Spectrochimica Acta Part A 79 (2011) 1573–1583

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, characterization, tautomerism and theoretical study of some new Schiff base derivatives

Gülşen Türkoğlu[a], Halil Berber[a,*], Hakan Dal[a], Cemil Öğretir[b]

[a] Anadolu University, Faculty of Science, Chemistry Department, 26470 Eskişehir, Turkey
[b] Eskişehir Osmangazi University, Faculty Arts and Sciences, Chemistry Department, 26040 Eskişehir, Turkey

ARTICLE INFO

Article history:
Received 25 February 2011
Received in revised form 30 March 2011
Accepted 10 April 2011

This paper is dedicated to Dear Professor Cemil Öğretir.

Keywords:
Schiff basel
Synthesis
Characterization
Tautomerism
Theoretical calculation
PM6 method

ABSTRACT

New Schiff base derivatives were prepared by the condensation of 5-chloro and 5-bromo salicylaldehyde with bis(*o*-aminophenol)ethers. Five bis(*o*-nitrophenol)ether compounds were synthesized using some ditosylate, 1,3-dibromopropane and 1,4-dibromobuthane with *o*-nitrophenol. These compounds were reduced to bis(*o*-aminophenol)ethers. The products have been characterized by elemental analysis, FTIR, ^{1}H, ^{13}C NMR, HETCOR and HMBC spectroscopic techniques. The tautomerisms of all of the Schiff bases compounds were determined in DMSO, $CHCl_3$, C_2H_5OH and C_6H_{12} solvents and in both acidic and basic media using the UV–vis spectrophotometric method. The heat of formation (ΔH_f), enthalpy (ΔH), entropy (ΔS), Gibbs free energy (ΔG_f and ΔG), stable isomers, conformations and tautomers of the synthesized compounds are calculated using the MOPAC2009 (PM6) program.

1. Introduction

The development of the so-called Schiff base compounds has attracted a lot of interest in the fields of coordination chemistry and material sciences [1,2]. Schiff bases that have a solvent dependent UV–vis spectrum (solvatochromicity) can be suitable NLO (non linear optical active) materials [3]. The Schiff base can accommodate different metal centers involving various coordination modes thereby allowing successful synthesis of homo and hetero metallic complexes with varied stereochemistry [4].

Schiff bases are important in diverse field chemistry owing to their biological activity [5]. Apart from the biological activity, photochromism is another characteristic of these materials leading to its application in various areas, such as the control and measurement of radiation intensity, display systems and optical computers [6].

Some crown ether-containing ortho hydroxylated Schiff bases have been synthesized and their complexation properties with transition metal cations have been investigated [7–9]. The Schiff base ligands are one of the most widely used ligands due to the ease of formation and remarkable versatility, and therefore they have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals [10]. Symmetrical diimines and their metal complexes have been used as models for biological systems for their antimicrobial and anticancer activities [11,12]. They have also been used in the catalytic reactions [13] and oxidation reactions [14,15]. Additionally, they have material properties and analytical applications such as ion selective electrodes [16].

The proton transfer equilibrium in 2-hydroxy Schiff bases in solution and solid state has been investigated using mass spectra [17], NMR [18–22], UV–vis [23–27] and X-ray crystallography [28–30]. Schiff bases with OH group in *ortho* position to the amino group are of interest mainly due to the existence of either O–H·····N or O·····N–H type of hydrogen bond and tautomerism between enol-imine and keto–amine form. In these compounds, short hydrogen bonds between the OH group in *ortho* position to the imino group and the imine nitrogen are due to stereochemistry.

In this study, we synthesized new Schiff bases (Fig. 1) and investigated using elemental analysis, FTIR, ^{1}H, ^{13}C NMR, HETCOR and HMBC spectroscopic techniques [31]. Then the tautomers of all of the Schiff bases compounds were determined using the UV–vis spectrophotometric method. Conformations and tautomers

* Corresponding author: Tel.: +90 222 335 05 80x4827; fax: +90 222 320 49 10.
E-mail address: hlberber@anadolu.edu.tr (H. Berber).

1386-1425/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2011.04.089

of the synthesized compounds are calculated using the MOPAC2009 (PM6) program.

2. Experimental

2.1. Reagents and materials

Chemicals used were 2-nitrophenol, diethyleneglycol dichloride, triethyleneglycol dichloride, 5-chlorosalicylaldeyde, 5-bromosalicylaldeyde, hydrazine hydrate (80%) and palladium/carbon (Pd/C) (5%). Solvents pyridine, ethanol (99%) and dimethylformamide (DMF) were dried by standard methods prior to use.

Carbon, nitrogen and hydrogen analysis were performed on a VarioEL III CHNS Elemental Analyzer. Melting points were measured on a Gallenkamp apparatus using a capillary tube. ^{1}H NMR, ^{13}C NMR, spectra were obtained on a Bruker DPX FT-NMR (500 MHz) spectrometer ($SiMe_4$ as internal Standard and 85% H_3PO_4 as an external Standard). The spectrometer was equipped with a 5 mm PABBO BB-inverse gradient probe. The concentration of the solute compounds was 150 mg in 1.0 mL $CDCl_3$ and DMSO-d_6. FTIR spectra were recorded on a Perkin Elmer Spectrum 100 Spectrometer in KBr discs and were reported in cm^{-1} units. The UV–visible spectra were measured using a SHIMADZU UV2101 Pc series spectrometer.

2.2. Synthetic procedures

Compounds were prepared according to basic synthesis procedures (Fig. 1). Bis(*o*-nitrophenol)ether and bis(*o*-aminophenol)ether compounds were prepared according to the published procedure [32].

2.3. Synthesis of compound (**1**)

1,3-Bis(*o*-aminophenoxy)-3-oxopropane (0.50 g, 1.9 mmol), was dissolved completely by heating in CH_3OH (25 mL). This solution was added dropwise to a stirred solution of 5-chlorosalicylaldehyde (0.606 g, 3.8 mmol) in CH_3OH (25 mL) over a period of 1 h. Compound (1) was obtained as a bright orange solid. It was crystallized from CH_3OH:THF (tetrahydrofuran) (1:1) as a bright orange solid. R_f = 0.72 (THF:n-hexane (1:2))

2.4. Synthesis of compound (**2**)

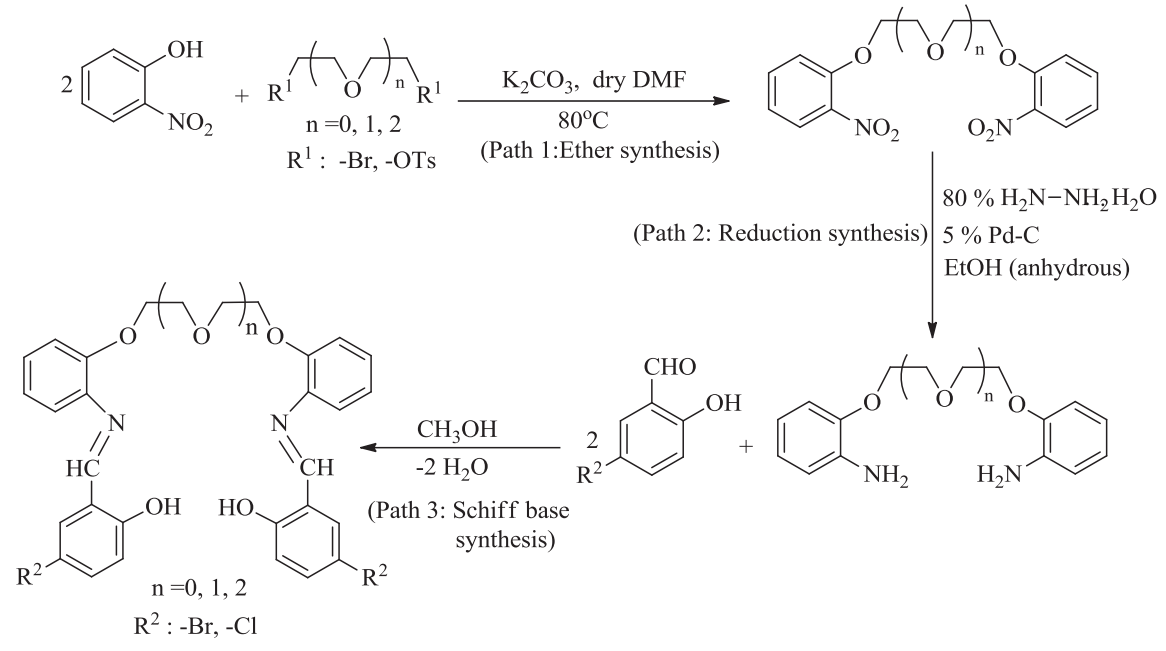
Compound (**2**) was prepared according to the compound (**1**). This reaction used 1,3-bis(*o*-aminophenoxy)-3-oxopropane (0.50 g, 1.9 mmol), 5-bromosalicylaldehyde (0.778 g, 3.8 mmol) and 50 mL methanol. It was crystallized from CH_3OH:THF (1:1) as an orange solid. R_f = 0.74 (THF:n-hexane (1:2)).

2.5. Synthesis of compound (**3**)

Compound (**3**) was prepared according to the compound (**1**). This reaction used 1,4-bis(*o*-aminophenoxy)-4-oxobutane (0.025 g, 0.159 mmol), 5-chlorosalicylaldehyde (0.0217 g, 0.319 mmol) and 50 mL methanol. It was crystallized from CH_3OH:THF (1:1) as a bright yellow-orange solid. R_f = 0.69 (THF:n-hexane (1:2)).

2.6. Synthesis of compound (**4**)

Compound (**4**) was prepared according to the compound (**1**). This reaction used 1,5-bis(*o*-aminophenoxy)-3-oxopentane (0.40 g, 1.38 mmol), 5-chlorosalicylaldehyde (0.434 g, 2.77 mmol) and 50 mL methanol. It was crystallized from CH_3OH:THF (1:1) as a bright orange solid. R_f = 0.62 (THF:n-hexane (1:2)).



(**1**) n=0, R^2: -Cl (**2**) n=0, R^2: -Br (**3**) n=0, R^2: -Cl

(**4**) n=1, R^2: -Cl (**5**) n=2, R^2: -Cl

Fig. 1. General procedure for synthesized compounds.

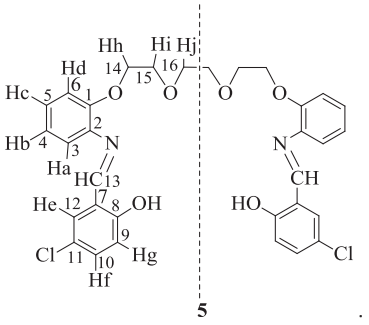
Table 1
Experimental and analytical data for synthesized compounds.

Compounds no	Empiric formula	MW (g/mol)	Yield (%)	m.p. (°C)	Calculated (found) %		
					C	H	N
1	$C_{29}H_{24}Cl_2N_2O_4$	535.42	98	178	65.76 (65.05)	4.60 (4.52)	5.00 (5.23)
2	$C_{29}H_{24}Br_2N_2O_4$	624.32	95	178	55.79 (56.57)	3.87 (3.63)	4.49 (4.63)
3	$C_{30}H_{26}Cl_2N_2O_4$	549.44	60	227–229	65.58 (66.46)	4.77 (4.25)	5.10 (5.40)
4	$C_{30}H_{26}Cl_2N_2O_5$	565.44	68	150–152	63.72 (64.32)	4.63 (4.55)	4.95 (5.53)
5	$C_{32}H_{30}Cl_2N_2O_6$	609.50	84	129	63.06 (63.63)	4.96 (5.00)	4.60 (4.86)

Table 2
Selected FTIR data for synthesized compounds (ν, cm^{-1}).

Compounds no	ν(C–H) aromatic	ν(C–H) aliphatic	ν(C=C) aromatic	ν(C–O–C) aromatic	ν(C–O–C) aliphatic	ν(O–H)	ν(C=N)
1	3064	2963–2884	1590–1478	1282–1252	–	3436–2746	1619
2	3061	2964–2884	1590–1474	1281–1252	–	3435–2747	1617
3	3065	2952–2875	1589–1478	1279–1252	–	3441–2740	1614
4	3079–3032	2953–2874	1592–1480	1297–1254	1145–1091	3438–2739	1620
5	3060–3027	2915–2873	1590–1481	1283–1257	1179–1091	3435–2743	1619

Table 3
^{1}H NMR data for synthesized molecules.



5

^{1}H NMR data					
H-type	δ (ppm)/J (Hz)				
	1[a]	**2**[a]	**3**[b]	**4**[a]	**5**[a]
Ha	7.23 (m, 1H)[c]	7.24 (m, 1H)	7.45 (dd, 1H) [^3Ja-b = 7.87] [^4Ja-c = 1.38]	7.21 (m, 2H)	7.23 (m, 2H)
Hb	7.01 (t, 1H) [^3Jb-c,a = 7.64]	7.00 (td, 1H) [^3Jb-c,a = 7.73] [^4Jb-d = 1,09]	7.03 (t, 1H) [^3Jb-c,a = 7.49]	7.01 (m, 2H)	7.01 (td, 1H) [$^3J_{Hb\text{-}Hc,a}$ = 7.74] [$^4J_{Hb\text{-}Hd}$ = 0.97]
Hc	7.23 (m, 1H)	7.24 (m, 1H)	7.25 (td, 1H) [^3Jc-b,d = 8.46] [^4Jc-a = 1.38[	7.21 (m, 2H)	7.23 (m, 2H)
Hd	7.06 (d, 1H) [^3Jd-c = 8.54]	7.06 (d, 1H) [^3Jd-c = 7.69]	7.13 (d, 1H) [^3Jd-c = 7.66]	7.01 (m, 2H)	6.96 (dd, 1H) [$^3J_{Hd\text{-}Hc}$ = 8.30] [$^4J_{Hd\text{-}Hb}$ = 0.78]
He	7,32 (m, 1H)	7,48 (d, 1H) [^3Je-g = 2, 41]	7,68 (d, 1H) [^3Je-g = 2, 69]	7,30 (d, 1H) [$^3J_{He\text{-}Hg}$ = 2, 57]	7,34 (d, 1H) [$^3J_{He\text{-}Hg}$ = 2, 58]
Hf	7.32 (m, 1H)	7.44 (dd, 1H) [^3Jg-h = 8.77] [^4Jg-e = 2.46]	7.40 (dd, 1H) [^3Jg-h = 8.83] [^4Jg-e = 2.69]	7.25 (dd, 1H) [$^3J_{Hg\text{-}Hh}$ = 8.83] [$^4J_{Hg\text{-}He}$ = 2.67]	7.26 (d, 1H) [$^3J_{Hg\text{-}Hh}$ = 8.81] [$^4J_{Hg\text{-}He}$ = 2.56]
Hg	6.98 (d, 1H) [^3Jh-g = 8.58]	6.92 (d, 1H) [^3Jh-g = 8.74]	6.94 (d, 1H) [^3Jh-g = 8.85]	6.89 (d, 1H) [$^3J_{Hh\text{-}Hg}$ = 8.81]	6.92 (d, 1H) [$^3J_{Hh\text{-}Hg}$ = 8.81]
Hh	4.33 (t, 2H) [^3Jk-l = 5.87]	4.30 (t, 2H) [^3Jk-l = 5.88]	4.15 (s, 2H)	4.24 (t, 2H) [$^3J_{Hk\text{-}Hl}$ = 4.74]	4.18 (tt, 2H) [$^3J_{Hk\text{-}Hl}$ = 4.68] [$^2J_{Hk\text{-}Hl,k'}$ = 25.29]
Hi	2.39 (m, 2H) [^3Jl-k = 5.82]	2.40 (m, 2H) [^3Jl-k = 5.88]	1.98 (m, 2H)	4.02 (t, 2H) [$^3J_{Hl\text{-}Hk}$ = 4.74]	3.91 (tt, 2H) [$^3J_{Hl\text{-}Hk}$ = 4.86] [$^2J_{Hl\text{-}Hk,l'}$ = 24.14]
Hj	–	–	–	–	3.78 (s, 2H)
–CH	8.62 (s, 1H)	8.62 (s, 1H)	9.00 (s, 1H)	8.60 (s, 1H)	8.70 (s, 1H)
–OH	14.00 (s, 1H)	14.10 (s, 1H)	14.10 (s, 1H)	13.80 (s, 1H)	13.80 (s, 1H)

[a] ^{1}H NMR data in $CDCl_3$.
[b] ^{1}H NMR data in DMSO-d_6.
[c] s = singlet, d = doublet, dd = doublet of doublet, t = triplet, tt = triplet of triplet, td = triplet of doublet, m = multiplets.

Table 4
^{13}C NMR data for synthesized molecules.

C-type	^{13}C NMR data δ (ppm)				
	1[a]	**2**[a]	**3**[b]	**4**[a]	**5**[a]
C1	152.40	152.40	152.45	152.29	152.26
C2	136.34	136.30	136.28	136.58	136.45
C3	120.25	119.39	120.14	119.92	120.31
C4	121.11	121.11	121.12	121.32	121.27
C5	128.57	128.60	128.58	128.33	128.29
C6	113.33	113.34	113.43	113.46	113.32
C7	118.94	120.90	118.98	120.28	118.85
C8	159.97	159.85	159.80	160.10	160.13
C9	119.04	119.03	119.32	118.85	120.31
C10	132.58	135.36	133.42	132.47	132.50
C11	123.23	110.08	120.23	123.16	123.17
C12	130.83	133.83	130.80	130.89	130.95
C13	160.25	160.73	160.78	160.73	160.94
C14	64.96	64.95	65.12	68.60	68.40
C15	29.37	29.36	29.35	70.02	69.63
C16	–	–	–	–	71.03

[a] ^{13}C NMR data in $CDCl_3$.
[b] ^{13}C NMR data in DMSO-d_6.

2.7. Synthesis of compound (**5**)

Compound (**5**) was prepared according to the compound (**1**). This reaction used 1,8-bis(*o*-aminophenoxy)-3,6-dioxooctane (0.50 g, 1.5 mmol), 5-chlorosalicylaldehyde (0.471 g, 3.0 mmol) and 50 mL methanol. It was crystallized from CH_3OH:THF (1:1) as an orange solid. R_f = 0.63 (THF:n-hexane (1:2)).

3. Result and discussion

3.1. Synthesis

The structures of the Schiff bases have been characterized by elemental analysis, ^{1}H, ^{13}C NMR and FTIR. All of these new compounds gave spectroscopic and analytical data in Tables 1–4. The structure of the Schiff bases have been characterized by elemental analysis. The new five compounds gave yields, melting points (m.p.) and elemental analysis data of calculated and found in Table 1.

3.2. Spectroscopy

3.2.1. IR spectra

Selected FTIR frequencies of various diagnostic bands of compounds are given in Table 2. The IR spectra of the Schiff bases exhibit various bands in the 250–4000 cm^{-1} region. All of the compounds (**1**–**5**) exhibit two medium intensity absorption signals at 3079–3061 and 3060–3027 cm^{-1} attributed to asymmetric and symmetric stretching vibrations of the Ar–H groups. The O–H stretching frequency of the all compounds is expected in the 3463–3433 cm^{-1} region, however, this frequency is generally displaced to the 2757–2723 cm^{-1} region due to the internal hydrogen bridge OH·····N=C [33]. All of the compounds (**1**–**5**) O–H stretching frequency are observed 3441–3435 cm^{-1}, internal hydrogen bridge OH·····N=C 2747–2739 cm^{-1} in accordance with the literature. As the hydrogen bond becomes stronger, the bandwidth increases, and this band is not always detected. Hydrogen bonds in these Schiff bases are usually very strong. These compounds are relatively planar with adequate intramolecular distance that favours intramolecular hydrogen bond formation [34]. Electron-donating groups on the phenolic ring increase the electron density on the hydroxyl oxygen making the H–O bond stronger and the absorption usually appears as a broad band in the IR spectrum. The ν(C=N) absorption bands are observed at 1620–1614 cm^{-1} region for all of the compounds. The ν(C–O) and ν(C–O, aromatic ethereal) vibrations bands overlap each other in the all compounds.

3.2.2. NMR spectra

All of the ^{13}C NMR and ^{1}H NMR assignments have been written on the ^{1}H NMR and ^{13}C NMR spectra (Figs. 2 and 3). All of the data shows that of the compounds have symmetric structures in the solution. The ^{1}H NMR data and coupling constant for the new Schiff bases are listed in Table 3. The broad signal around δ = 13.80–14.10 ppm are assigned to the protons of the hydroxyl groups. This peak is due to hydrogen bonded phenolic protons and the integration is generally less than 2.0 due to this intramolecular hydrogen bonding. Signals for the methine protons of the characteristic azomethine group for Schiff bases, –N=C(H)– were observed between 9.0 and 8.6 ppm. In the region of 7.48–6.8 ppm chemical shifts were assigned for hydrogen of the aromatic ring. The alkyl protons O–CH_2–CH_2–O were observed between 4.24 and 3.77 ppm. The ^{1}H NMR data for all the compounds shows the tautomeric equilibrium favours the phenol-imine in solution (δ = 13.80–14.10 ppm, singlet for OH; δ = 9.0–8.60 ppm, singlet for –N=C(H)–).

The ^{13}C NMR data for the new Schiff bases are listed in Table 4. Aliphatic carbon atoms (O–CH_2–CH_2–O): δ = 71.01–64.95 ppm for compounds, aromatic carbons were observed between 152.36 and 110.08 ppm.Assignments of the protonated carbons were made by HETCOR using delay values which correspond to ^1J(C,H). As an example, only the HETCOR spectrum of compound (**1**) is depicted in Fig. 4. The C1 carbon atom adjacent to the more electronegative oxygen atom of the aliphatic ring is shifted further downfield when compared to the neighbouring C6 atom. In addition, C5 and C4 atoms are more shielded than the the others. On the other hand, the aromatic carbons were also determined using delays in two dimensional HETCOR and HMBC experiments to emphasize the long range coupling either ^2J(C,H), ^3J(C,H) or ^4J(C,H) between the carbons and protons (Tables 3 and 4). The absence of non-protonated carbon atoms (C1, C2, C7, C8, and C11) in the HETCOR have supported the assignments, C1: at δ = 152.40 ppm, C2: δ = 136.30 ppm, C7: δ = 118.94 ppm, C8: δ = 159.97 ppm, C11: δ = 123.23 ppm for compound (**1**). Others carbon atoms (C3, C4, C5, C6, C9, C10 and C12)

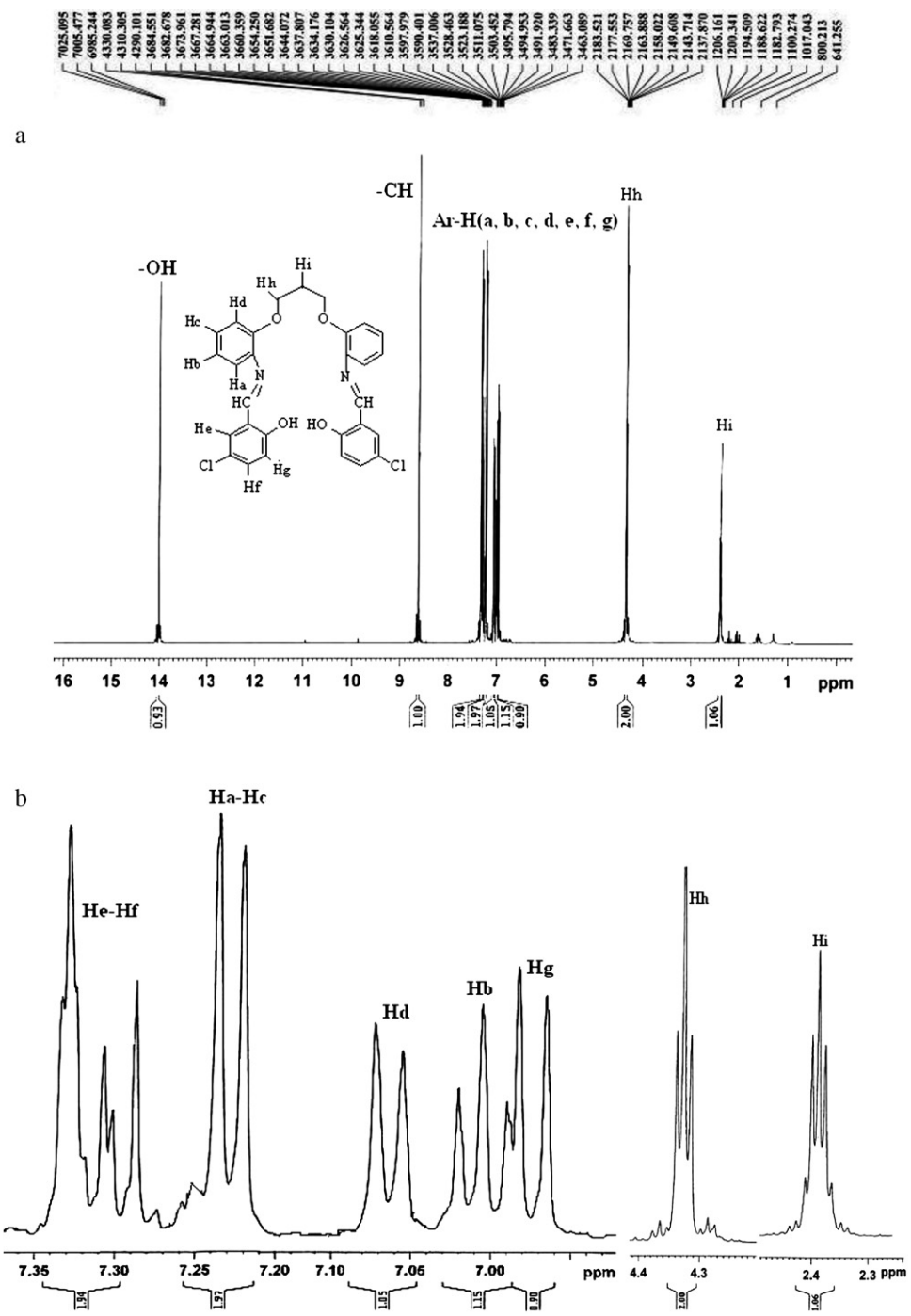


Fig. 2. (a) ^{1}H NMR spectrum of compound (**1**), (b) The CH_2, OCH_2 groups region (4.40–2.30 ppm) and the region aromatic protons (6.80–7.40 ppm).

have been assigned respectively, according to the HMBC and HETCOR spectrum for compound (**1**).

3.3. Tautomerism

In solutions, the tautomerism depends on the solvent polarity and the ability of the solvents to form hydrogen bonds. The Schiff bases show absorption in the range greater than 400 nm in polar and nonpolar solvents. Keto–amine tautomeric forms are present for the compounds **1**–**5.** The spectra measured in non-polar solvent (C_6H_{12}) contain two bands at approximately 280 and 332–380 nm. These bands are due to π–π^* transitions. In polar solvents (DMSO, C_2H_5OH and $CHCl_3$), one additional band emerges at approximately 450 nm (n–π), which has logically been linked with the shift of the tautomeric equilibrium to the keto–amine form. There is a decrease in imino nitrogen basicity followed by a weakening of the intramolecular hydrogen bond (O–H·····N) and a decreased tendency of the tautomeric inter conversion to keto–amine [34]. The UV–visible spectra of compounds (**1**–**5**) were studied in polar and non-polar solvents both in acidic (CF_3COOH) and basic (Et_3N) media. The parameters of the spectra for all of the Schiff bases in polar and non-polar solvents both in acidic and basic media are

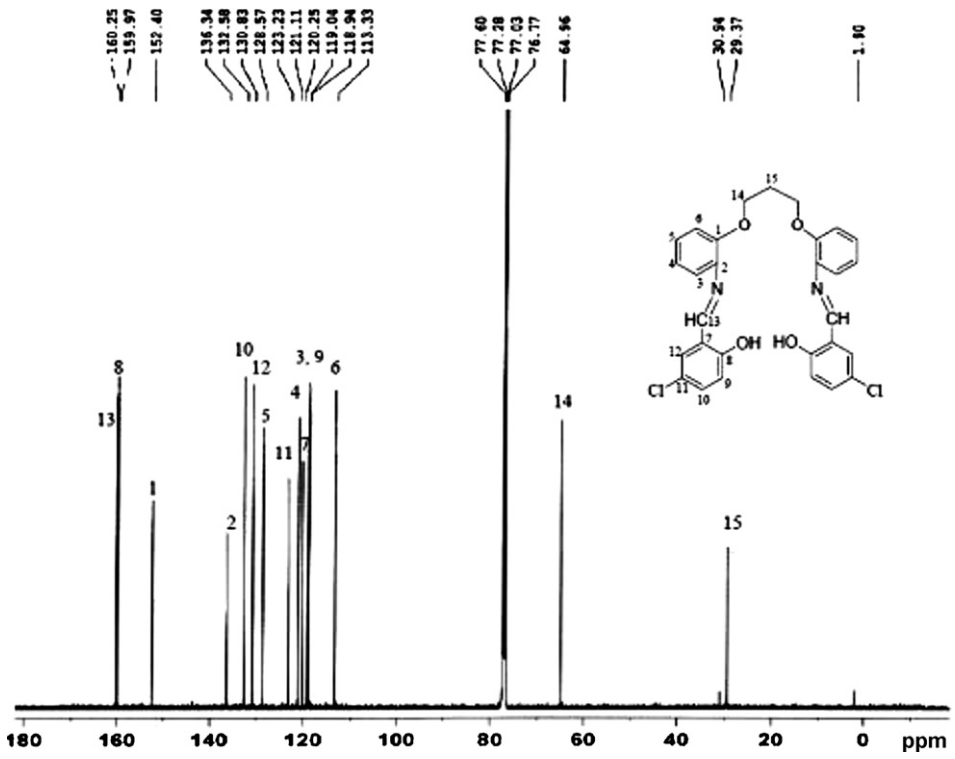


Fig. 3. ^{13}C NMR spectrum of compound (**1**).

listed in Table 5. Fig. 5 shows the UV spectra for compound **1** in different solvents both in acidic and basic media. The calculated keto–amine tautomeric equilibrium of all the compounds are given in Table 6.

In pure solvent media C_6H_{12}, the keto–amine tautomers were only observed for compound **5**. In basic media C_6H_{12}, the keto–amine tautomers (%) were only measured for compound **4**. Interestingly, when acid was added to a non-polar solvent (C_6H_{12}), the keto–amine forms were observed for the compounds **1**–**5,** but when the acid was added to polar solvent (DMSO), the phenol-imine forms were dominant for all of the compounds. In pure solvent media DMSO, the ratios of the keto–amine tautomers of the (**1**–**5**) are higher than in C_2H_5OH, $CHCl_3$ and C_6H_{12}. In acidic solutions $CHCl_3$ and C_6H_{12}, keto–amine tautomers (%) all of the compounds are observed as higher than the DMSO and C_2H_5OH solutions. The bathochromic shifts both above and below 400 nm in all of the solvents studied (DMSO, C_2H_5OH, $CHCl_3$ and C_6H_{12}) do not depend on solvent polarities for compounds (**1**–**5**). The absence of a keto–amine form in the acidic solutions of $CHCl_3$ and C_6H_{12} may be explained by the hydrogen bonding to CF_3COOH.

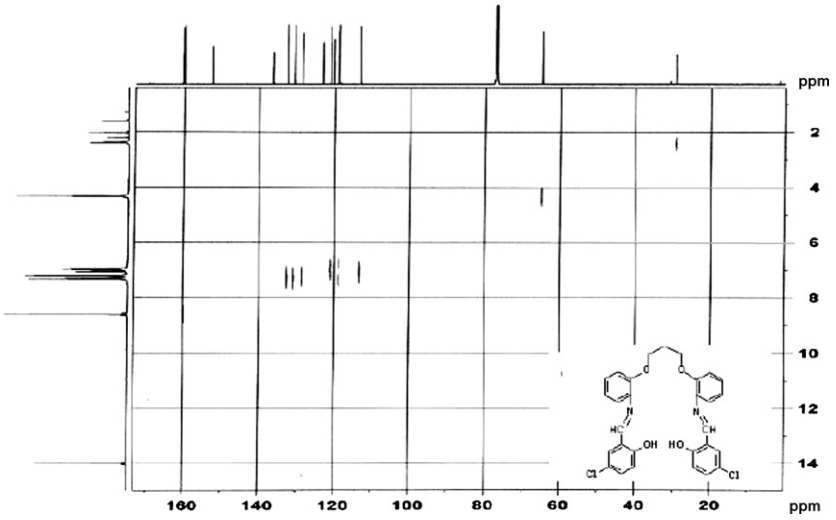


Fig. 4. HETCOR spectrum of compound (**1**).

Table 5
The acid and base effects in the different solvents for tautomerism ($T = 298 \pm 1\,^{\circ}C$).

Compounds no	Solvent	$\lambda_{max.\,(nm)\,(Absorbance)}$		
		Solvent media[a]	Acidic media[b]	Basic media[c]
1	DMSO	359 (*A* = 0.876)	335 (*A* = 0.583)	360 (*A* = 0.792)
		257 (*A* = 1.237)	264 (*A* = 0.910)	274 (0.684)
		457 (*A* = 0.056)	415 (*A* = 0.029)	363 (*A* = 0.561)
	C_2H_5OH	347 (*A* = 0.730)	341 (*A* = 0.259)	262 (*A* = 0.796)
		279 (*A* = 0.613)		
		473 (*A* = 0.021)	418 (*A* = 0.618)	458 (*A* = 0.017)
	$CHCl_3$	361 (0.807)	322 (*A* = 0.433)	362 (*A* = 0.537)
		270 (*A* = 0.613)		280 (*A* = 3.082)
	C_6H_{12}	359 (*A* = 0.696)	413 (*A* = 0.487)	360 (*A* = 0.402)
		269 (*A* = 0.575)	322 (*A* = 0.446)	267 (*A* = 0.274)
2	DMSO	360 (*A* = 0.650)	335 (*A* = 0.273)	360 (*A* = 0.550)
		275 (*A* = 0.499)		264 (*A* = 1.031)
	C_2H_5OH	343 (*A* = 0.185)	339 (*A* = 0.045)	366 (*A* = 0.127)
		285 (*A* = 0.166)		262 (*A* = 0.860)
		457 (*A* = 0.016)	419 (*A* = 0.536)	458 (*A* = 0.015)
	$CHCl_3$	362 (*A* = 0.580)	322 (*A* = 0.383)	362 (*A* = 0.389)
				294 (*A* = 0.334)
	C_6H_{12}	359 (*A* = 0.375)	417 (*A* = 0.120)	362 (*A* = 0.220)
			341 (*A* = 0.089)	268 (*A* = 0.579)
3	DMSO	36 2 (*A* = 0.406)	334 (*A* = 0.154)	365 (*A* = 0.281)
		275 (*A* = 0.297)		279 (*A* = 0.110)
		346 (*A* = 0.252)	411 (*A* = 0.084)	553 (*A* = 0.007)
	C_2H_5OH	285 (*A* = 0.275)	341 (*A* = 0.128)	364 (*A* = 0.176)
				289 (*A* = 0.143)
		361 (*A* = 0.667)	421 (*A* = 0.868)	458 (*A* = 0.015)
	$CHCl_3$	271 (*A* = 0.527)	323 (*A* = 0.598)	360 (*A* = 0.449)
			277 (*A* = 0.218)	278 (*A* = 2.512)
		458 (*A* = 0.005)	411 (*A* = 0.080)	343 (*A* = 0.109)
	C_6H_{12}	356 (*A* = 0.109)	343 (*A* = 0.059)	267 (*A* = 0.085)
		285 (*A* = 0.067)		
4	DMSO	361 (*A* = 0.725)	335 (*A* = 0.323)	551 (*A* = 0.037)
		272 (*A* = 0.595)	257 (*A* = 1.209)	362 (*A* = 0.668)
		555 (*A* = 0.005)	341 (*A* = 0.079)	532 (*A* = 0.011)
	C_2H_5OH	342 (*A* = 0.339)		371 (*A* = 0.229)
		282 (*A* = 0.318)		
		555 (*A* = 0.016)	417 (*A* = 0.686)	533 (*A* = 0.011)
	$CHCl_3$	359 (*A* = 0.802)	323 (*A* = 0.515)	359 (*A* = 0.611)
		270 (*A* = 0.647)		
		539 (*A* = 0.002)	431 (*A* = 0.059)	356 (*A* = 0.876)
	C_6H_{12}	356 (*A* = 0.608)	270 (*A* = 0.029)	277 (*A* = 0.298)
		269 (*A* = 0.766)		
5		552 (*A* = 0.001)	275 (*A* = 0.545)	359 (*A* = 0.693)
	DMSO	359 (*A* = 0.786)		335 (*A* = 0.165)
		271 (*A* = 0.665)		
		460 (*A* = 0.021)	339 (*A* = 0.067)	397 (*A* = 0.204)
	C_2H_5OH	356 (*A* = 0.398)	260 (*A* = 0.500)	271 (*A* = 0.343)
		280 (*A* = 0.198)		
	$CHCl_3$	360 (*A* = 0.730)	415 (*A* = 0.396)	360 (*A* = 0.713)
		269 (*A* = 0.601)	320 (*A* = 0.314)	270 (*A* = 0.525)
	C_6H_{12}	356 (*A* = 0.525)	356 (*A* = 0.296)	405 (*A* = 0.320)
		270 (*A* = 0.444)	311 (*A* = 0.368)	268 (*A* = 0.308)

[a] Without acid and base.
[b] Acid effects in solvents.
[c] Basic effects in solvents.

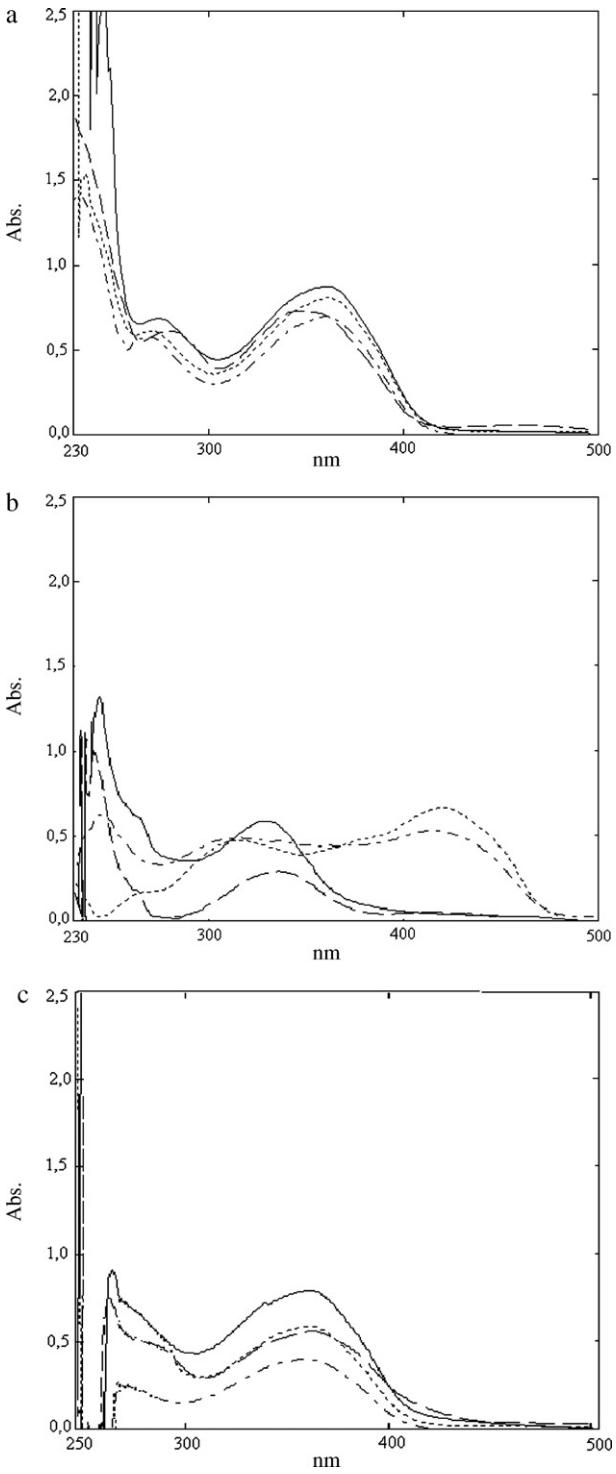


Fig. 5. The typical UV–vis spectra of compound **1** ($c = 5 \times 10^{-5}$ mol L^{-1}). (a) Different solvents effect in neutral media. (b) in acidic media by addition of CF_3COOH (1 mL) to the given solution. (c) in basic media by addition of Et_3N (1 mL) to the given solution. (DMSO_____, C_2H_5OH ——, $CHCl_3$ · · · · ·, C_6H_{12} — · — · — .)

Table 6
keto–amine tautomer (%) in solvent, acidic and basic media for the compounds.

Compounds no	Solvent	Keto–amine tautomer, % [a]		
		Solvent media	Acidic media[b]	Basic media[c]
1	DMSO	56.2	–	–
	C_2H_5OH	8.4	10.1	–
	$CHCl_3$	3.3	58.8	1.0
	C_6H_{12}	–	52.2	–
2	DMSO	56.6	–	–
	C_2H_5OH	–	–	–
	$CHCl_3$	–	58.3	4.3
	C_6H_{12}	–	57.4	–
3	DMSO	57.8	–	71.9
	C_2H_5OH	–	39.6	4.7
	$CHCl_3$	55.9	80.0	0.6
	C_6H_{12}	6.9	42.3	–
4	DMSO	54.9	–	–
	C_2H_5OH	1.6	–	–
	$CHCl_3$	2.4	57.1	–
	C_6H_{12}	–	67.1	67.1
5	DMSO	0.2	–	56.0
	C_2H_5OH	5.8	–	50.7
	$CHCl_3$	–	55.6	57.6
	C_6H_{12}	54.2	46.5	–

[a] Keto isomer (%) = $(A_2/A_2 + A_1) \times 100$ where, A_1 = the absorbance of the phenol-imine isomer (π–π^*); A_2 = the absorbance of the keto–amine isomer (n–π^*).
[b] Acidic media is attained by addition of CF_3COOH(~1 mL) to the given solution (molecules concentration 1×10^{-5} mol L^{-1}).
[c] Basic media is attained by addition of Et_3N(~1 mL) to the given solution (molecules concentration 1×10^{-5} mol L^{-1}).

No noticeable increase or decrease in the keto–amine tautomers (%) were observed by changing the solvent polarities for the compounds (**1**–**5**).

3.4. Theoretical calculations

The theoretical calculations were carried out by the MOPAC2009 pocket program at Restricted Hartree–Fock level using PM6 semi-empirical SCF-MO methods [35]. An Intel Pentium Pro. 400 MHz computer was used. The initial data for geometry optimization (bond lengths, bond angles and dihedral angles) were estimated by a molecular mechanic program (ChemOffice) [36].

ΔH_f, ΔH, ΔS, ΔG_f and ΔG are listed in Table 7. It is observed that **e** tautomeric forms of the compounds are more stable than **k** tautomeric forms depending on Gibss free energies (ΔG_f) (Table 7).

In theoretical tautomeric equilibrium calculations, **e** (phenol forms) of all the studied compounds are more stable than **k** (keto forms) (Fig. 6, Table 8).

Any meaningful correlation could not be observed between the tautomeric equilibrium and the solvent polarities (Table 9).

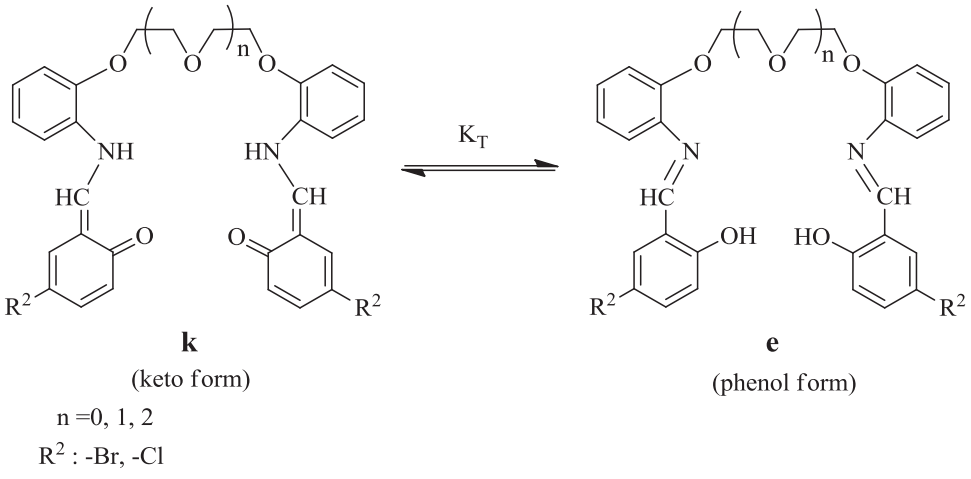


Fig. 6. Tautomeric structures of the compounds used in the theoretical calculations.

Table 7
Thermodynamic parameters of the studied compounds by PM6 method in liquid phase (T = 298 K).

Compounds no	ΔH_f (kcal mol^{-1})	ΔH (cal mol^{-1})	ΔS (kcal mol^{-1})	ΔG_f[a] (kcal mol^{-1})	ΔG[b]	Compounds no	ΔH_f (kcal mol^{-1})	ΔH (cal mol^{-1})	ΔS (kcal mol^{-1})	ΔG_f[a] (kcal mol^{-1})	ΔG[b] (kcal mol^{-1})
DMSO						DMSO					
1e	−64.352	21804.085	131.442	−103.522	−17.366	**1k**	−55.966	21939.810	131.688	−95.209	−17.303
2e	−42.004	22099.692	132.214	−81.404	−17.300	**2k**	−34.101	22674.554	133.072	−73.756	−16.981
3e	−70.950	23056.370	137.216	−111.840	−17.834	**3k**	−61.163	23078.875	136.837	−101.940	−17.699
4e	−106.477	23489.021	140.084	−148.222	−18.256	**4k**	−94.928	23813.799	140.611	−136.830	−18.088
5e	−151.099	25766.653	153.163	−196.742	−19.876	**5k**	−145.890	25400.401	152.594	−191.363	−20.073
C_2H_5OH						C_2H_5OH					
1e	−63.652	21790.406	131.396	−102.808	−17.366	**1k**	−55.299	21932.350	131.647	−94.530	−17.299
2e	−41.291	22091.046	132.170	−80.678	−17.296	**2k**	−33.171	22670.458	133.026	−72.813	−16.971
3e	−70.275	23051.763	137.180	−111.155	−17.828	**3e**	−60.336	23071.354	136.801	−101.103	−17.695
4e	−105.707	23474.077	140.054	−147.443	−18.262	**4k**	−94.082	23812.252	140.579	−135.974	−18.080
5e	−150.435	25755.419	153.121	−196.065	−19.875	**5k**	−145.252	25395.208	152.553	−190.713	−20.066
$CHCl_3$						$CHCl_3$					
1e	−58.311	21723.786	131.053	−97.365	−17.330	**1k**	−50.299	21860.476	131.311	−89.430	−17.270
2e	−35.835	22037.117	131.867	−75.131	−17.259	**2k**	−26.271	22615.920	132.677	−65.809	−16.922
3e	−65.111	23008.303	136.875	−105.900	−17.781	**3k**	−54.129	23056.826	136.553	−94.822	−17.636
4e	−99.867	23390.856	139.837	−141.538	−18.281	**4k**	−87.751	23763.353	140.373	−129.582	−18.068
5e	−145.338	25684.354	152.855	−190.889	−19.866	**5k**	−140.369	25351.877	152.273	−185.746	−20.025
C_6H_{12}						C_6H_{12}					
1e	−51.309	21642.261	130.647	−90.242	−17.290	**1k**	−43.956	21783.219	130.903	−82.965	−17.226
2e	−28.650	21961.493	131.494	−67.835	−17.224	**2k**	−17.674	22503.743	132.264	−57.089	−16.911
3e	−58.313	22895.935	136.321	−98.937	−17.728	**3k**	−46.254	22950.595	136.243	−86.854	−17.650
4e	−92.289	23308.134	139.552	−133.876	−18.278	**4k**	−79.730	23737.145	140.114	−121.484	−18.017
5e	−138.582	25590.157	152.516	−184.032	−19.860	**5k**	−133.933	25317.572	151.952	−179.215	−19.964

[a] $\Delta G_f = \Delta H_f - T\Delta S$.
[b] $\Delta G = \Delta H - T\Delta S$.

Table 8
Tautomeric equilibrium constants (KT) by PM6 method in liquid phase.

Process[a]	$\delta\Delta G_f$[b]	K_{Tf}[c]	pK_{Tf}[d]	$\delta\Delta G$[e]	K_T[f]	pK_T[g]
DMSO						
1k-1e	−8.313	1.25×10^6	−6.097	−0.062	1.111	−0.046
2k-2e	−7.647	4.06×10^5	−5.609	−0.319	1.714	−0.234
3k-3e	−9.900	1.82×10^7	−7.261	−0.135	1.257	−0.099
4k-4e	−11.392	2.27×10^8	−8.355	−0.168	1.327	−0.123
5k-5e	−5.379	8.80×10^3	−3.945	0.197	0.717	0.144
C_2H_5OH						
1k-1e	−8.278	1.18×10^6	−6.072	−0.067	1.120	−0.049
2k-2e	−7.865	5.87×10^5	−5.768	−0.324	1.728	−0.238
3k-3e	−10.052	2.36×10^7	−7.373	−0.133	1.251	−0.097
4k-4e	−11.469	2.58×10^8	−8.412	−0.182	1.359	−0.133
5k-5e	−5.352	8.43×10^3	−3.926	0.191	0.724	0.140
$CHCl_3$						
1k-1e	−7.935	6.61×10^5	−5.820	−0.060	1.106	−0.044
2k-2e	−9.323	6.88×10^6	−6.838	−0.337	1.768	−0.248
3k-3e	−11.078	1.33×10^8	−8.125	−0.144	1.276	−0.106
4k-4e	−11.956	5.88×10^8	−8.769	−0.213	1.432	−0.156
5k-5e	−5.142	5.91×10^3	−3.772	0.159	0.764	0.117
C_6H_{12}						
1k-1e	−7.277	2.17×10^5	−5.337	−0.064	1.115	−0.047
2k-2e	−10.747	7.62×10^7	−7.882	−0.313	1.696	−0.229
3k-3e	−12.082	7.27×10^8	−8.862	−0.078	1.141	−0.057
4k-4e	−12.392	1.23×10^9	−9.089	−0.262	1.556	−0.192
5k-5e	−4.817	3.41×10^3	−3.533	0.105	0.838	0.077

[a] Process; **k** form ⇌ **e** form. Calculated in equality.
[b] $\delta\Delta G_f$; $\delta\Delta G_f = \Delta G_{f(e)} - \Delta G_{f(k)}$.
[c] K_{Tf}; $K_{Tf} = e^{(-\delta\Delta Gf/RT)}$. Calculated in equality.
[d] $pK_{T(f)}$; $pK_{T(f)} = -\log K_{Tf}$ Calculated in equality.
[e] $\delta\Delta G$; $\delta\Delta G = \Delta G_{(e)} - \Delta G_{(k)}$. Calculated in equality.
[f] K_T; $K_T = e^{(-\delta\Delta G/RT)}$. Calculated in equality.
[g] pK_T; $pK_T = -\log K_T$. Calculated in equality. $R = 1.987 \times 10^{-3}$ kcal mol^{-1} K ve $T = 298$ K (the plus sign indicates the stability of keto form).

Table 9
The PM6 and experimental tautomeric equilibrium constants (K_T) in different solvents.

Compounds no	Experimental tautomeric equilibrium constants	Calculated tautomeric equilibrium constants					
	$K_{T(exp.)}$	$\delta\Delta G_f$	K_{Tf}	pK_{Tf}	$\delta\Delta G$	K_T	pK_T
DMSO							
1	56.20	−8.313	1.25×10^6	−6.097	−0.062	1.111	−0.046
2	56.60	−7.647	4.06×10^5	−5.609	−0.319	1.714	−0.234
3	57.80	−9.900	1.82×10^7	−7.261	−0.135	1.257	−0.099
4	54.90	−11.392	2.27×10^8	−8.355	−0.168	1.327	−0.123
5	0.15	−5.379	8.80×10^3	−3.945	0.197	0.717	0.144
C_2H_5OH							
1	8.40	−8.278	1.18×10^6	−6.072	−0.067	1.120	−0.049
2	–	−7.865	5.87×10^5	−5.768	−0.324	1.728	−0.238
3	–	−10.052	2.36×10^7	−7.373	−0.133	1.251	−0.097
4	1.60	−11.469	2.58×10^8	−8.412	−0.182	1.359	−0.133
5	5.80	−5.352	8.43×10^3	−3.926	0.191	0.724	0.140
$CHCl_3$							
1	3.30	−7.935	6.61×10^5	−5.820	−0.06	1.106	−0.044
2	–	−−9.323	6.88×10^6	-6.838	−0.337	1.768	−0.248
3	55.90	−11.078	1.33×10^8	−8.125	−0.144	1.276	−0.106
4	2.40	−11.956	5.88×10^8	−8.769	−0.213	1.432	−0.156
5	–	−5.142	5.91×10^3	−3.772	0.159	0.764	0.117
C_6H_{12}							
1	–	−7.277	2.17×10^5	−5.337	−0.064	1.115	−0.047
2	–	−10.747	7.62×10^7	−7.882	−0.313	1.696	−0.229
3	6.90	−12.082	7.27×10^8	−8.862	−0.078	1.141	−0.057
4	–	−12.392	1.23×10^9	−9.089	−0.262	1.556	−0.192
5	54.20	−4.817	3.41×10^3	−3.533	0.105	0.838	0.077

4. Conclusion

The structures of the synthesized compounds in the present study have been characterized by elemental analysis, FTIR, ^{1}H and ^{13}C NMR spectroscopic techniques. The structures of compounds synthesized were also determined using the HETCOR and HMBC spectroscopic techniques.

The tautomeric equilibrium constants of the compounds were calculated experimentally and theoretically in different solvent media. No meaningful correlation between the experimental and the theoretical tautomeric results were observed.

Acknowledgements

We are grateful to Medicinal Plants and Medicine Research Center of Anadolu University Eskişehir (Turkey) for NMR and 2D NMR spectrums and to Anadolu University for ChemOffice 2010 program. We are also grateful for MOPAC2009 free package program.

References

[1] C.P. Johnson, J.L. Atwood, J.W. Steed, C.B. Bauner, R.D. Rogers, Inorg. Chem. 35 (1996) 2602–2610.
[2] N. Alizadeh, S. Ershad, H. Naeimi, H. Shargi, M. Shamsipur, Pol. J. Chem. 73 (1999) 915–925.
[3] A.A. Alemi, B. Shaabani, Acta Chim. Slov. 47 (2000) 363–369.
[4] H. Naeimi, K. Rabiei, F. Salimi, Dyes Pigments 75 (2007) 294–297.
[5] J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena, Coord. Chem. Rev. 119 (1992) 67–88.
[6] A. Elmalı, M. Kabak, E. Kavlakoğlu, Y. Elerman, T.N. Durlu, J. Mol. Struct. 510 (1999) 207–214.
[7] W. Zeng, J. Li, Z. Mao, Z. Hong, S. Qin, Adv. Synth. Catal. 346 (11) (2004) 1385–1391.
[8] Z. Hayvali, N. Gunduz, Z. Kilic, E. Weber, J. Prakt. Chem. 341 (6) (1999) 568–573.
[9] X. Wei, Z. Mao, J. Li, S. Qin, Synthetic Commun. 34 (2004) 1237–1246.
[10] H. Keypour, P. Arzhangi, N. Rahpeyma, M. Rezaeivala, Y. Elerman, H.R. Khavasi, Inorg. Chim. Acta 367 (2011) 9–14.
[11] L. Shi, H.M. Ge, S.H. Tan, H.Q. Li, Y.C. Song, H.L. Zhu, R.X. Tan, Eur. J. Med. Chem. 42 (2007) 558–564.
[12] S.M. Abdallah, G.G. Mohamed, M.A. Zayed, M.S. Abou El-Ela, Spectrochim. Acta Part A 73 (2009) 833–840.
[13] D.M. Boghaei, S. Mohebi, Tetrahedron 58 (2002) 5357–5366.
[14] M.L.P. Santos, A. Faljoni-Alario, A.S. Mangrich, A.M.C. Ferreira, J. Inorg. Biochem. 71 (1–2) (1998) 71–78.
[15] S. Arunachalam, N.P. Priya, C. Jayabalakrishnan, V. Chinnusamy, Spectrochim. Acta Part A 74 (2009) 591–596.
[16] C. Hazneci, K. Ertekin, B. Yenigul, E. Cetinkaya, Dyes Pigments 62 (2004) 35–41.
[17] S.R. Salman, F.S. Kamounah, Spectrosc. Lett. 35 (2002) 327–335.
[18] J.-C. Zhuo, Magn. Reson. Chem. 37 (1999) 259–268.
[19] S.H. Alarcon, A.C. Olivieri, G.R. Labadie, R.M. Cravero, M. Gonzalez-Sierra, Tetrahedron 51 (1995) 4619–4626.
[20] S.H. Alarcon, D. Pagani, J. Bacigalupo, A.C. Olivieri, J. Mol. Struct. 475 (1999) 233–240.
[21] Z. Rozwadowski, T. Dziembowska, A. Filarowski, P.E. Hansen, Magn. Reson. Chem. 39 (2001) 67–80.
[22] Z. Rozwadowski, W. Schilf, B. Kamienski, Magn. Reson. Chem. 43 (2005) 573–577.
[23] Z. Hayvali, D. Yardimci, Transition Met. Chem. 33 (2008) 421–429.
[24] Z. Hayvali, N. Gunduz, Z. Kilic, E. Weber, Z. Naturforsch 55b (2000) 975–981.
[25] Z. Hayvali, M. Hayvali, Z. Kilic, T. Hokelek, E. Weber, J. Incl. Phenom. Macrocycl. Chem. 45 (2003) 285–294.
[26] M. Hayvali, Z. Hayvali, Synth. React. Met. Org. Chem. 34 (2004) 713–732.
[27] H. Unver, M. Yildiz, N. Ocak, T.N. Durlu, J. Chem. Crystallogr. 38 (2008) 103–108.
[28] S. Sharif, D.R. Powell, D. Schagen, T. Steiner, M.D. Toney, E. Fogle, H.H. Limbach, Biochemistry 38 (1999) 311–320.
[29] M. Yildiz, H. Unver, D. Erdener, N. Ocak, A. Erdonmez, T.N. Durlu, Cryst. Res. Technol. 41 (2006) 600–606.
[30] J. Ribas, C. Diaz, R. Costa, Y. Journauv, C. Mathoniere, O. Kahn, A. Gleizes, Inorg. Chem. 29 (1990) 2042–2047.
[31] G. Türkoğlu, 'Synthesis of Some Diphenolic Schiff Base Compounds and Their Structural Characterization' Master of Science Thesis, Anadolu University, Sciences Institute, Eskişehir, Turkey, (2007).
[32] J.P. Dutasta, J.P. Declercq, C.E. Calderon, B. Tinant, J. Am. Chem. Soc. 111 (18) (1989) 7136–7144.
[33] H.H. Freedman, J. Am. Chem. Soc. 83 (1961) 2194–2195.
[34] M. Yıldız, Z. Kılıç, T. Hökelek, J. Mol. Struct. 441 (1998) 1–10.
[35] MOPAC2009, James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO. USA. http://OpenMOPAC.net (2008).
[36] CS Chemoffice Pro for Microsoft Windows, Cambridge Scientific Computing, Inc. 875 Massachusetts Avenue, Suite 61, Cambridge, MA 2139, USA.