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Spectroscopic Properties of 2,2′-[Thiobis(P-Phenylenenitrilomethylidyne)]Bis(4-Chloro/Bromo/Methyl/Nitro/Methoxy)Phenol

2,2′-[Tiyobis(P-Fenilennitrilometilidin)]Bis(4-Kloro/Bromo/Metil/Nitro/Metoksi)Fenol'ün Spektroskopik Özellikleri

Research Article

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ABSTRACT

Novel Schiff base has been synthesized from the reaction of 4,4′-diaminodiphenyl sulfide with 2-hydroxy-5-substituebenzaldehyde and 2-hydroxynaphtaldehyde. The compounds were characterized by elemental analysis, FT-IR, ^{1}H NMR,^{13}C NMR. The UV-visible spectra of the compounds were studied in polar and nonpolar solvents in acidic and basic media. İt is point out that the enol-imine tautomer is dominant only in the solution form the compound 1a-e.

Key Words
Schiff base, Diamine compounds, Benzaldehyde, Keto-enol tautomer

ÖZET

4,4′-diaminodifenil sülfit ile 2-hidroksi-5-sübstitüebenzaldehit ve 2-hidroksinaftaldehitin tepkimesi ile yeni Schiff bazları sentezlendi. Bileşiklerin yapıları elementel analiz, FT-IR, ^{1}H NMR, ^{13}C NMR ile aydınlatıldı. Bileşiklerin polar ve apolar çözücülerdeki asidik ve bazik ortamlardaki UV-vis. spektrumları incelendi. UV-vis. sonuçlarına göre çözücü ortamında enol-imin tautomerinin daha baskın olduğu görüldü.

Anahtar Kelimeler
Schiff bazı, Daimin bileşikleri, Benzaldehit, Keto-enol tautomer

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INTRODUCTION

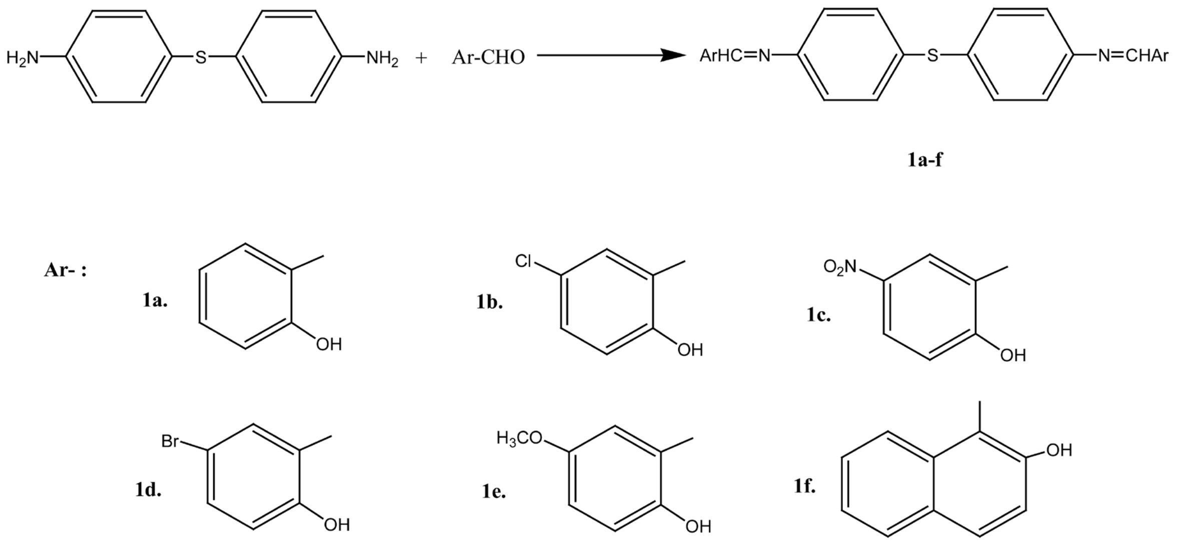
It has well been documented that Schiff bases are important in diverse fields of chemistry and biochemistry owing to their biological activities [1,2]. Schiff bases derived from aromatic o-hydroxy aldehydes, such as salicylidenanilines, may exist either as a single tautomer or a mixture of two in equilibrium: a cis-quinonoid structure (enamine or keto tautomer) characterized by an O/H• • •N intramolecular hydrogen bonding and a benzenic structure (imine or enol tautomer) possessing the alternative O• • •H/N intramolecular bonding. The presence of ortho hydroxyl group, for instance, has been regarded as one of the importance elements which favours for the existence of intramolecular hydrogen bonding (O–H• • •N and O• • •H–N) and also the tautomerism which accounts for the formation of either enol-imino or keto-amino tautomer[3]. In the field of coordination chemistry, this type of ortho hydroxylated Schiff bases has received an overwhelming attention particularly on the study of complex formation [4–7]. Schiff bases derived from aromatic o-hydroxyaldehydes are well known models for the study of keto–enol tautomerism as well as proton transfer mechanisms [8–11]. Proton transfer equilibrium is considered to have a major impact on the physicochemical properties of these compounds (e.g. thermochromism and photochromism) [12–14]. The tautomeric form can be altered by introduction of electron withdrawing/donating substituent (s) on the salicylidene ring [15]. Several spectroscopic methods have been employed for the characterization of keto–enol tautomerism such as IR [16], UV–vis [17], Raman [18], ^{1}H and ^{13}C NMR spectroscopy [19], mass spectrometry [29], spectrophotometry [30] and HPLC [31]. Recently, Gilli et al. reported the X-ray crystallographic structures of keto–enol tautomers and their H-bonding effects [23,24]. Kenar et al. synthesized long-chain b-diketone compounds and investigated their keto–enol tautomeric equilibrium [25].

EXPERIMENTAL

All carbonyl compounds and other chemicals were purchased from Merck and Aldrich. All melting points were determined in sealed capillaries and are uncorrected. FT-IR spectra were recorded on a Nicolet 6700 FT-IR Spectrometer with ATR. 1H-NMR spectra were recorded on a Varian Gemini 400 (400 MHz) NMR spectrometer in d6-DMSO. The UV-vis spectra were measured using a SHIMADZU 1208 series spectrometer. Carbon, nitrogen and hydrogen analyses were performed by using a LECO CHNS-932 analyzer.

NMR measurements

Spectra of 10 mg/mL in d6-DMSO solutions for ^{1}H and ^{13}C, with TMS as an internal reference, in 2.5 mm or 5.0 mm o.d. tubes, were recorded on a



Scheme 1. Synthesis of imine compounds.

Bruker AVANCE spectrometer equipped with a 2.5 mm direct probe with z-field gradient operating at 400 MHz (^{1}H) and 100 MHz (^{13}C) or on a Bruker AVANCE DRX 400 MHz spectrometer.

FT-IR Spectroscopy

The FT-IR data of the compound are given in synthetic procedures. Except that 1a compound, the vibration bands with the wave numbers of 3645, 3612, 3603, 3611, 3602 (γO-H). 3074, 3084, 3084, 3060 (γC-H, Ar-H), 1613, 1614, 1614, 1613, 1617(γCH=N) were observed for he compound, respectively. The C=N bond which is accountable partially for the existence enol-imine form can also be inferred from the FT-IR spectra of the compound.

Uv-visible Spectroscopy

The Uv-visible spectrum of the compound was studied in polar and nonpolar solvents in both acidic and basic media. The Schiff bases show absorption in the range greater than 350 nm in polar and nonpolar solvent [26, 27]. Compound 1a-d showed no absorption above 400 nm in polar and nonpolar solvents. However, the band was observed with value greater than 400 nm in basic solutions of DMF and ethanol. Compound 1a-d showed no absorption above 400 nm in basic solutions of benzene and acetonitrile. It can be pointed out that the new band belongs to the keto-amine form of the Schiff bases with OH group in ortho position to the imine group in DMF and ethanol. The Uv-visible spectra of 1f was studied in same solutions both in acidic and basic media. This compound (1f) show absorption in the range greater than 400 nm in polar and nonpolar solvents. It is pointed out that the new band belongs to the keto-amine form of the this compound with OH group in ortho position to the imino group in polar and nonpolar solvents in both acidic and basic media. So the enol-imine tautomer is dominant only in the solution form the compound.

^{1}H NMR and ^{13}C NMR spectroscopy

The ^{1}H NMR and ^{13}C NMR data are given in the experimental section. ^{1}H NMR spectra of 1b-f showed broad peak at 12.78, 13.78, 12.90, 12.27 ppm (Ar-OH), respectively. Imine proton signals are observed 8.97, 9.15, 8.97, 8.94, 9.68 ppm (CH=N), respectively. Aromatic proton signals showed δ 6.60-7.96 ppm. The ^{13}C NMR spectral data on synthesized compounds are also in accordance with the proposed structures. ^{13}C NMR spectra expected number of carbon were observed.

General method for the synthesis of imine compounds

A solution of 4,4′-diaminodiphenyl sülfite (2.16 g, 10 mmol) and the appropriately substituted salycil aldehyde (20 mmol) in anhydrous ethanol (25 mL) was refluxed for 3 h. Then the mixture was cooled at room temperature and then gave a precipitate which was removed by filtration and purified by recrystallization in ethanol.

α,α'-[thiobis(p-phenylenenitrilo)]di-o-Cresol (1a). Yield; 72%, Found : m.p: 215-216 ^{0}C. 215-216 [28]. 216-217 [29],

2,2′-[thiobis(p-phenylenenitrilomethylidyne)] bis(4-chlorophenol) (1b). Yield; 70%, mp : 250-251 ^{0}C, FT-IR (ATR, cm^{-1}) : 3645 (Ar-OH), 3074 (Ar-H), 1613 (CH=N). ^{1}H NMR (d6-DMSO, ppm) : 7.45 (m, 5H, Ar-H), 8.97 (s, ^{1}H, CH=N), 12.78 (b, 1H, Ar-OH). ^{13}C NMR : 116, 117, 120, 121, 123, 130, 133, 147, 152, 154, 162. Anal.Calcd. For $C_{26}H_{18}Cl_2N_2O_2S$: C; 63.29%, H; 3.68%, Cl; 14.37%, N; 5.68%, O; 6.49%, S; 6.50%. Found: C; 63.12%, H; 3.938%, N; 5.43%.

2,2′-[thiobis(p-phenylenenitrilomethylidyne)] bis(4-nitrophenol) (1c). Yield; 63%, mp : 262-264 ^{0}C, FT-IR (ATR, cm^{-1}) : 3612 (Ar-OH), 3084 (Ar-OH), 1614 (CH=N). ^{1}H NMR (d6-DMSO, ppm): 7.44 (m, 5H, Ar-H), 9.15 (s, 1H, CH=N), 13.78 (b, 1H, Ar-OH). ^{13}C NMR: 117, 120, 121, 123, 127, 132, 133, 148, 152, 156, 163. Anal. Calcd. For $C_{26}H_{18}N_4O_6S$: C; 60.70%, H; 3.53%, N; 10.89%, O; 18.66%, S; 6.23%. Found: C; 59.92%, H; 3.71%, N; 10.22.

2,2′-[thiobis(p-phenylenenitrilomethylidyne)] bis (4-bromophenol) (1d).

Yield; 67%, mp : 278-279 °C. FT-IR (ATR, cm^{-1}) : 3603 (Ar-OH), 3084 (Ar-H), 1614 (CH=N). ^{1}H NMR (d6-DMSO, ppm): 7.44 (m, 5H, Ar-H), 8.97 (s, ^{1}H, CH=N), 12.90 (b, 1H, Ar-OH). ^{13}C NMR : 115, 118, 122, 123, 127, 128, 132, 136, 144, 156, 162. Anal.Calcd.For $C_{26}H_{18}Br_2N_2O_2S$: C; 53.63%, H; 3.12%, Br; 27.44%, N; 4.81%, O; 5.50%, S; 5.51 %. Found: C; 53.53%, H; 3.38%, N; 4.49%.

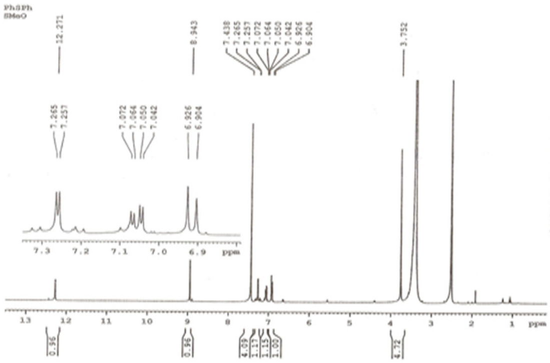


Figure 1. ^{1}H NMR spectrum of the compound 1e.

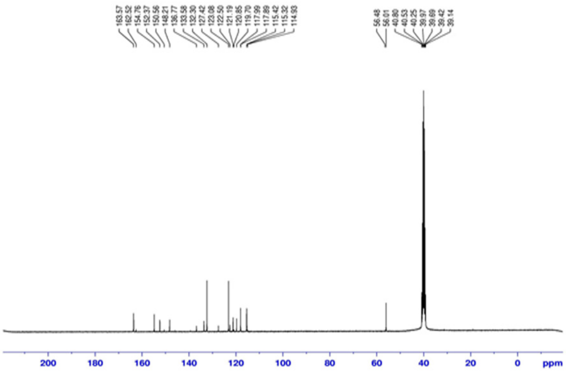


Figure 2. ^{13}C NMR spectrum of the compound 1e.

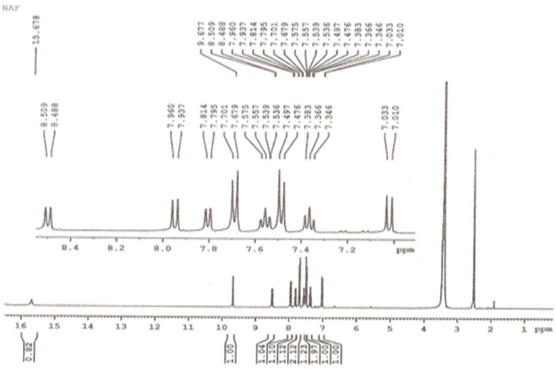


Figure 3. ^{1}H NMR spectrum of the compound 1f.

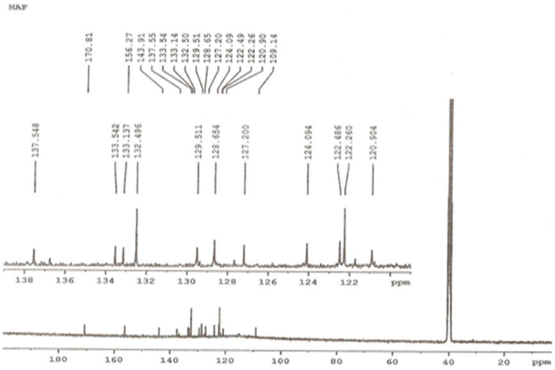


Figure 4. ^{13}C NMR spectrum of the compound 1f.

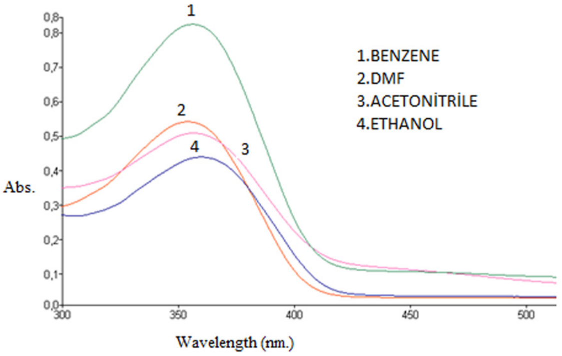


Figure 5. UV-vis. Spectrum of the compound 1c in different solvents.

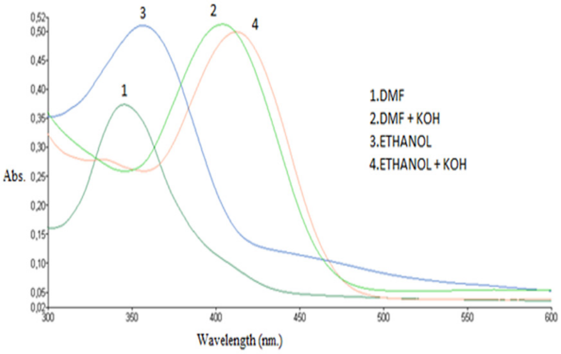


Figure 6. Base effect on compound 1d.

2,2′-[thiobis(p-phenylenenitrilo-methylidyne)]bis(4-methylphenol) (1e).

Yield; 73%, mp: 197-199 ^{0}C. FT-IR (ATR, cm^{-1}): 3611 (Ar-OH), 3060 (Ar-H), 1613 (CH=N). ^{1}H NMR (d6-DMSO, ppm) : 3.75 (s, 3H, OCH_3), 7.17 (m, 5H, Ar-H), 8.94 (s, 1H, CH=N), 12.27 (b, 1H, Ar-OH). ^{13}C NMR : 56, 115, 117, 119, 121, 123, 132, 133, 148, 152, 154, 163. Anal. Calcd.For $C_{28}H_{24}N_2O_4S$: C; 69.40%, H; 4.99%, N; 5.78%, O; 13.21%, S; 6.62%. Found: C; 69.42%, H; 5.04%, N; 5.56%.

1,1′-[thiobis(p-phenylenenitrilomethylidyne)] di-2-Naphthol (1f).

Yield; 67%, Found. mp: 228-230 ^{0}C. mp: 227 ^{0}C [29]. ^{1}H and ^{13}C NMR we found different. FT-IR (ATR, cm^{-1}): 3602 (Ar-OH), 3061 (Ar-H), 1617 (CH=N). ^{1}H NMR (d6-DMSO, ppm) : 7.48 (m, 8H, Ar-H), 9.68 (s, 1H, CH=N), 15.68 (b, 1H, Ar-OH). ^{13}C NMR: 109, 120, 122, 122, 123, 124, 127, 128, 129, 132, 133, 133, 137, 156, 170.

Table 1. Influence of solvent on λmax. of compound 1a-f.

Cmp. no	DMF	(DMF+KOH)	Acetonitrile	Benzene	Ethanol	(Ethanol+KOH)
1a	356	392	356	359	363	389
1b	359	394	362	371	360	392
1c	354	394	356	361	358	394
1d	345	403	355	370	356	412
1e	356	397	358	393	358	397
1f	389	453	393	404	397	458

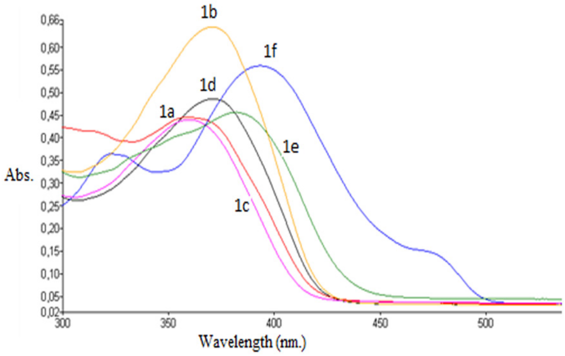


Fig. 7. UV-vis. Spectrum of the compound 1a-f in benzene.

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