

Quantum -Chemical and Experimental Study of Synthesis a new imine ligand

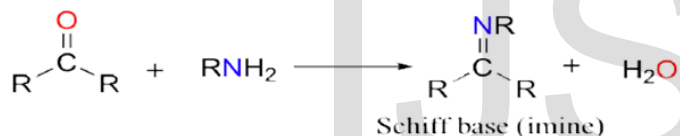
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Abstract— A novel imine ligand TBTM [N,N'-(2,3,5,6-tetramethyl-1,4-phenylene)bis (1-(thiophen-2-yl)methanimine)] which has not been described in the literature Previously was synthesized by the condensation reaction of 2,3,5,6-tetramethylbenzene-1,4-diamine(TMBA)with thiophene-2-carbaldehyde (ThCA) then it was investigated using the density functional theory (DFT/B3LYP(6-311++ G(2d)) by finding the optimal structures for reacting and resulting compounds and also the calculation of cohesion and reaction energies in addition to the thermodynamic properties of these compounds . The calculations of the characterized thermodynamic functions for this reaction showed that the reaction is endothermic and It is found that the molar ratio of reaction is 1: 2. The analyzing of MO's energies, especially the energies of HOMO and LUMO of the reacting and resulting compounds showed that the formation reaction of this compound is not spontaneously. It is necessary to use a catalyst (as heat or chemical catalysis...etc.) for occurrence the reaction.

Index Terms— DFT, imine,IR , NMR, structure, synthesis, UV-visible.

1 INTRODUCTION

An imine, known as azomethine or Schiff base is a functional group or chemical compound containing a carbon-nitrogen double bond . Imines are a result of reaction between aldehydes or ketones with amines . The electrophilic carbon atoms of aldehydes and ketones can be targets of nucleophilic attack by amines then C=O double bond is replaced by a C=N double bond.



Imines derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, e.g., biological, inorganic and analytical chemistry [1]. Schiff's bases of o-phenylenediamine and its complexes have a variety of applications including biological, analytical [2] and clinical [3]. Aromatic amines catalyze reactions on oxygenation [4,5], hydrolysis [6], electro-reduction [7] and decomposition [8]. Moreover, imines compounds have been extensively used in analytical chemistry for the detection and separation of metal ions [9]. Nowadays DFT is being applied as a computational method for calculating the structural properties of molecular systems; it provides greater accuracy in reproducing the experimental values of molecular geometry, vibrational frequencies, atomic charges, dipole moment ,etc. [10-11].

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2 QUANTUM-CHEMICAL STUDY:

Using a Gaussian 09 package [12] have been carry out the DFT/B3LYP [6-311++G(2d)] [13-14] calculations for the reacting and possible resulting compounds in the reactions of synthesis of a new imine ligand.

2.1 Optimized structures:

The optimized structure parameters [bond lengths(Ao) and bond angles(o)] of reactants and resultants were obtained using quantum chemical method DFT/B3LYP[6-311++G(2d)], GaussView5 and Gaussian09 programs , the optimized structures of reactants and resultants are shown in figure 1.

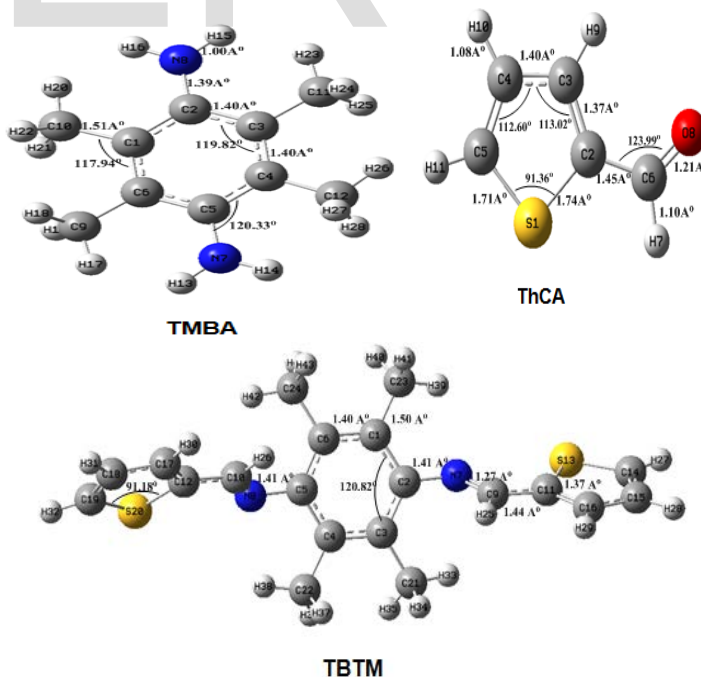


Figure 1: The optimized structures of reactants and resultants

2.

Table 1 :Dipole moment ,total electronic energy (Ei) , energy of highest occupied molecule orbital (εHOMO) , energy of lowest unoccupied molecule orbital (εLUMO) and energy gap (εgap).

compound	Dipole moment In Debye	Energies in KJ/mol			
		E _i	ε _{HOMO}	ε _{LUMO}	ε _{gap}
ThCA	3.682178	-1749718.36	-696.48	-220.33	476.15
TMBA	0.064133	-1313602.04	-418.84	-16.67	402.17
TS	1.038595	-2862624.58	-498.60	-166.71	331.89
H ₂ O	2.163600	-200720.03	-840.02	-61.14	778.88
TBTM	3.086300	-4411600.18	-526.54	-185.28	341.26

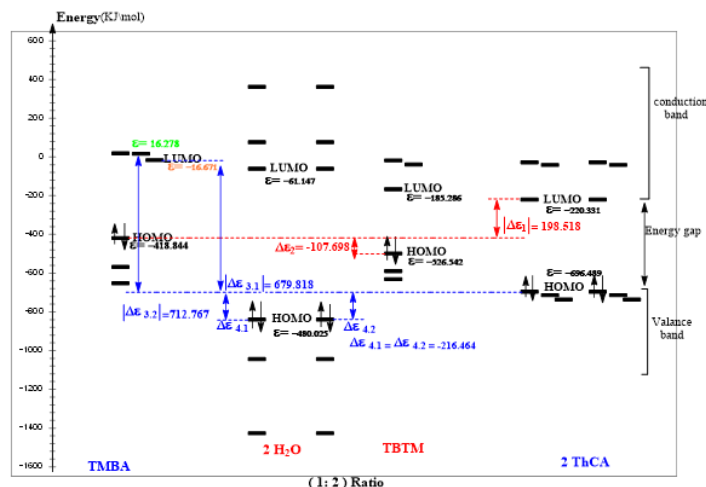


Figure 3: MO's energies for reactants and resultants when the reaction ratio (1: 2).

2. 2 Frontier Molecular Orbitals:

The HOMOs and LUMOs are known as Frontier molecular orbitals (FMOs), which played an important role for evaluating molecular chemical stability, chemical reactivity and the hardness/softness of the molecule [15]. The HOMO acts as an electron donor, while the LUMO is an electron acceptor. The energy gap (ε_{gap}) represents the chemical reactivity of compounds. For a system, a lower value of (ε_{gap}) makes it more reactive or less stable. To judge the spontaneity of the reaction in the liquid state and the stability of the resulting compound, the energies of MO's, especially the energies of HOMO and LUMO of the reactants and resultants was analyzed as in the following figure 2 and figure 3.

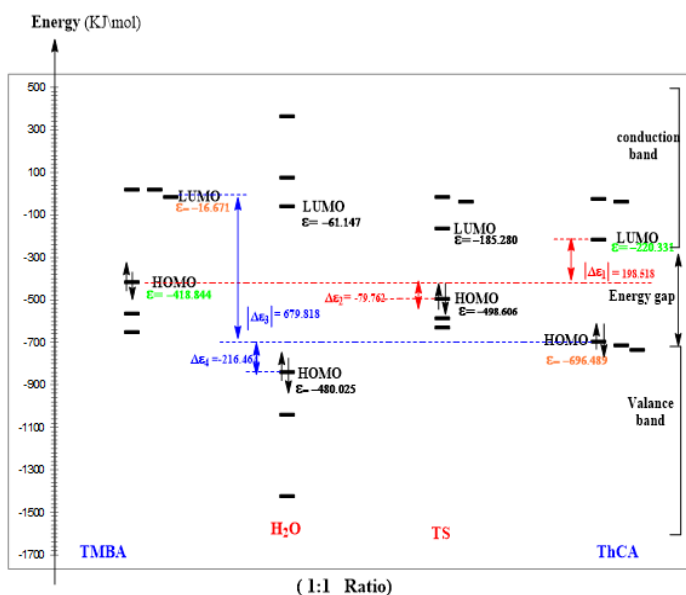


Figure 2: MO's energies for reactants and resultants when the reaction ratio (1: 1).

An analyze of MO's energies, especially the energies of the HOMO and LUMO orbitals in each of the reactants and resultants from the reaction in the ratio of (1: 1), shows that the energy difference between LUMO in ThCA(thiophene-2-carbaldehyde) and HOMO in TMBA(2,3,5,6-tetra methylbenzene-1,4-diamine) is large ($\Delta\epsilon_1 = 198.518$ kJ/mol) and therefore the interactions between them is weak ($\Delta\epsilon_2 = -79.762$ kJ/mol). The energy difference between LUMO in TMBA and HOMO in ThCA is very large ($\Delta\epsilon_3 = 679.818$ kJ/mol) and therefore the interactions between them is very weak ($\Delta\epsilon_4 = -216.464$ kJ/mol). We conclude that the average energy difference between the HOMO and LUMO orbitals in reactants (439.168 kJ/mol) is large and the interactions is weak (-148.113 kJ/mol). This indicates that TBTM can be formed, but the reaction is very slow, so we need hard conditions (temperature ,photo catalyze,.....etc.) to make the LUMO in reactants lower.

In the case of the ratio (2: 1), the energy difference between LUMO in ThCA and HOMO in TMBA is large ($\Delta\epsilon_1 = 198.518$ kJ/mol) and therefore the interactions between them is weak ($\Delta\epsilon_2 = -107.698$ kJ/mol). The energy difference between LUMO in TMBA in ThCA is very large ($\Delta\epsilon_{3.1} = 679.818$, $\Delta\epsilon_{3.2} = 712.767$ kJ/mol) and therefore the interactions between them is very weak ($\Delta\epsilon_{4.1} = -216.464$, $\Delta\epsilon_{4.2} = -216.464$ kJ/mol).

We conclude that the average energy difference between HOMO and LUMO in the reactants (530.367 kJ/mol) is very large and the interactions is very strong (-270.313 kJ/mol) , the comparison of interaction between both cases, indicate to the stability of the resulting compound TBTM (Ratio 2:1), the compound with ratio (1:1) is likely to be the intermediate compound through which the reaction occurs. This explains the use of heating to accelerate the reaction.

2.3 Synthesis reactions:

Table 2 : Energies and enthalpies* of possible reactions.

The reaction	Reaction energy in KJ/mol	
ThCA + TMBA \longrightarrow TS+H ₂ O	ΔH_{R1}	10.32
	ΔE_{R1}	-24.21
TS+ ThCA \longrightarrow TBTM+ H ₂ O	ΔH_{R2}	-1.06
	ΔE_{R2}	+22.73
2ThCA+TMBA \longrightarrow TBTM+2H ₂ O	ΔH_{R}	9.26
	ΔE_{R}	-1.48

(*): $H=EA +KbT$, where EA: total thermal energy.

The values of reaction enthalpies indicate that the reaction is endothermic ($\Delta H_{R} > 0$), while values of reaction energies show that the favorite reaction path is through formation of the intermediate compound (TS) (figure 4).

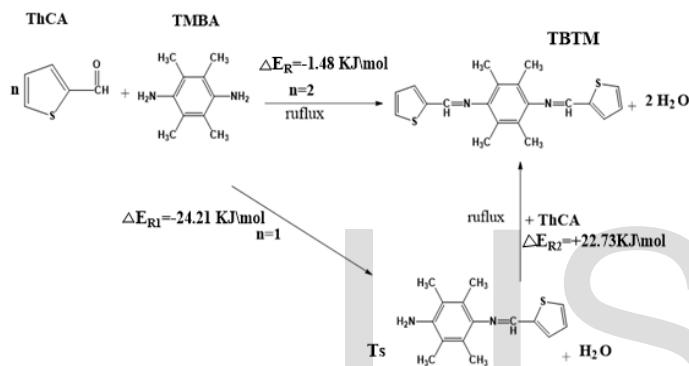
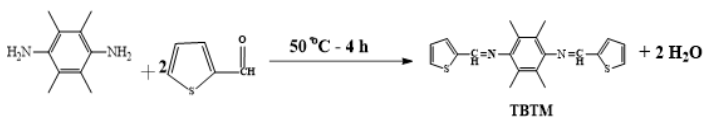


Figure 4: formation mechanism of TBTM.

3. EXPERIMENTAL STUDY:

3.1 Synthesis of imine ligand TBTM :

A warm solution of 2,3,5,6-tetramethylbenzene-1,4-diamine (2 mmol) in (10ml) absolute ethanol was added drop wise into a warm solution of thiophene-2-carbaldehyde (4.4 mmol) in (5ml) absolute ethanol with constant stirring and heating (50 °C) . After the addition of 2,3,5,6-tetramethylbenzene-1,4-diamine was completed, the solution was stirred for 1 hours in room temperature .The resulting solid compound was filtered off, washed with absolute ethanol then dried in vacuum oven. A precipitate is obtained with a yellow crystalline yield of (52%) and a melting point of (212 °C) .



3.2 characterization of reactants and resultants ,by comparison with quantum spectra:

- FT-IR spectrophotometer by theoretical and experimental methods:

The harmonic vibrational frequencies for reactants and resultants were calculated by using (DFT/B3LYP(6-311++ G(2d)) method and measured by experimentally . (Figures 5,6,7,8), (tables 2,3) explain vibration values for the basic functional groups for reactants calculated by theoretical and experimental methods.

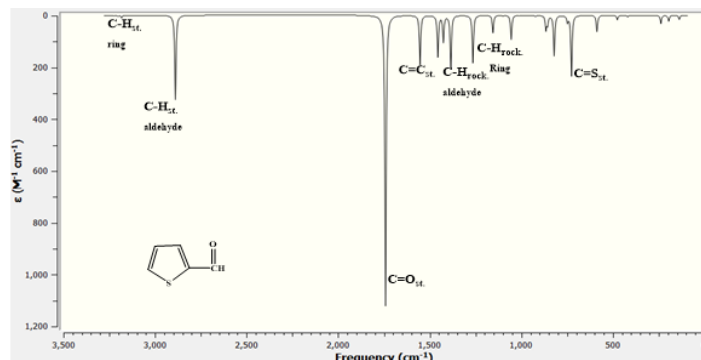


Figure 5: IR spectrum for ThCA by theoretical method.

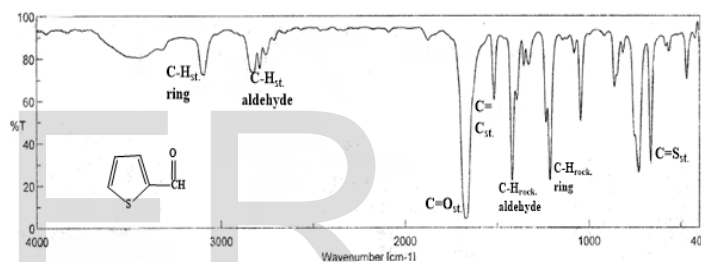


Figure 6: IR spectrum for ThCA by experimental method.

Table 2: Vibrations of ThCA calculated by theoretical and experimental method.

ThCA	Theoretical Value cm ⁻¹	Experimental value cm ⁻¹
C-H _{st} aldehyde	2889	2822
C-H _{rock} aldehyde	1426	1418
C-H _{st} ring	3182	3091
C-H _{rock} ring	1265	1213
C=O _{st}	1741	1671
C=C _{st}	1550	1515
C-S _{st}	588	664

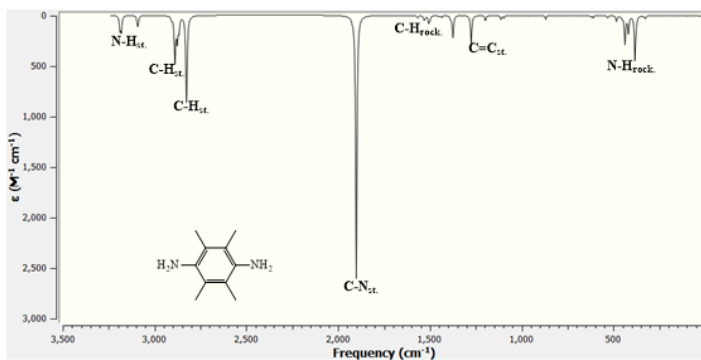


Figure 7: IR spectrum for TMBA by theoretical method.

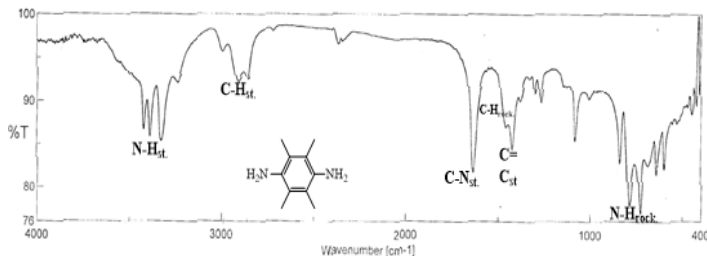


Figure 8: IR spectrum for TMBA by experimental method.

Table 3: Vibrations of TMBA calculated by theoretical and experimental method.

TMBA	Theoretical Value Cm^{-1}	Experimental value Cm^{-1}
N-H _{st}	3190-3180-3090	3424-3389-3327
C-H _{st}	2891-2876-2824	2990-2911-2890
C-H _{rock}	1500	1490
C-N _{st}	1679	1632
C=C _{st}	1275	1423
N-H _{rock}	420-457	787-727

Vibrations of TBTM were calculated by theoretical method and measured by experimental method. (Figures 9,10), (table 4) explain vibration values for the basic functional groups for reactants calculated by theoretical and experimental methods.

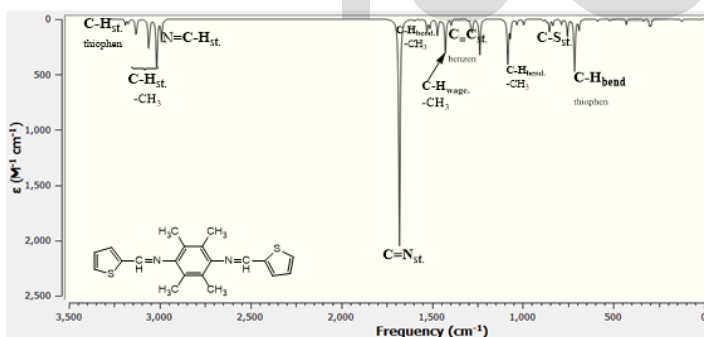


Figure 9: IR spectrum for TBTM by theoretical method.

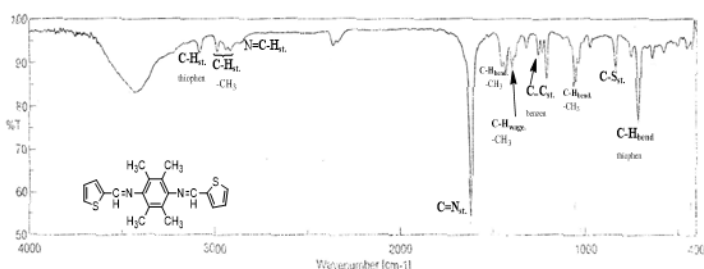


Figure 10: IR spectrum for TBTM by experimental method.

Table 4: Vibrations of TBTM calculated by theoretical and experimental method.

TBTM	Theoretical Value Cm^{-1}	Experimental value Cm^{-1}
C-H _{st} thiophen.	3189	3090
C-H _{bend} thiophen.	714	713
C-H _{st} -CH ₃	3132-3060-3017	2990-2920-2900
C-H _{wag} -CH ₃	1425	1400
C-H _{bend} -CH ₃	1527-1519 1082	1450-1432 1059
-N=C-H _{st}	2990	2840
C=N _{st}	1682	1617
C=C _{st} benzene	1283	1256
C-S _{st}	755	839

From (table 4) we notice converge between theoretical and experimental values for an imine ligand TBTM. It can be seen that the experiment has a better correlation with the calculations.

- Electronic Absorption Spectra by theoretical and experimental methods:

UV-Visible spectra were calculated by theoretical method (figure 11) and measured by experimental method (figure 12) for an imine ligand TBTM.

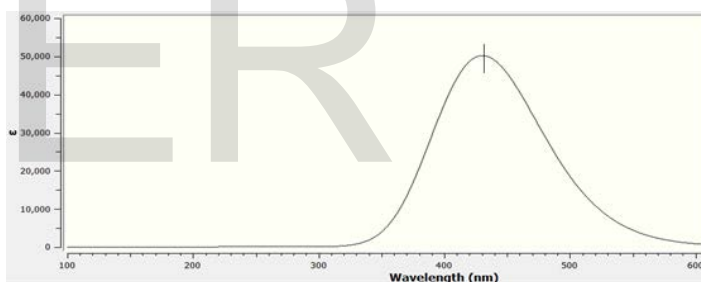


Figure 11: UV spectrum for TBTM by theoretical method.

The spectra of TBTM shows a broad and very strong band and peak at 431 nm which is assigned to a ($n \rightarrow \pi^*$) transition .

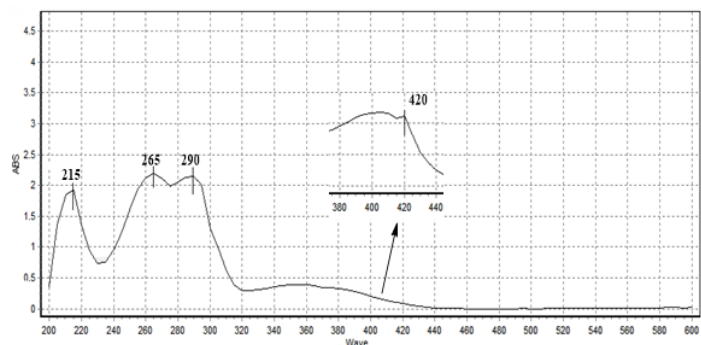


Figure 12: UV spectrum for TBTM by experimental method.

Within the UV spectrum of the ligand TBTM in ethanol shows the existence of 4 absorption bands assigned to the transitions

215 nm ($\pi \rightarrow \pi^*$) transition, 265 nm ($\pi \rightarrow \pi^*$ benzene) transition, 290 nm ($n \rightarrow \pi^*$) transition, 420 nm ($n \rightarrow \pi^*$)

transition due to nitrogen atom and sulfur atom in the compound.

- $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra in DMSO :

In the $^1\text{H-NMR}$ spectrum of the ligand (TBTM) we notice double chemical shifts recognize every two symmetric protons, for example two protons S-CH=CH- (28,31) observed at (7.20-7.23 ppm). The signals of $^{13}\text{C-NMR}$ are consistent with the structure of the ligand (TBTM), nine chemical shifts appeared of nine types of corresponding carbon atoms, for example four carbon atoms of methyl groups observed at (14.52 ppm). Table 5 clears the chemical shifts of proton and carbon atoms.

Table 5: chemical shifts of proton and carbon atoms in $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra.

Chemical shift in ppm, δ		Chemical shift in ppm, δ	
Groups	$^1\text{H NMR}$	Groups	$^{13}\text{C NMR}$
$-\text{CH}_3$ (12 H)	2.00	CH_3 (21,22,23,24)	14.52
S-CH=CH- (28,31)	7.20-7.23 (d,2H)	S-CH=CH- (15,18)	112.38
S-C=CH- (29,30)	7.56-7.64 (d,2H)	S-C=CH- (16,17)	123.76
S-CH=CH- (27,32)	7.75-7.82 (d,2H)	Ar-C- (1,6,3,4)	134.21
N=CH-C-S (25,26)	8.23-8.35 (d,2H)	Ar-C- (2,5)	141.76
		N=CH- (9,10)	149.20
		S-CH=CH- (14,19)	156.12
		N=CH-C-S (11,12)	157.10

4 SUMMARY AND CONCLUSIONS:

In this work, a new imine compound, namely (TBTM) [N,N'-(2,3,5,6-tetramethyl-1,4-phenylene)bis(1-(thiophen-2-yl)methanimine)] has been synthesized and characterized by various techniques including IR, NMR, UV-Vis. The Synthesis of imine ligand TBTM were carried out by the condensation reaction of 2,3,5,6-tetramethylbenzene-1,4-diamine(TMBA) with thiophene-2-carbaldehyde (ThCA). Theoretically, two pathway mechanisms were proposed for this process, which consists of formation of intermediate compound (IS) before the ligand (TBTM) is formed (I) and formation of this ligand directly (II). These two mechanisms were studied with the density functional theory (DFT/B3LYP(6-311++G(2d))). The theoretical calculations demonstrate that Pathway I is a more dominant route than Pathway II.

The DFT/B3LYP theory has been successfully employed to support the experimental findings and to evaluate some important parameters, bond length, bond angle, frequency, Mulliken charge distribution, HOMO-LUMO energy gap (ϵ

gap), etc. The molar ratio of reaction was 1: 2 and the reaction was endothermic and slow, the yield was 52%. Figures may only appear in color for certain journals. Please verify with IJSER that the journal you are submitting to does indeed accept color before submitting final materials.

5 EXPERIMENTAL APPARATUS AND CHEMICALS MATERIALS:

Quantum method (DFT/B3LYP(6-311+G(2d))), GaussView5 and Gaussian09 programs. spectrum NMR proton and carbon device 400 MHz model Bruker by Switzerland company - Atomic Energy Commission Damascus Syria -, optical absorption spectrum infrared device model FT-IR-4100 from the Japanese company Jasco -Al Baath university -, UV/Vis spectroscopy (model: Optizen 2120 UV)- Al Baath university-, thin layer chromatographic of aluminum coated by Silica Gel 60F254 measuring 20 X 20 from the German company Merc.

Table 5: Chemicals Materials

Material	company	Assay %
Thiophene-2-carbaldehyde	Sigma-Aldrich	98
2,3,5,6-tetramethylbenzen-1,4-diamine	Sigma-Aldrich	99
ethanol	BHD	99
dichloromethan	Sigma-Aldrich	98

ACKNOWLEDGMENT

I would like to thank the scientific supervisors for my research, and I especially thank Dr. Mohammed Al- Noaymi for his help in publishing this research.

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