

Synthesis, Spectral, and Thermal Analysis of a new Schiff-base Derived from Terephthalaldehyde

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ABSTRACT

A Schiff bases were prepared by the condensation of 1,4-terephthalaldehyde with aromatic amine and characterized by spectroscopic techniques namely IR, HNMR and EI-mass. the results revealed the condensation between aldehyde and amine in 1:2 molar ratio. The thermal stability and kinetic parameters were studied by TG/DTA analysis and the Coats- Redfern methods was applied to evaluate the activation energy (E), enthalpy of activation (ΔH), entropy of activation (ΔS) and Gibbs free energy (ΔG)

Keywords: Coats- Redfern, Schiff base, Terephthalaldehyde, Thermal Analysis.

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INTRODUCTION

Schiff bases, also known as azomethine -imine are condensation products of carbonyl compounds and primary amines.¹ Schiff bases show a broad range of biological activities such as antibacterial, antifungal, anti-inflammatory etc.²⁻⁵ Schiff bases have ability as a ligand due to the presence of lone pair of electrons on nitrogen atoms of azomethane group and behave as a Lewis base in donating an electron pair to a metal atom in the formation of a coordination compound.⁶

MATERIALS AND METHODS

Materials

All solvents employed in synthesis were of extra pure and used as received. 1,4-terephthalaldehyde, and 4-Amino azo benzene were obtained from Merck, 4-Aminobenzoic acid and 5-nitro-2-hydroxy aniline from BDH company.

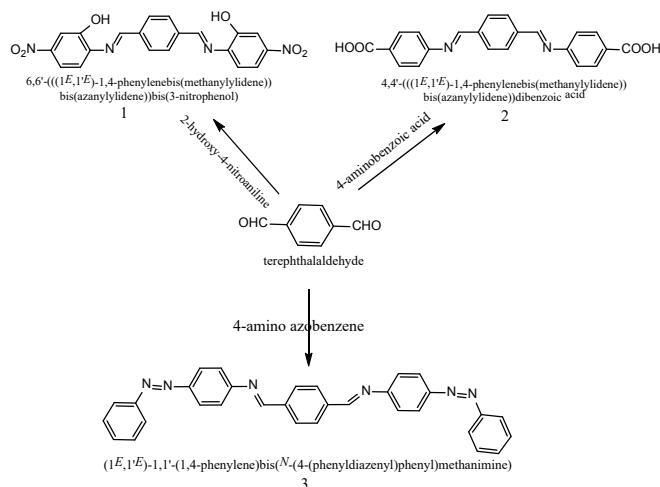
Instruments

IR spectra were recorded on a Shimadzu FT-IR 8400s spectrophotometer as a KBr pellet. The H NMR spectra were recorded at room temperature on (Bruker, 500 MHz), in DMSO-d₆ and TMS as the internal reference. EI-mass (70 eV) were recorded on Agilent Technologies 5973C. The thermal analyses (TG) were conducted in dynamic N₂ atmosphere (20 mL/min) from room temperature to 600°C with heating rate 10°C/min using a perkin-Elmer Thermal Analyzer.

Synthesis Methods

Preparation of Schiff Bases (1-3)

The Schiff bases (1-3) were synthesized by the condensation of 1,4-terephthalaldehyde with different aromatic amine in molar ratio 1:2 by refluxing in absolute ethanol. The reaction proceeded smoothly producing the corresponding Schiff bases in good yield. The synthesis of Schiff bases was performed in accordance with reaction Scheme 1.



Scheme 1: Synthesis of compounds

Synthesis of 6,6'-(((1E,1'E)-1,4-phenylenebis(methanylylidene)) bis(azanylylidene))bis(3-nitrophenol)(1)

2 mmole of 5-nitro-2-hydroxy aniline was add to 1 mmole of hot ethanolic solution of 1,4-terephthalaldehyde, the resulting mixture was reflexed for 3 hours and solid precipitate which obtained filtered hot and washed with warm ethanol several times and dried at 50°C, the product is light yellow scales, m.p.=325°C, yield 78%, EI-mass m/z= 406 (M⁺).

Synthesis of 4,4'-(((1E,1'E)-1,4-phenylenebis(methanylylidene)) bis(azanylylidene))dibenzoic acid(2)

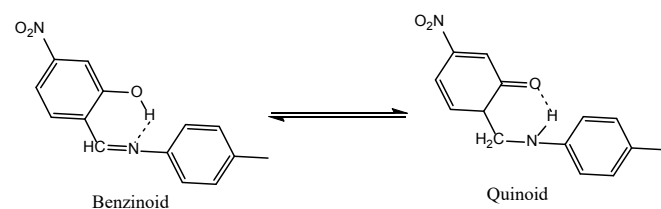
2 mmole of 4-Aminobenzoic acid was add to 1 mmole of hot ethanolic solution of 1,4-terephthalaldehyde (25 mL), the resulting mixture was reflexed for 2.5 hrs and the reaction monitored by TLC(ethyl acetate :benzene 6:4).the mixture was filtered and the yellow solid was collected and recrystallized from hexane to give a pale yellow solid with m.p.=407°C, yield 63%, EI-mass m/z= 372 (M⁺).

Synthesis of (1E,1'E)-1,1'-(1,4-phenylene)bis(N-(4-phenyldiazenyl)phenyl)methanimine(3)

2 mmole of 4-Amino azo benzene added to 1 mmole of hot ethanolic solution of 1,4-terephthalaldehyde and the mixture was reflexed for 4.5 hours and the orange precipitated which obtained was filtered hot and recrystallized from ethyl acetate to give an orange crystals m.p.=250–251°C, yield 63%, EI-mass m/z= 492(M⁺).

RESULTS AND DISCUSSION

The prepared compounds are stable and non-hygroscopic with high melting points, insoluble in common organic solvents such ethanol, methanol, benzene, chloroform at room temperature,



Scheme 2: Benzenoid -Quinoid tautomerization

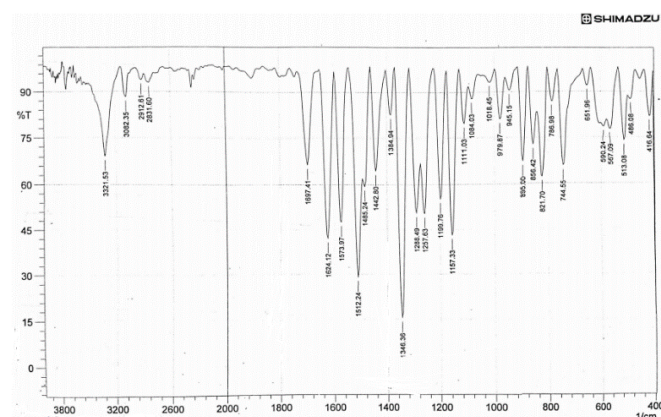


Figure 1: FT-IR spectrum of compound (1)

and springily soluble in hexane, ethyl acetate, but very soluble in DMF and DMSO.

I.R Spectra

The IR spectrum of compound (1) (Figure 1)show a very strong band at ν 1624 cm^{-1} attributed to stretching vibration of (HC=N) and indicate the formation Schiff base the strong band at ν 1697 cm^{-1} together with that at ν 1624 cm^{-1} and the broad band at ν 3321 cm^{-1} indicated the presence of the two form benzenoid and quinoid form (Scheme 2).^{1,7}

the IR spectrum of compound (2) show also the very strong band at ν 1605 cm^{-1} attributed to stretching vibration of (HC=N) and a very strong band at ν 1681 cm^{-1} attributed to ν (C=O) stretching of carboxylic group.

the IR spectrum of compound (3) show strong band at ν 1616 cm^{-1} attributed to C=N and a moderate band at ν 1485 cm^{-1} which may be attributed to N=N stretching.⁸

Mass Spectra Analysis:

The mass spectra of all prepared compounds show the molecular ions and confirms the proposed formula where the condensation reaction between the 1,4-terephthalaldehyde condensed with amins in 2:1 molar ratio (Figure 2).

¹H-NMR Spectra

The HNMR spectrum of compound (1) (Figure 3) shows a signal at δ 8.91 ppm which attributed to azomethane proton,

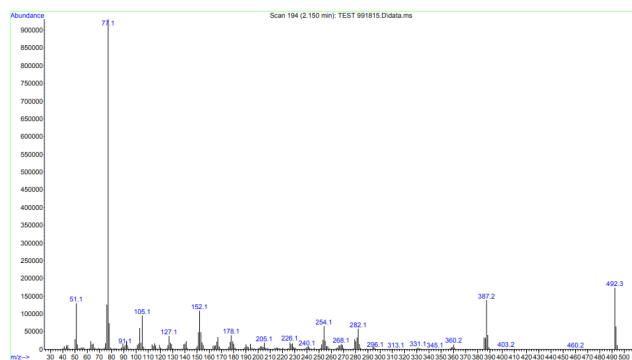


Figure 2: The mass spectrum of synthesized compounds (3)

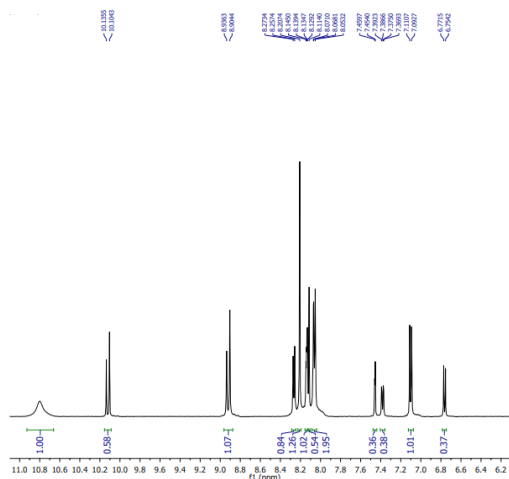
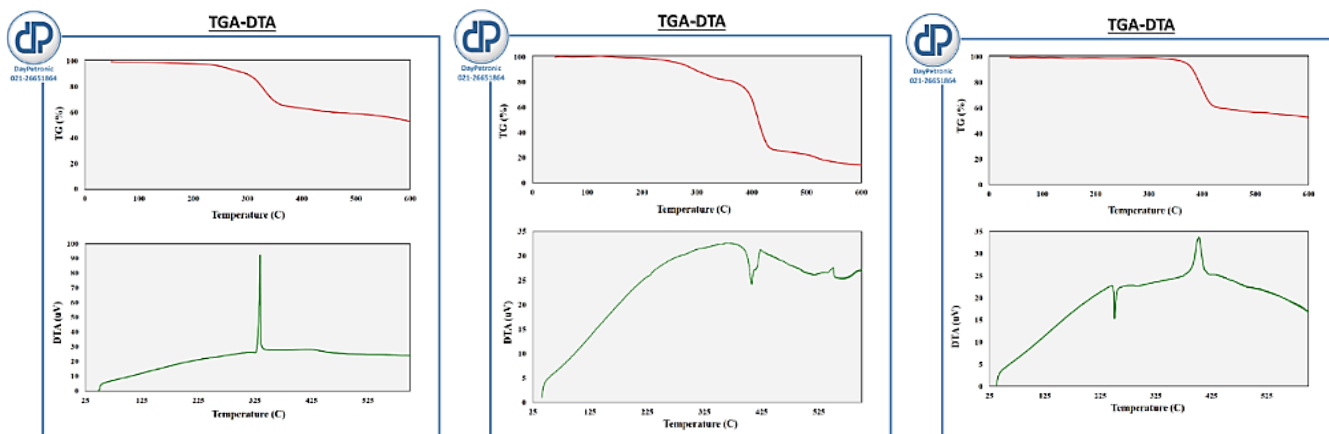


Figure 3: The ¹H NMR spectrum of compound (1)

Table 1: TG data and kinetic parameters of the complexes using the Coats-Redfern equation

Complex	Step	A (S ⁻¹)	E (KJmol ⁻¹)	ΔH (KJmol ⁻¹)	ΔS (KJmol ⁻¹ K ⁻¹)	ΔG (KJmol ⁻¹)	r
1	1 st	5.334289	45.82907	40.78247	-0.2369	184.5817	0.963
2	1 st	4.100291	47.90864	42.2468	-0.24005	205.7177	0.961
3	1 st	767687.5	113.7746	109.4181	-0.13693	181.1714	0.950


Figure 4: TG -. DTA curves of synthesis compounds (1-3)

two signal was observed in the region at δ 10.1–10.8 ppm which may be attributed to free OH proton and broad signal at δ 10.8 ppm which may be attributed to bonded OH.^{2,9} The aromatic protons appear in the expected region (7.1–8.2)ppm equivalent to 10 proton which confirm the 1:2 condensation of aldehyde with amine.

The HNMR spectrum of compound (2) shows a signal at δ 12.84 ppm which attributed to proton of carboxylic group, also a sharp signal at δ 8.7 ppm confirms the formation of Schiff base, the aromatic protons appear in the region δ 7.3–8.17 ppm.

Thermal Analysis

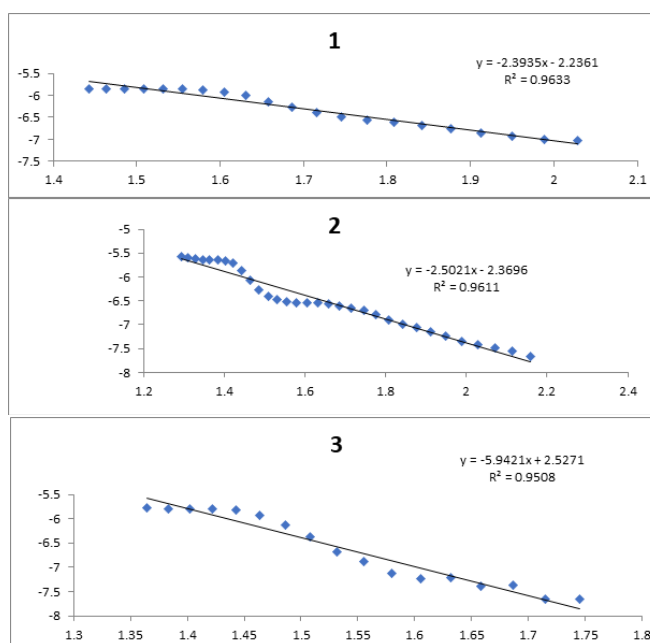
The TG/DTA analysis for the compounds were carried out within the temperature range from room temperature to 600°C under nitrogen atmosphere. The TG curve of compound (1) (Figure 4) shows no loss until ~200°C and then the compound began to decompose as indicated by the sharp exothermic peak in DTA at ~325°C.

The TG curve of compound (2) (Figure 5) shows no weight loss until ~200°C and then the first mass loss of about 20% which may be attributed to dehydration process as indicated by small broad peak above 300°C in DTA curve, after that the decomposition of compound continue to remain about 20%.

The TG curve of compound (3) (Figure 6) the high stability where no mass loss up 300°C. The first sharp endothermic peak in DTA curve at 250°C attributed to melting point and the second exothermic peak at ~410°C for the decomposition.

To describe the thermal stability of the compounds the thermodynamic parameters were calculated by using an integral method (Coats-Redfern).¹⁰

$$\ln \left[-\frac{\ln(1-\alpha)}{T^2} \right] = -\frac{E_a}{RT} + \ln \left[\frac{AR}{\beta E_a} \right] \quad [1]$$


Figure 5: Coats–Redfern plots for major decomposition of synthesis compounds 1, 2 and 3

where α represents the decomposed fraction at temperature T in kelvin, β is the heating rate, A is a Arrhenius factor, E is the activation energy and R is the gas constant ($R=8.314 \times 10^{-3}$ KJ/mol K).

A plot of the left-hand side of Coats-Redfern equation versus $1000/T$ shows a best fit for first-order reaction kinetics.¹¹ The slope which obtained from the straight line equation (Figure 7). The slope equal E/R the Arrhenius factor was determined from the intercept, $\Delta S, \Delta H$, and ΔG have been calculated by using the following relation.¹²

$$\Delta S = R \ln \left(\frac{A h}{k T} \right) \quad [2]$$

Where h is plank constant (6.66×10^{-34} J.S), K is Boltzmann constant (1.3806×10^{-23} J/K)

$$\Delta H = \Delta E - RT \quad [3]$$

$$\Delta G = \Delta H - T\Delta S \quad [4]$$

The high value of activation confirm the high thermal stability and compound (3) show the highest value (110 KJ/mole) which may be due to high conjugated and linearity of the molecules. The negative value of ΔS and positive values of ΔG indicates the nonspontaneous decomposition. The enthalpy change (ΔH) in all compound is positive which reveal endothermic decomposition processes.¹³ The thermal analysis data are summarized in Table 1.

CONCLUSIONS

Application of Coats-Redfern was employed to determine the thermodynamic parameters, high stability of the prepared compound was shown in the results of thermogravimetric analysis. The spectroscopic data revealed the 2:1 mole ratio (amine-aldehyde).

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