Theoretical Treatment, Microwave Synthesis and Spectroscopic Analysis of New Schiff Bases Derived from 4-Aminoantipyrene

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Abstract. The new Schiff base was obtained compounds (I, II, III, IV) derived from 4-aminoantipyrene were synthesized by using microwave technique. And these Schiff bases were verified by some spectral data (IR, UV). HyperChem release 8.0 program was used to calculate the heat of formation (ΔH°f) binding energy (ΔEb) and dipole moment (µ) for all compounds, also theoretical vibration frequencies and electronic spectra of compounds were calculated.

Key words: Schiff base, 4-Aminoantipyrene, Microwave, 4,4'-Diaminodiphenyl methane

1-Introduction
There are many chemists which are very much focused on the Schiff bases derived from heterocyclic ring with carbonyl compounds. As has been the center of attraction in many areas like biological, clinical, medical, analytical and pharmacological [¹,²]. Play as Schiff bases a central role in the field of coordination chemistry and their metal complexes are of great interest for many years [³-⁵]. Used also for preparation super-conducting [⁶]. There are many methods for synthesis Schiff bases one of this using a microwave technique. Where the synthesis microwave-assisted is a branch of green chemistry. The application of microwave-assist synthesis in organic chemistry continued to develop at an astonishing pace. Microwave irradiated reactions under solvent free or less solvent conditions are attractive contributory, reduced pollution, low cost and offer high yields together with clarity in processing and handling. The most important advantages of microwave approach are shorter reaction times, simple reaction conditions and enhancements in yields [⁷-¹¹]. In this study, we report the synthesis a new Schiff base derived from 4-aminoantipyrene by using microwave techniques.
2. Materials and Methods

2.1 Materials

All chemicals and solvents used in the present work were supplied by Merck, BDH, Fluka and Sigma Aldrich and the thermionic device were used to measure the melting point of all prepared compounds and are uncorrected (Table 1). Also element C.H.N analyzer was carried out on a EM-017. Mth instrument in laboratory of Chemistry Department, College of Science, Al-Muthanna University. The FTIR spectra in the range (4000-400) cm⁻¹were recorded as KBr disc on FT-IR-8000, single beam path laser, Shimadzu Fourier transform infrared spectrophotometer. The spectra were recorded in the laboratory of Chemistry Department, Al-Muthanna University. UV-Visible spectrophotometer in range (200-600) nm. The microwave irradiation was complete using microwave oven-Panasonic. NN-ST300W in the laboratory of Science Department/College of Basic Education/AL-Muthanna University.

2.2 Methods

2.2.1 Synthesis of new Schiff base compounds

All materials were used further purification.

2.2.2 Synthesis of mono-imines [12,13]

The mono-imines (I,II) prepared by the reaction of the mixture of 0.005 mole of 4-aminoantipyrene with 0.005 mole of aldehyde were dissolved in absolute ethanol (15mL). The mixture was irradiated in microwave oven for 1min. and 300W, then cooled at room temperature, a Schiff base. Finally, a suitable solvent is used to recrystallize the products.

- 4-((4-(Chloro)benzylidene)amino)-1,5-dimethyl-2-phenyl-pyrazol-3-one (I): Prepared by reacting 4-aminoantipyrene (1.01gm, 0.005mol) with 4-Chlorobenzaldehyde (0.70gm, 0.005mol). Yield = 81%, m.p = 210-212 °C. IR (υ, cm⁻¹, KBr disk): 1610 (C=N). Recrystallized with ethanol.

- 4-((4-(Dimethylamino)benzylidene)amino)-1,5-dimethyl-2-phenyl-pyrazol-3-one (II): Prepared by reacting 4-aminoantipyrene (1.01gm, 0.005mol) and 4-dimethylamino benzaldehyde (0.74gm, 0.005mol). Yield = 81%, m.p = 246-248 0C. IR (υ, cm-1, KBr disk): 1593 (C=N). Recrystallized with ethanol.

2.2.3 Synthesis of Bis-imines [14,15]

The bis-imines (II) prepared by the reaction of the mixture of 0.001 mole of 4,4'-Diaminodiphenylmethane with 0.002 mole of mono-imine were dissolved in absolute chloroform (15mL). The reaction mixture was irradiated in microwave oven for 2min. And 300W, then cooled at room temperature, a good of Schiff base. Finally, a suitable solvent used to recrystallize the products.

- 3,3'-((methylenebis(4,1-phenylene))bis(azanylylidene))bis(N-(4-chlorobenzylidene)-2,5-dimethyl-1-phenyl-2,3-dihydropyrazol-4-amine)(III):Prepared by reacting 4,4'-Diaminodiphenylmethane (0.198gm, 0.001mol) and compound I (0.65gm, 0.002mol), were dissolved in chloroform (15mL). Yield = 86%, m.p = 190-192 °C. IR (υ, cm⁻¹, KBr disk): 1651 (C=N). Recrystallized with ethanol.

- 3,3'-((methylenebis(4,1-phenylene))bis(azanylylidene))bis(N-(4-dimethyl amino)benzylidene)-2,5-dimethyl-1-phenyl-2,3-dihydropyrazol-4-amine)(IV): Prepared by reacting 4,4'-Diaminodiphenylmethane (0.198gm, 0.001mol) and compound II (0.66gm, 0.002mol). Yield = 86%, m.p = 200-202 °C. IR (υ, cm⁻¹, KBr disk): 1649 (C=N). Recrystallized with ethanol.
3. Result and discussion
The compounds (I, II, III, IV) were synthesized by using the microwave technique the reactions involve two steps. The first step involves of the reaction of 4-aminoantipyrene with 4-substituted benzaldehyde to give compounds I and II. The second step involves the reaction of compounds I and II with 4,4′-Diaminodiphenylmethane to give compounds III and IV. The purity of the compounds was checked by TLC. The strategies adopted to obtain the target compounds are:

Scheme 1. Mechanism suggested for synthesis of mono-imines
Scheme 2. Mechanism suggested for synthesis of Bis-imines

The analytical data together with some physical properties of the compounds are summarized in Table (1). The calculated values of C.H.N analysis were in a good agreement with the experimental values.

Table 1. Physical data of Schiff base compounds

| Comp | Color      | Molecular formula | Found (calculated1) | M.wt (g. Mol-1) |
|------|------------|-------------------|---------------------|-----------------|
|      |            |                   | C% | H% | N% |                      |
| I    | Pale yellow| C18H16N3OCl       | 65.42 | 5.10 | 11.9 | 325.79 |
|      |            |                   | (66.30) | (4.91) | (12.89) |
| II   | Yellow     | C20H22N4O         | 70.50 | 5.60 | 15.81 | 344.13 |
|      |            |                   | (71.76) | (6.57) | (16.74) |
| III  | Brown      | C49H78N8Cl2       | 70.65 | 8.46 | 13.43 | 850.10 |
|      |            |                   | (69.17) | (9.17) | (13.17) |
| IV   | Dark yellow| C53H90N10         | 74.51 | 9.43 | 17.10 | 867.34 |
|      |            |                   | (73.33) | (10.30) | (16.14) |
The important IR spectral data are given in Table (2). The spectrum of Compound (I) indicated the appearance of bands in the region 1593.95, 1570.79, 1649.92 and 3060.75 cm$^{-1}$ which could be attributed to $\nu$(C=N), $\nu$(C=C)$_{\text{aromatic}}$, $\nu$(C=O) and $\nu$(C-H)$_{\text{aromatic}}$ respectively $^{[16]}$. The spectrum of the compound (II) exhibits the absorption bands for $\nu$(C=N), $\nu$(C=C)$_{\text{aromatic}}$, $\nu$(C=O) and $\nu$(C-H)$_{\text{aromatic}}$ at 1610.61, 1589.40, 1647.26 and 3070.78 cm$^{-1}$ respectively $^{[17]}$. Figures (1 and 2). The IR spectra of the compounds III and IV are complex due to the large number of the groups which have overlapping regions, however few bands have been chosen in order to observe the complement of reaction. The spectra of compounds III and IV characterized by disappearance of stretching frequency of $\nu$(C=O) and appearance of another band due to stretching frequency of $\nu$(C=N) in the region 1651.12 cm$^{-1}$ for compound III and 1649.19 cm$^{-1}$ for compound IV make us a good sign that we are on the correct way in the synthesis. Figures (3 and 4).

The experimental UV-VIS. Spectra of compounds I, II, III, and IV, exhibited $\lambda_{\text{max}}$ in 323, 326, 333, 370 nm respectively this absorption band due to (n–$\pi^*$) transition may be located on the nitrogen atom of the (-C=N-) $^{[18]}$.

![Figure 1. FTIR spectrum of compound I](image1)

![Figure 2. FTIR spectrum of compound II](image2)
4. Theoretical calculation
HyperChem offers ten semi-empirical molecular orbital methods, with options for organic and main group compounds for spectrum simulation [19]. Zerner’s INDO (ZINDO/1) level of semi-empirical method was used for evaluating the heat of formation ($\Delta H^{\text{f}}$) and binding energy ($\Delta E_b$) for Schiff base compounds. Parameterization method3 (PM3) level also used to calculate vibration frequencies and ZINDO/S compound used to calculate the electronic spectra table 2.
Table 2. The calculated energies(in KJmol$^{-1}$) and dipole moment (in Debye) for Schiff base compounds.

| Comp. | ΔH$_f$ | ΔE$_b$ | μ   |
|-------|--------|--------|-----|
| I     | -35670.78 | -53817.60 | 4.1 |
| II    | -41370.26 | -62606.58 | 4.5 |
| III   | -98231.99 | -146447.88 | 8.6 |
| IV    | -110153.99 | -164548.83 | 21.4 |

All computational chemistry techniques energy such that the system with the lowest energy is more stable. Thus the shape of a molecule corresponds to the shape with the lowest energy [20]. As shown in the table the compounds can be arranged according to the increase in thermodynamic stability as follows: IV > III > II > I.

Table 3. Experimental and theoretical vibration frequencies of Schiff base compounds

| Symbol | ū (C-H) aromatic | ū (C=O) | ū (C=N) | ū (C=C) alkene |
|--------|------------------|---------|---------|----------------|
| I      | 3060.75*         | 1649.92* | 1593.95* | 1570.79*       |
|        | 3086.67**        | 1790.95** | 1677.67** | 1600.10*       |
|        | (0.8)            | (7.9)   | (4.9)   | (1.8)          |
| II     | 3070.78 *        | 1647.26* | 1610.61* | 1589.40*       |
|        | 3051.19**        | 1779.95** | 1679.84** | 1631.78**      |
|        | (-0.6)           | (7.5)   | (4.1)   | (2.6)          |
|        | 3059.20*         | ------- | 1595.18* | 1572.04*       |
|        | 3151.31 (2.9)   | ------- | 1622.21** | 1610.35**      |
|        | (2.9)            |         | (1.6)   | (2.4)          |
| III    | 3059.20*         | ------- | 1649.19* | 1574.75*       |
|        | 3010.22**        | ------- | 1610.61* | 1666.32**      |
|        | (-0.16)          |         | (2.4)   | (5.5)          |
| IV     | 3010.22**        | ------- | 1650.22** | 1650.22**      |
|        | (2.9)            |         | (2.4)   | (5.5)          |

Where *: Experimental frequency, **: Theoretical frequency ( ) :Error%.

The theoretical UV-spectrum of compounds were calculated using ZINDO/S method and appeared some deviations from the experimental values but these deviations in generally acceptable in theoretical calculations [21]. The electronic spectrum of compounds I,II,III, and IV , exhibited λmax at 309.48, 316.12, 320.34, and 368.31 nm respectively. Figures (5-8).
5. Conclusions:
The compounds I, II, III, and IV were successfully synthesized by microwave irradiation technique. The physical data as well as FTIR and UV-VIS. Proposed the compounds synthesized. The value calculated energy for the compounds suggested that the compound IV is more stable than the other compounds. The value of theoretical vibrational frequencies and electronic transitions which obtained practically approximately similar to the experimental values.
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