calculating the refractive index. It would be interesting to develop a model that can be applied to all models without distinguishing energy gaps. While researchers are conducting experimental and theoretical studies to find the refractive indices for many different types of materials, the technologies that have many applications are based on the refractive index and band gap. In recent years, the interest of researchers has increased in application areas such as nanotechnology and biotechnology (Tauc and Menth 1972; Tauc 2000). The optical band gap or forbidden bandwidth of the optical transition (E_g) depends on the absorption coefficient $\alpha (\text{cm}^{-1})$ and photon energy ($h\nu$ (eV)). Optical band gap (E_g) can be evaluated from the absorption spectrum using Tauc law of optical transitions,

$$(\alpha h\nu) = A * (h\nu - E_g)^n \quad (3)$$

Here, A^* is constant and n is the parameter relevant to the measuring of the type of band gap. When it is examined by taking 1/2 and 2 in this equation, it gives us information about the direct and indirect transitions from the optical band gap, respectively.

The relationship between refractive index n and E_g (energy band gap) is determined using Moss (Moss 1985, 1950), Ravindra (Ravindra et al. 1979), Hervé-Vandamme (Herve and Vandamme 1994), Kumar–Singh (Kumar and Singh 2010) and Reddy (Reddy and Anjaneyulu 1992) relations.

In this study, we tried to calculate the refractive index of new TSCs with five different methods. These methods are listed below.

$$\begin{aligned} n^4 &= (95 \text{ eV} / E_g) \text{ for Moss approximation,} \\ n &= (4.084 - 0.62 E_g) \text{ for Ravindra,} \\ n^2 &= 1 + (A / (E_g + B))^2 \text{ for Hervé-Vandamme} \end{aligned}$$

where $A = 13.6 \text{ eV}$ and $B = 3.47 \text{ eV}$,

$$\begin{aligned} n &= (3.3668 / (E_g))^{0.32234} \text{ for Kumar-Singh,} \\ n &= (154 / (E_g - 0.365))^{(1/4)} \text{ for Reddy.} \end{aligned}$$

3 Result and discussion

3.1 Absorption spectra and electronic transitions

Electronic absorbance spectra of the investigated five thiosemicarbazone derivatives in Fig. 2 can be seen in different solvents. UV–vis. spectra data are listed in Table 1. As seen from Fig. 2, main band was observed with slightly shifts due to solvent. Two main bands were observed in all the investigated compounds. In the first band, maxima of three peaks were observed in the 257–285 nm range. This transition corresponds to the electronic transitions in the indole ring.

The maximum absorbance band is observed in the range of 364 nm (3.406 eV)–377 nm (3.289 eV). This maximum absorbance band can be attributed to π - π^* electronic transition due to thiosemicarbazone resonance. As the solvent polarity of this wavelength increases, it is seen that the wavelength shifts towards smaller values, albeit slightly. Thus, the hypsochromic effect was realized at the maximum wavelength.

We can see from Table 1 and Fig. 2 that TSCs have broad main absorbance band. This band indicates the π - π^* electronic absorption transition in thiosemicarbazone for all the molecules studied. This transition also comes from conjugation on the entire molecule.

As can be seen from Table 1, this global electronic transition causes the hypsochromic effect for TSC-A when the polarity increases, and the wavelength as the wavelength shifts from 376 nm (3.29 eV) to 369 nm (3.36 eV). Absorption maxima of TSC-B shifts from 371 nm (3.34 eV) toward 369 nm (3.36 eV) indicating hypsochromic effect with the increase of solvent polarity.

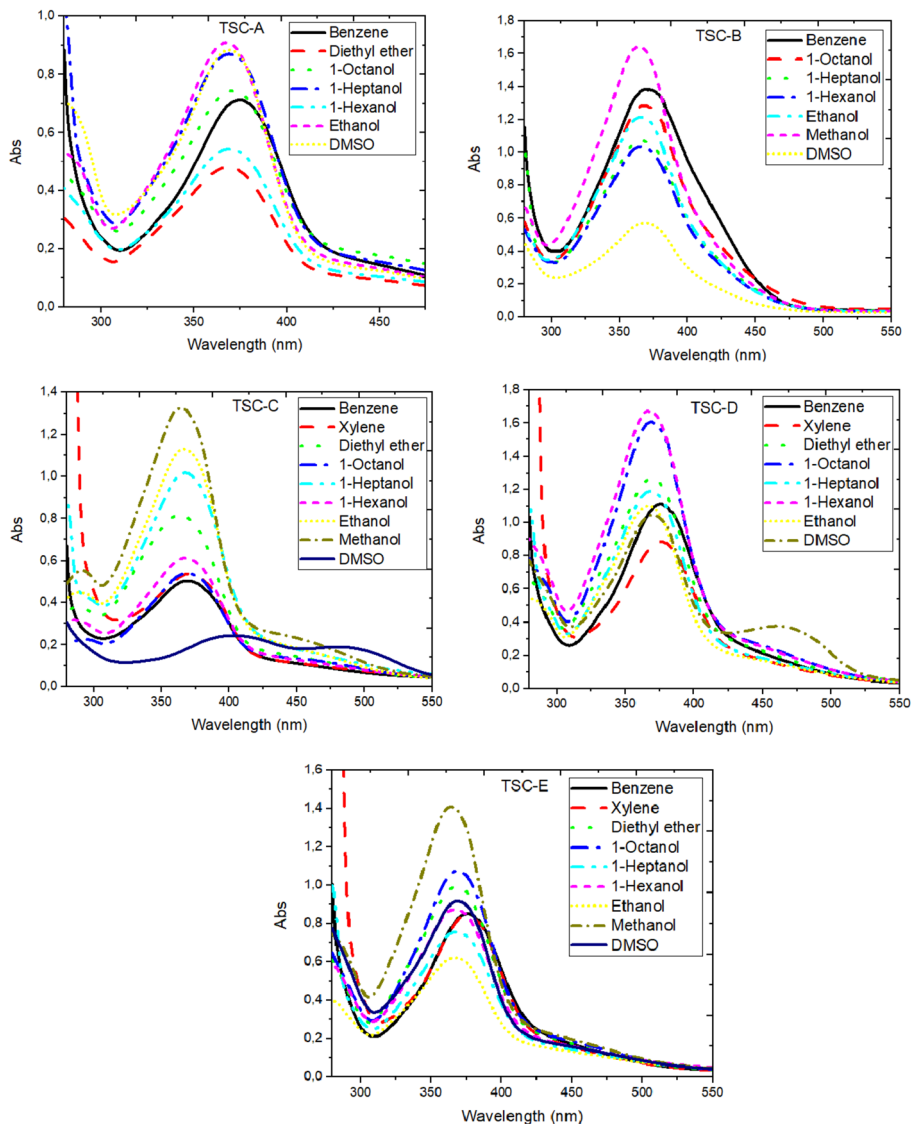


Fig. 2 The absorbance spectra in different solvent medium of TSCs

As the solvent polarity increases for the TSC-C compound, it is observed that the wavelength shifts from 371 nm (3.34 eV) to 403 nm (3.07 eV) showing bathochromic effect occurred with the increase of solvent polarity.

In the TSC-D compound, a shift occurred from 376 to 371 nm wavelength band, and in the TSC-E compound, from 377 nm (3.28 eV) to 370 nm (3.35 eV) with the observed hypsochromic effect. The hypsochromic effect is that the energy difference between the molecular orbitals of the electronic absorbent chromophore of the molecule increases as the polarity of the solvent increases. The ability to form intermolecular hydrogen

Table 1 The UV–Visible spectral data in different solvent medium of the investigated TSC derivatives

Solvent	TSC-A		TSC-B		TSC-C		TSC-D		TSC-E	
	λ_{ABS1}	λ_{ABS2}	λ_{ABS1}	λ_{ABS2}	λ_{ABS1}	λ_{ABS2}	λ_{ABS1}	λ_{ABS2}	λ_{ABS1}	λ_{ABS2}
Benzene	–	376	–	371	–	371	–	376	–	377
o-Xylene	–	–	–	–	–	370	–	375	–	376
Diethyl Ether	260,268	369	249,259,270	365	256,266,290	365	257,267,286	369	259,269	369
1-Octanol	260,269,287	371	251,260,272	369	261,294	370	259,267,284	369	259,269	369
1-Heptanol	270,280	370	260,272	367	272,279	368	268	369	272	368
1-Hexanol	258,268,283	370	250,260,273	366	252,289	367	259,267,281	368	261,268	367
Ethanol	260,267,282	368	249,259,271	367	256,264,286,296	367	257,266,285	367	260,268	367
Methanol	257,265,282	366	249,257,272	365	255,264,287,295	365	256,265,282	366	258,266,286	365
DMSO	285	369, 465	–	369	–	403,480 (sh)	285	370, 460	–	370,439

bonding (H-bond) interactions with both hydrogen donor and hydrogen acceptor sites has been reported. The literature on semicarbazones (e.g., ethane-1-one semicarbazone for (E)-1-(4-fluorophenyl) (Fun et al. 2009)) and thiosemicarbazone (e.g., 2-acetylpyridine thiosemicarbazones (Ibrahim et al. 2018; Singh and Singh 2015)) compounds are structurally similar to those studied in this study.

Shoulder absorbance bands around 465, 480, 460 and 439 nm was observed for TSC-A, TSC-C, TSC-D and TSC-E compounds, only in the polar aprotic solvent DMSO. This could mean an H-bond interaction that can occur as a result of solvent–solute interaction.

A shift of 7 nm for TSC-A, 3 nm for TSC-B, 32 nm for TSC-C, 6 nm for TSC-D, and 7 nm for TSC-E correspond to the global electronic transition has been observed in benzene and the DMSO solvents. The compound with the highest spectral shift is observed for TSC-C, with the methoxy group attached to the quinolone ring, and the nitro group on the benzene ring. The methoxy group has more electron donor character more than the nitro group, and it can be said that because one end of the TSC-C compound is the donor and the other end is the acceptor, as the polarity of the solvent increases, the conjugation has a direct effect on the TSC group.

3.2 Linear solvation energy relationships

Solvatochromism is one of the most valid methods to numerically determine both specific and non-specific interactions of solvent–solute interactions (Sıdır and Gülseven Sıdır 2011, 2015; Gülseven Sıdır and Sıdır 2013; Gülseven Sıdır et al. 2011). Here, using the Kamlet-Abboud-Taft and Catalán solvent parameters, which include four parameters, using the linear solvation energy relationship statistical method, the values as a result of statistical calculation are given in Table 2. As can be seen from Table 2, linear solvation energy relationships were investigated in eight solvents for TSC-A, TSC-B and TSC-C and 9 solvents for TSC-D and TSC-E. In the LSER models found, $R > 0.99$, $R^2 > 0.98$. The large the F value and the P value close to zero indicates that this statistical model is the more accurate.

Table 2 The statistical parameters and results of Kamlet-Abboud-Taft and Catalán solvatochromism of investigated TSC derivatives

Kamlet-Abboud-Taft	N	C ₀	C ₁	C ₂	C ₃	C ₄	R	R ²	F	P
TSC-A	8	27,665	−3880	571	−27	−103	0.99	0.98	41.82	0.006
TSC-B	8	28,377	−4279	−282	241	−64	0.92	0.86	4.75	0.116
TSC-C	8	29,085	−6001	−792	114	146	0.94	0.89	6.49	0.078
TSC-D	9	27,698	−3759	225	224	23	0.99	0.99	238.90	0.000
TSC-E	9	27,748	−4169	192	344	51	0.99	0.98	76.12	0.000
Catalán	N	C ₅	C ₆	C ₇	C ₈	C ₉	R	R ²	F	P
TSC-A	8	27,832	−1801	635	−232	211	0.99	0.97	35.82	0.07
TSC-B	8	28,380	−1886	201	−239	149	0.90	0.82	3.54	0.164
TSC-C	8	29,003	−2496	−101	21	−63	0.93	0.86	4.96	0.109
TSC-D	9	27,733	−1581	382	17	341	0.99	0.99	147.38	0.000
TSC-E	9	27,726	−1685	405	103	438	0.99	0.98	64.19	0.001

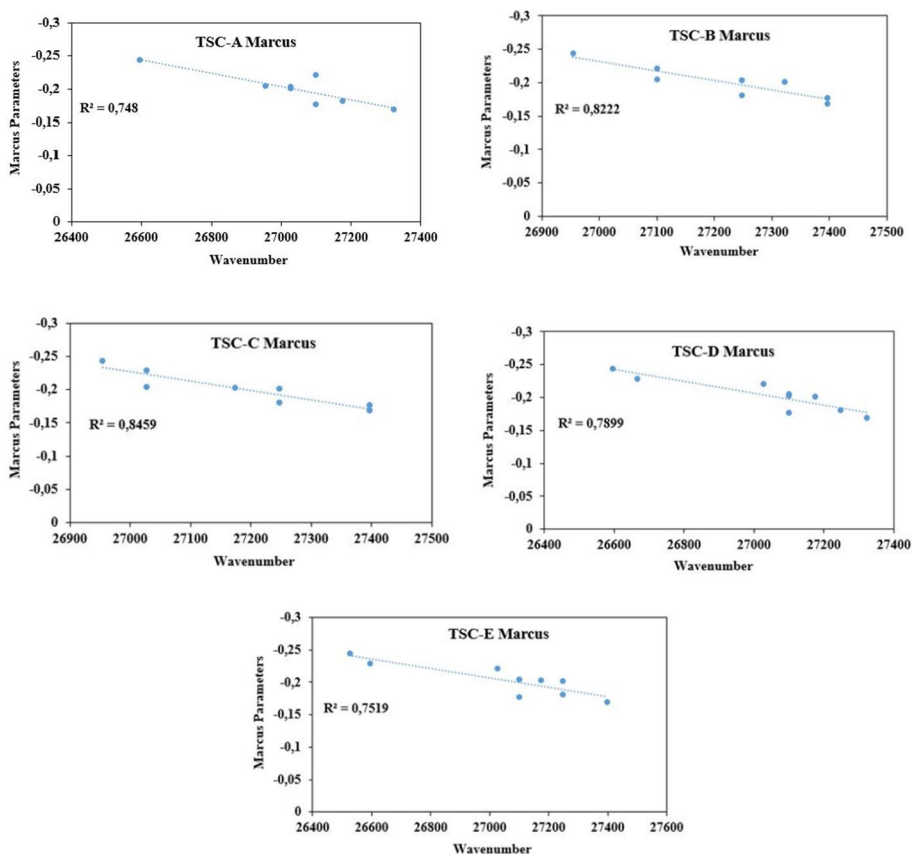


Fig. 3 The correlation graphs between electronic transition wavenumbers with Marcus parameters of investigated thiosemicarbazide derivatives

The C coefficients give the contributions of the individual solvent parameters to the total spectral shift. The C_0 and C_5 coefficients correspond to the electronic transitions of the investigated compounds in the gas phase or isolated medium, respectively. The C_1 value shows the contribution of the dispersion-polarization interaction, while the C_2 value gives the contribution of the orientation-induction interaction.

The C_0 is the gas phase wave number found from Kamlet-Abboud-Taft solvatochromism; 27,665 cm^{-1} (361 eV) for TSC-A, 28,377 cm^{-1} (352 eV) for TSC-B, 29,085 cm^{-1} (344 eV) for TSC-C, 27,698 (361 eV) for TSC-D and 27,748 cm^{-1} (360 eV) for TSC-E, respectively. As can be seen from Table 2, the value of C_1 coefficient is greater than C_2 coefficient. It can be said that the contribution of orientation dispersion-polarization interaction is high. The C_2 coefficient has negative values only for TSC-B and TSC-C. The C_3 value indicates the interaction of the hydrogen bond acceptor parameter, while the C_4 describes the effect of the hydrogen bond donor parameter. Except for TSC-A and TSC-C compounds, the C_3 coefficient is quite large compared to C_4 coefficient. Thus, we can say that those of the hydrogen bond acceptor ability of solvents is more effective than those of hydrogen bond donor ability of solvents.

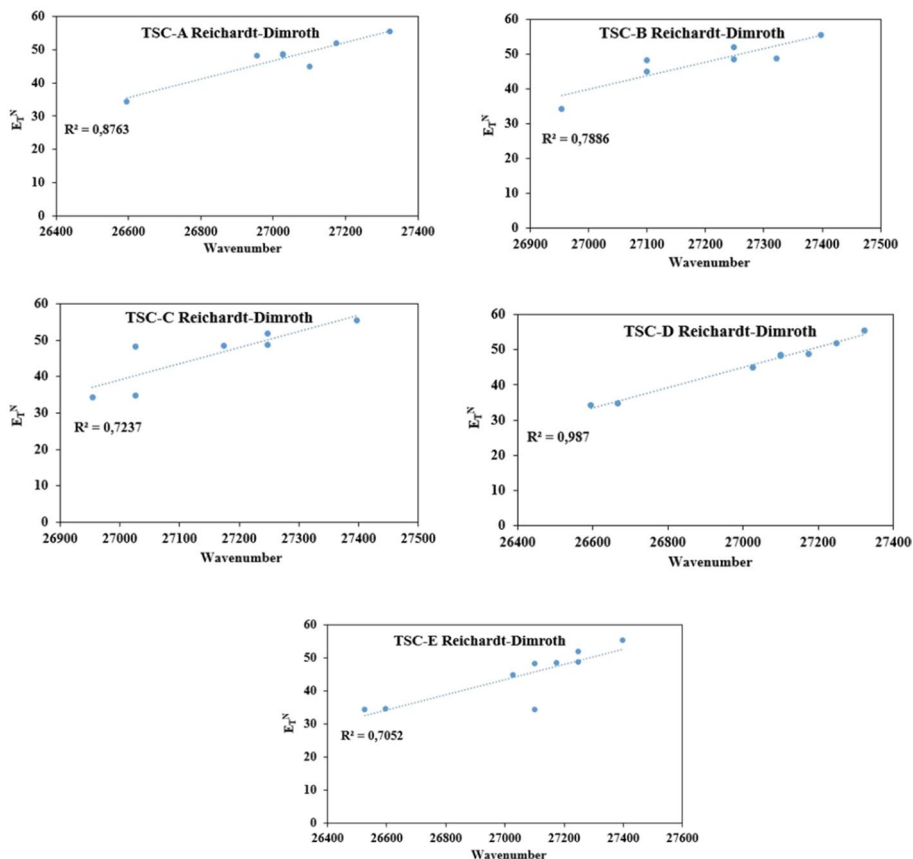


Fig. 4 The correlation graphs between electronic transition wavenumbers with Reichardt parameters of investigated thiosemicarbazide derivatives

The results of the LSER calculations applicative according to the Catalán parameters are listed in Table 2. The C_5 is the gas phase wave number found in Catalán solvatochromism. C_5 values according to Catalán solvatochromism are $27,832 \text{ cm}^{-1}$ (359 eV) for TSC-A, $28,380 \text{ cm}^{-1}$ (352 eV) for TSC-B, $29,003 \text{ cm}^{-1}$ (344 eV) for TSC-C, $27,733 \text{ cm}^{-1}$ (360.58 eV) for TSC-D and $27,726 \text{ cm}^{-1}$ (360.67 eV) for TSC-E, respectively. While the C_6 coefficient describes the effect of the solvent of polarizability parameter on the global electronic transitions, the C_7 coefficient gives information about the polarity coefficients of the solvents. As can be seen from Table 2, the value of the C_6 coefficient is greater than that of C_7 . Thus, the effect of solvent polarizability on electronic absorbance transitions occurring in the studied TSC molecules is greater than that of solvent polarity. While the value of the C_8 coefficient estimated for TSC-A and TSC-B is higher than the C_9 coefficient, the C_9 coefficient in TSC-C, TSC-D and TSC-E is considerably higher than C_8 . Thus, it was observed that TSC-A and TSC-B were more affected by solvent acidity than solvent basicity, while TSC-C, TSC-D and TSC-E compounds were more effective solvent basicity than solvent acidity. However, as can be seen from the LSER equations, solvents have a complex effect on electronic absorbance transitions. According to the correlation graph of wavenumbers obtained from the result of Kamlet-Abboud-Taft and Catalán solvatochromism in Fig. 1S–2S, there are quite consistent

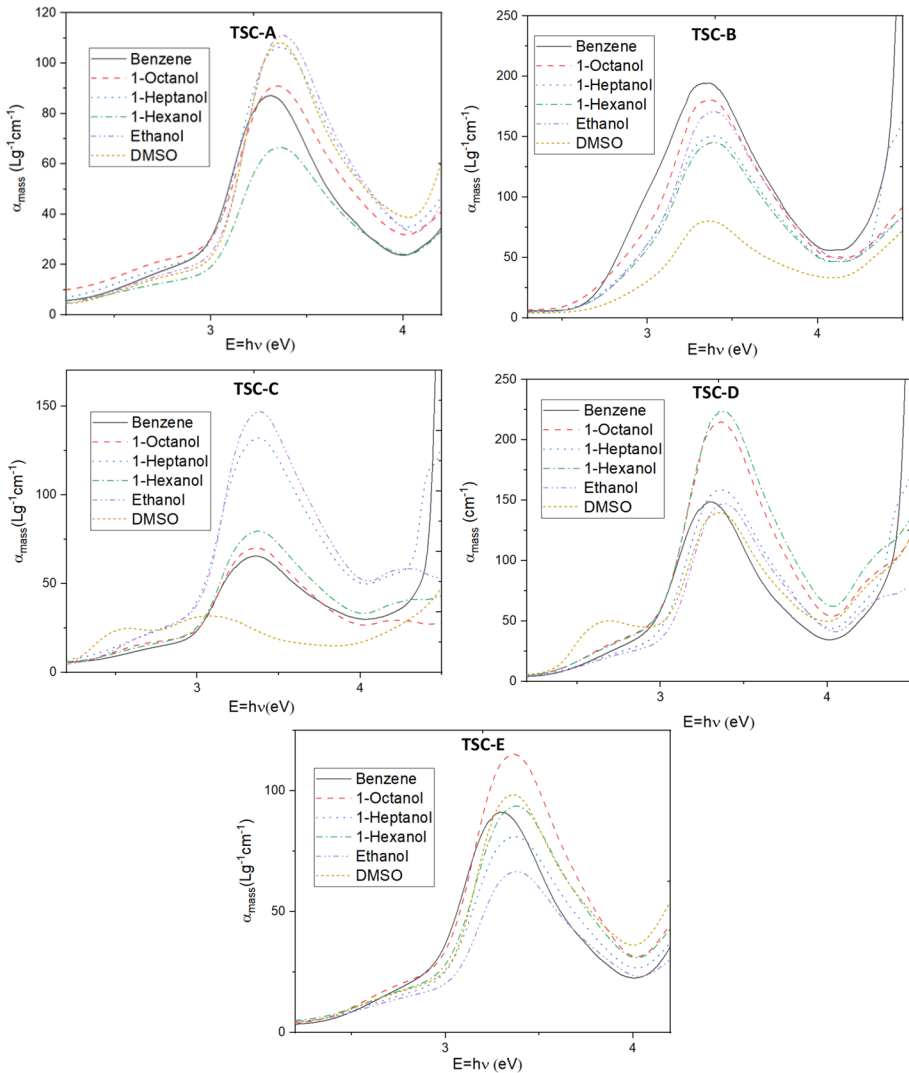


Fig. 5 The graph of $E = h\nu$ versus α_{mass} of TSCs

results between the experimental wavenumbers and the wavenumbers obtained from the LSER result.

Charge transfer is one of the most important chemical processes that play an important role in biological, physical and chemical systems. The correlation plots between the Marcus optical dielectric function and electronic absorbance wavenumbers are given in Fig. 3 and the correlation values are obtained as $R^2 = 0.748$ for TSC-A, 0.8222 for TSC-B, 0.8459 for TSC-C, 0.7899 for TSC-D and 0.7519 for TSC-E. Thus, we can say that the charge transfer between the ground and excited state is opposite to each other, in that, the excited state dipole moment direction and the ground state dipole moment direction are opposite of each other.

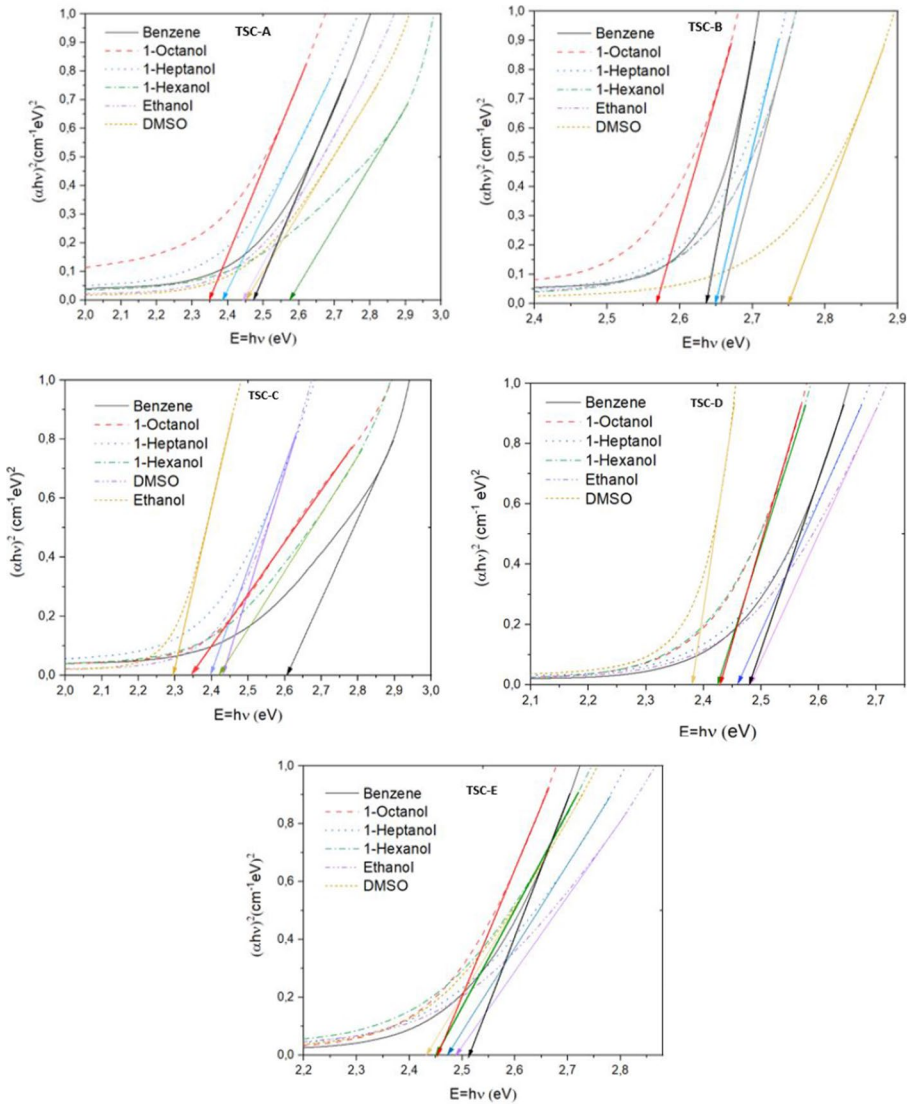


Fig. 6 The correlation graphs drawn for found E_g values of TSCs (x-axis absorbed photon energy ($E = h\nu$ (eV)) and y-axis $(\alpha h\nu)^2$ ($\text{cm}^{-1} \text{eV}^2$))

The correlation graphs between Reichardt-Dimroth solvent parameter (E_T^N) and wavenumbers can be seen in Fig. 4. As seen from Fig. 4, $R^2 = 0.8763$ for TSC-A, $R^2 = 0.7886$ for TSC-B, $R^2 = 0.987$ for TSC-C, $R^2 = 0.987$ for TSC-D and $R^2 = 0.7052$ for TSC-E. As seen in Fig. 4, the wavelength decreases with change of as the E_T^N parameter increases, so it can be said that the solvent effects give rise to a hypsochromic effect the Reichardt-Dimroth solvent parameter.

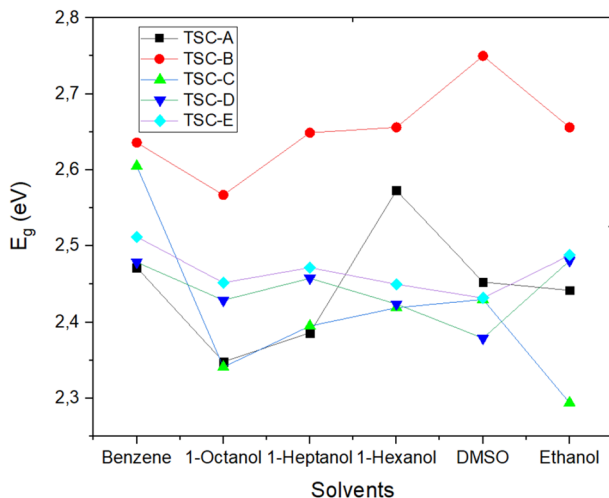
Table 3 Some optoelectronic properties, forbidden energy band gap and refractive index according to Moss, Ravindra, Herve-Vandamme, Kumar, Singh, and Reddy relationships for the investigated new TSC compounds

Solvents	TSC-A E_g	Moss	Ravindra	Hervè-Vandamme	Kumar-Singh	Reddy
Benzen	2.472	2.489	2.551	2.497	2.514	2.923
1-Octanol	2.348	2.522	2.628	2.542	2.556	2.968
1-Heptanol	2.386	2.511	2.604	2.528	2.543	2.954
1-Hexanol	2.573	2.465	2.488	2.462	2.482	2.889
DMSO	2.453	2.494	2.563	2.504	2.521	2.930
Ethanol	2.442	2.496	2.567	2.506	2.523	2.933
Solvents	TSC-B E_g	Moss	Ravindra	Hervè-Vandamme	Kumar-Singh	Reddy
Benzen	2.636	2.450	2.449	2.441	2.463	2.869
1-Octanol	2.567	2.466	2.492	2.464	2.484	2.891
1-Heptanol	2.649	2.447	2.441	2.437	2.459	2.865
1-Hexanol	2.656	2.445	2.437	2.434	2.457	2.863
DMSO	2.750	2.424	2.379	2.404	2.429	2.834
Ethanol	2.656	2.445	2.437	2.434	2.457	2.863
Solvents	TSC-C E_g	Moss	Ravindra	Hervè-Vandamme	Kumar-Singh	Reddy
Benzen	2.605	2.457	2.468	2.451	2.472	2.879
1-Octanol	2.341	2.523	2.630	2.543	2.558	2.970
1-Heptanol	2.395	2.508	2.597	2.524	2.539	2.950
1-Hexanol	2.419	2.502	2.582	2.515	2.531	2.941
DMSO	2.430	2.500	2.576	2.512	2.528	2.938
Ethanol	2.294	2.537	2.662	2.563	2.576	2.989
Solvents	TSC-D E_g	Moss	Ravindra	Hervè-Vandamme	Kumar-Singh	Reddy
Benzen	2.479	2.487	2.546	2.494	2.512	2.921
1-Octanol	2.429	2.501	2.578	2.513	2.529	2.939
1-Heptanol	2.458	2.493	2.559	2.502	2.519	2.928
1-Hexanol	2.424	2.502	2.581	2.514	2.530	2.940
DMSO	2.379	2.513	2.608	2.530	2.545	2.956
Ethanol	2.481	2.487	2.545	2.494	2.511	2.920
Solvents	TSC-E E_g	Moss	Ravindra	Hervè-Vandamme	Kumar-Singh	Reddy
Benzen	2.512	2.479	2.525	2.483	2.501	2.909
1-Octanol	2.452	2.494	2.563	2.504	2.521	2.930
1-Heptanol	2.472	2.489	2.551	2.497	2.514	2.923
1-Hexanol	2.450	2.495	2.565	2.505	2.522	2.931
DMSO	2.432	2.500	2.576	2.511	2.528	2.937
Ethanol	2.488	2.485	2.541	2.492	2.509	2.918

3.3 Optoelectronic properties

Let optoelectronics be both materials, which specifically describes the quantum mechanical effect on semiconductor and composite structures. The quantum mechanical effect can be

Fig. 7 The graph of E_g (eV) values changed as dependent to solvent of TSCs compounds



defined as finding, detecting and controlling light. In many systems, optoelectronic features, especially imaging technology, form the basis of the production of electronic circuit elements in devices such as integrated computers. Optoelectronic devices are devices such as LED, photodetectors (photodiode and phototransistors). Optoelectronics are devices that can convert optical signals into electrical signals and electrical signals into optical signals. They are used in a wide variety of application areas of optoelectronics, optical fiber communication, laser technology and all types of light measurements. Absorbance, mass extinction coefficient, mass absorption coefficient, forbidden energy gap, refractive index, transmittance and reflectance can be counted as optoelectronic properties. Here, several different optoelectronic properties of 2-oxo-2H-indole-3(3OH)-ylidene thiosemicarbazide compounds with five main structures but substituent added were investigated.

The correlation graphs of α_{mass} versus photon energies of TSCs compounds have been given in Fig. 5. Despite the solutions prepared in the same molarities according to Fig. 5, molar extinction coefficients have been found as $111.03 \text{ Lg}^{-1} \text{ cm}^{-1}$ in ethanol for TSC-A, $194.45 \text{ Lg}^{-1} \text{ cm}^{-1}$ in benzene for TSC-B, $146.77 \text{ Lg}^{-1} \text{ cm}^{-1}$ in ethanol solvent for TSC-C, $223.45 \text{ Lg}^{-1} \text{ cm}^{-1}$ in 1-hexanol for TSC-D and $115.11 \text{ Lg}^{-1} \text{ cm}^{-1}$ in 1-hexanol for TSC-E, respectively. The highest molar extinction coefficient is obtained for TSC-D compound.

The graphs of absorbance coefficient (α (cm^{-1})) and photon energy ($h\nu$ (eV)) are shown in Fig. 3S. The forbidden energy gaps have been found by using the correlation graph plotted against the energy of the photon absorbed with $(\alpha h\nu)^2$ with using Eq. 3 of studied TSCs compounds. As seen in Fig. 6, For each TSC compound have drawn benzene as the non-polar solvent, 1-octanol, 1-heptanol, 1-hexanol and ethanol as polar protic solvents and DMSO as polar aprotic solvent. The experimental refractive index values of TSC compounds have been calculated using the Moss, Ravindra, Hervè-Vandamme, Kumar-Singh and Reddy relations in like benzene, 1-octanol, 1-heptanol, 1-hexanol, DMSO and Ethanol solvents. Determined refractive index values have been tabulated in Table 3.

From the data given in Table 3, it can be said that the forbidden energy range of the compounds changes depending on the solvent. According to the analyzed solutions, the highest E_g value was estimated in benzene solvent. As seen that the band gap of the studied TSC compounds of non-polar solvents is larger than the other solvents. We can say that

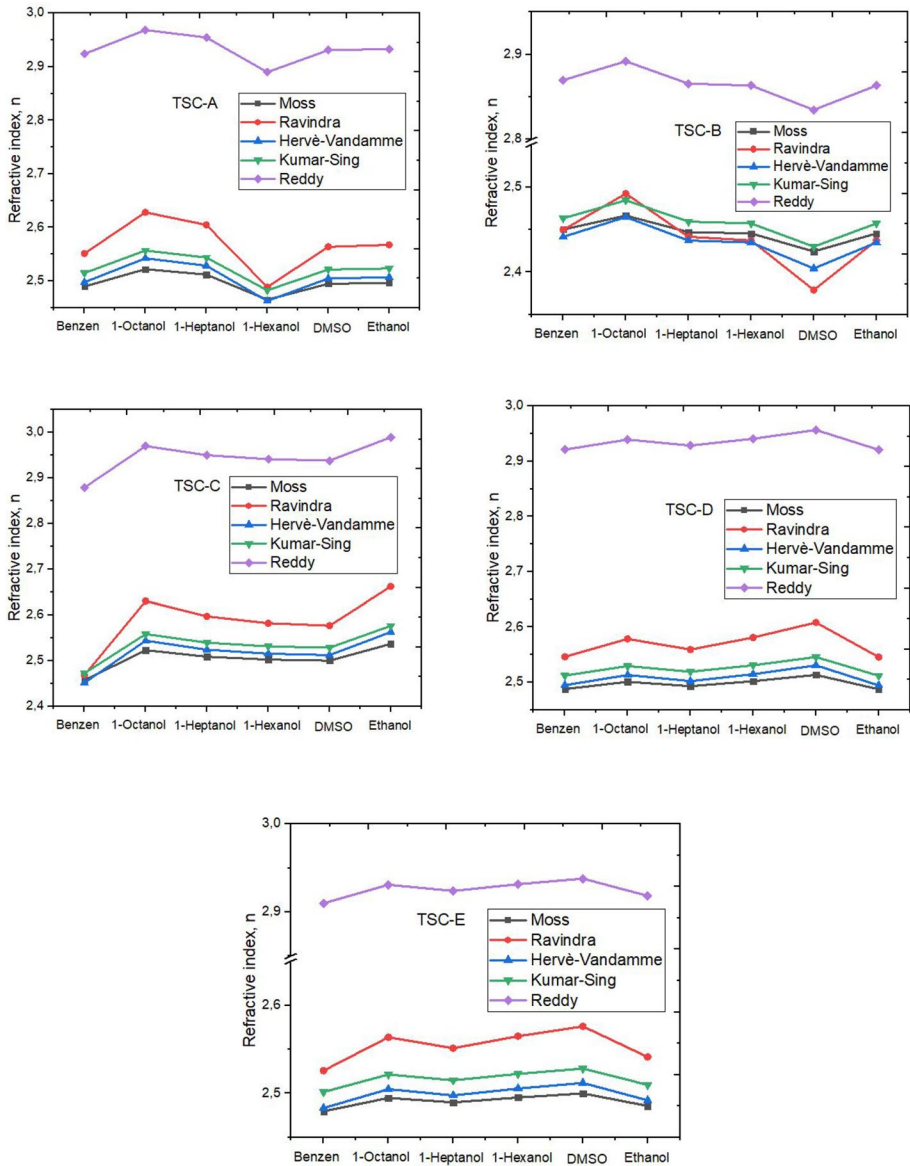


Fig. 8 The shape of relationship between refractive index of TSCs

polar solvents reduce the forbidden energy gap values. The graph of the E_g (eV) values of the studied TSCs compounds depending on the solvent can be seen in Fig. 7. From this graph, we can say that TSC-B compound with NO_2 group and indole on the other side has the highest band gap energy, while TSC-C has the lowest forbidden band gap in ethanol solvent. The TSC-C compound has NO_2 and the methoxy group. The forbidden band gap

energy of this compound showed a great variation depending on the solvent, for example, it is 2.6 eV in benzene, while it is around 2.29 eV in ethanol.

The experimental index of refraction can be calculated using the quantum theory of scattered light near the fundamental absorbance limit of semiconductor compounds. The refractive index has been calculated in benzene, 1-octanol, 1-heptanol, 1-hexanol, DMSO and ethanol solvent. From Table 3, we can say that while the refractive index varies between 2.4 and 2.6, the refractive index calculated only by the Reddy relationship have found to be between 2.8 and 2.9. The graphs of the new TSCs for which we calculated the refractive index with five different methods are shown in Fig. 8. It can be seen that the refractive index values calculated with the Reddy approach were larger than the other approaches. Generally, the lowest refractive index values for all molecules except TSC-B were obtained by Moss approximation.

4 Conclusions

The electronic, solvatochromism and some optoelectronic properties of five TSC compounds were investigated from electronic absorption spectra obtained from different solvents. The global electronic absorbance transitions of the examined TSC derivatives originate from the conjugation in the thiosemicarbazide group and occur in the range of 365–376 nm depending on the substituent. Linear solvation free energy (LSER) relationships of the studied TSC compounds were investigated using Kamlet-Abboud-Taft parameters, Catalán parameters, Reichardt-Dimroth solvent parameter and Marcus optodielectric coefficients. The derived LSER models explained the absorbance transition mechanism and solvent effects with very high statistical correlation. Some electronic properties like forbidden band gap values and refractive indices were found by five different methods. According to the forbidden energy range, TSC compounds can be considered to be a candidate of semiconductor organic compounds. Although the refractive index showed little change according to the methods examined, the refractive index changed in the range of 2.5 and 2.9.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11082-024-06301-1>.

Authors' contributions YGS: experimental study, analysis, methodology, and writing; YEK: Investigation, IS: Spectroscopic analysis; FK: Synthesis and characterization.

Funding Open access funding provided by the Scientific and Technological Research Council of Türkiye (TÜBİTAK). YGS thanks to Bitlis Eren University for the support given to the BEBAP 2013.04 and BEBAP 2014.05 projects.

Availability of data and materials All data and materials are available from the corresponding author.

Declarations

Ethical approval Not applicable.

Competing interests The authors declare that they have no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence,

and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Abboud, J.L.M., Kamlet, M.J., Taft, R.W.: An examination of linear solvation energy relationships. *Prog. Phys. Org. Chem.* **13**, 485–630 (1981)
- Ateş, D., Gulcan, M., Gümüş, S., Şekerci, M., Özdemir, S., Şahin, E., Çolak, N.: Synthesis of bis (thiosemicarbazone) derivatives: Definition, crystal structure, biological potential and computational analysis. *Phosphorus Sulfur Silicon Relat. Elem.* **193**, 14–22 (2018)
- Benosmane, A., Gündüz, B., Benaouida, M.A., Boukentoucha, C., Merziç, H.: Experimental structural and optoelectronic properties and theoretical investigation of novel square planar nickel (II) complex with (o-tolyldiazenyl) naphthalen-2-ol ligand. *J. Mol. Struct.* **1273**, 134254 (2023)
- 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)
- Dimroth, K., Reichardt, C., Siepmann, T., Bohlmann, F.: Über Pyridinium-N-phenol-betaïne und ihre Verwendung zur Charakterisierung der Polarität von Lösungsmitteln. *Justus Liebigs Ann. Chem.* **661**, 1–37 (1963)
- Fun, H.-K., Yeap, C.S., Padaki, M., Malladi, S., Isloor, A.M.: (E)-1-(4-Fluorophenyl)ethan-1-one semicarbazone. *Acta Crystallogr. Sect. E Crystallogr. Commun.* **65**, 1619–1620 (2009)
- Ganim, M.A., Baloglu, M.C., Aygun, A., Celik Altunoglu, Y., Sezgin Sayiner, H., Kandemirli, F., Sen, F.: Analysis of DNA protection, interaction and antimicrobial activity of isatin derivatives. *Int. J. Biol. Macromol.* **122**, 1271–1278 (2019)
- Gatti, A., Habtemariam, A., Romero-Canelón, I., Song, J.I., Heer, B., Clarkson, G.J., Rogolino, D., Sadler, P.J., Carcelli, M.: Half-sandwich arene ruthenium (II) and osmium (II) thiosemicarbazone complexes: solution behavior and antiproliferative activity. *Organometallics* **37**(6), 891–899 (2018)
- Gülseven Sıdır, Y., Sıdır, İ. Solvent effect on the absorption and fluorescence spectra of 7-acetoxy-6-(2,3-dibromopropyl)-4,8-dimethylcoumarin: determination of ground and excited state dipole moments. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **102**, 286–296 (2013)
- Gülseven Sıdır, Y., Sıdır, İ., Taşal, E., Ermiş, E.: Studies on the electronic absorption spectra of some monoazo derivatives. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **78**, 640–647 (2011)
- Herve, P., Vandamme, L.K.J.: General relation between refractive index and energy gap in semiconductors. *Infrared Phys. Technol.* **35**(4), 609–615 (1994)
- Ibrahim, A.B.M., Farh, M.K., Plaisier, J.R., Shalaby, E.M.: Synthesis, structural and antimicrobial studies of binary and ternary complexes of a new tridentate thiosemicarbazone. *Future Med. Chem.* **10**(21), 2507–2519 (2018)
- Jiménez-Pulido, S.B., Linares-Ordóñez, F.M., Moreno-Carretero, M.N., Quirós-Olozábal, M.: Versatile coordinative abilities of a new hybrid pteridine– thiosemicarbazone ligand: crystal structure, spectroscopic characterization, and luminescent properties. *Inorg. Chem.* **47**(3), 1096–1106 (2008)
- 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**(377), 2886 (1976)
- 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.* **48**, 2877–2887 (1983)
- Kandemirli, F., Saracoğlu, M., Bulut, G., Ebenso, E., Arslan, T., Kayan, A.: Synthesis and Theoretical study of Zinc(II) and Nickel(II)- complexes of 5-methoxyisatin 3-[N-(4-chlorophenyl)thiosemicarbazone]. *J. Math. Fundam. Sci.* **44**(1), 35–50 (2012)
- Kandemirli, F., Rasheed, S., Sayiner, H., Akkaya, Y., Vurdu, C.D.: Synthesis, biological activity and theoretical study of some isatin, and their metal complexes. *J. Chem. Pharm. Res.* **7**(3), 44–55 (2015)
- Kumar, V., Singh, J.K.: Model for calculating the refractive index of different materials. *Indian J. Pure Appl. Phys.* **48**(8), 571–574 (2010)
- Lobana, T.S., Sharma, R., Bawa, G., Khanna, S.: Bonding and structure trends of thiosemicarbazone derivatives of metals—an overview. *Coord. Chem. Rev.* **253**(7–8), 977–1055 (2009)

- Marcus, R.A.: Free energy of nonequilibrium polarization systems. III. Statistical mechanics of homogeneous and electrode systems. *J. Chem. Phys.* **39**, 1734 (1963)
- 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)
- Marini, A., Munoz-Losa, A., Biancardi, A., Mennucci, B.: What is solvatochromism? *J. Phys. Chem. B* **114**(51), 17128–17135 (2010)
- Moss, T.S.: A relationship between the refractive index and the infra-red threshold of sensitivity for photoconductors. *Proc. Phys. Soc. London, Sect. B* **63**(3), 167–176 (1950)
- Moss, T.S.: Relations between the refractive index and energy gap of semiconductors. *Phys. Status Solidi B* **131**, 415 (1985)
- Netalkar, P.P., Netalkar, S.P., Revankar, V.K.: Transition metal complexes of thiosemicarbazone: synthesis, structures and in vitro antimicrobial studies. *Polyhedron* **100**, 215–222 (2015)
- Paduszynski, K., Domanska, U.: Limiting activity coefficients and gas–liquid partition coefficients of various solutes in piperidinium ionic liquids: measurements and LSER calculations. *J. Phys. Chem. B* **115**(25), 8207–8215 (2011)
- Pelosi, G., Bisceglie, F., Bignami, F., Ronzi, P., Schiavone, P., Re, M.C., Casoli, C., Pilotti, E.: Antiretroviral activity of thiosemicarbazone metal complexes. *J. Med. Chem.* **53**, 8765–8769 (2010)
- Prajapati, N.P., Patel, H.D.: Novel thiosemicarbazone derivatives and their metal complexes: recent development. *Synth. Commun.* **49**(21), 2767–2804 (2009)
- Ravindra, N.M., Auluck, S., Srivastava, V.K.: On the Penn Gap in semiconductors. *Phys. Status Solidi B* **93**(2), K155–K160 (1979)
- Reddy, R., Anjaneyulu, S.: Analysis of the Moss and Ravindra relations. *Phys. Status Solidi B* **174**, K91 (1992)
- Reichardt, C.: Solvatochromic dyes as solvent polarity indicators. *Chem. Rev. Chem. Rev.* **94**, 2319–2358 (1994)
- Reichardt, C.: Solvents and Solvent Effects in Organic Chemistry. VCH, New York (2008)
- Reichardt, C., Welton, T.: Solvents and Solvent Effects in Organic Chemistry. Wiley, Weinheim (2011)
- Sidir, İ., Gülseven Sidir, Y.: Ground state and excited state dipole moments of 6,8-diphenylimidazo[1,2- α]pyrazine determined from solvatochromic shifts of absorption and fluorescence spectra. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **79**, 1220–1225 (2011)
- Sidir, İ., Gülseven Sidir, Y.: Estimation of ground and excited state dipole moments of Oil Red O by solvatochromic shift methods. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **135**, 560–567 (2015)
- Sidir, İ., Sidir, Y.G., Berber, H., Demiray, F.: Electronic structure and optical properties of Schiff base hydrazone derivatives by solution technique for optoelectronic devices: synthesis, experiment and quantum chemical. *J. Mol. Struct.* **1176**, 31–46 (2019)
- Sidir, İ., Sidir, Y.G., Khan, N., Berber, H.: Optoelectronic and photonic properties of π -conjugated benzonitrile derivative bis-Schiff base by solution technique. *Optik* **241**, 166825 (2021)
- Sidir, Y.G., Sidir, İ., Berber, H.: Optoelectronic properties by solution technique and comprehensive solvatochromism of novel fluorescent Schiff base derivatives. *J. Mol. Liq.* **357**, 119110 (2023)
- Singh, R.K., Singh, A.K.: Synthesis, molecular structure, spectral analysis, natural bond order and intramolecular interactions of 2-acetylpyridine thiosemicarbazone: a combined DFT and AIM approach. *J. Mol. Struct.* **1094**, 61–72 (2015)
- Tauc, J.: Amorphous and Liquid Semiconductors. Plenum Press, New York (2000)
- Tauc, J., Menth, A.: States in the gap. *J. Non-Cryst. Solids* **8–10**, 569–585 (1972)