WORLD JOURNAL OF PHARMACY AND PHARMACEUTICAL SCIENCES
SJIF Impact Factor 6.647
Volume 7, Issue 1, 71-76 Research Article ISSN 2278 – 4357

# SYNTHESIS AND SPECTRAL CHARACTERIZATION OF SOME NEW PYRAZOLINE DERIVATIVES

**Abdul –Wahhab J. Al-Hamdany and Ameera M. Farag**

Dep. of Chemistry, Coll. of Science, Univ. of Mosul, Mosul/IRAQ.

Article Received on
30 October 2017,
Revised on 20 Nov. 2017,
Accepted on 11 Dec. 2017
DOI: 10.20959/wjpps20181-10170

***Corresponding Author**
**Abdul –Wahhab J. Al-Hamdany**
Dep. of Chemistry, Coll. of Science, Univ. of Mosul, Mosul/IRAQ.

## ABSTRACT

The title compounds were synthesized by condensation azachalcones with ethylacetoacetate to get intermediate 3-(pyridyl)-5-aryl-6-ethylcarboxylate-2-cyclohexenone which were subsequently treated with hydrazine hydrate to afford the title compounds 4-(pyridyl)-6-aryl-7one-5,6-dihydro-1Hindazol or pyrazoline derivatives.[1-10] The sructures of the final products were supported by spectral data (UV, IR, $^1$HNMR) in addition to their physical properties.

**KEYWORDS:** Azachalcones, Cyclohexenones, condensation, Indazol, Pyrazoline.

## INTRODUCTION

In recent year asignificant portion of research in heterocyclic chemistry has been devoted to pyrazolines containing different aryl group as substituents.[1] Pyrazolines are compounds with noteworthy application pyrazolines are well known and important nitrogen-containing five member heterocyclic compounds.[2] Numerous pyrazoline derivatives have been found to posses considerable biological activities. Which stimulated the research activity in this field.[3] it has been demonstrated to have an important therapeutic potentiale mainly as anti-inflammatory[4], antidepressant[5], molluscicidal[6], antibacterial[7], antifungal[8] and antitumor[9] agensts been cited in literature. pyrazoline derivatives such as antipyrine, aminopyrine and dipyrone are known as antipyretic and analgesic substances and their pharmacological action.[10]

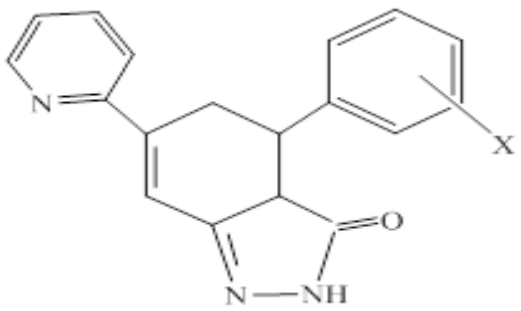
### Instrumentation

Melting points were measured on an electro thermal (Stuart melting point spm 30). IR spectra were recorded on a Bruker optics (FT –IR) spectrophotometer co. using KBr – disk. $^1$H-NMR

spectra were recorded on B. Bruker Avance III400- MHz spectrometer (Gazi Osman basa University / Turkey) using TMS as an internal standard and DMSO – d6 as a solvent. UV spectra were recorded by Shimadzu UV – visible recording UV -160 spectrophotometer. Theoretical study of the heat of formation (H.F) and steric energy (S.E) was achieved by using AM1(Austin–Model1) to explain the effect of different groups (electron donating or drawing) on the reaction.

General method for the synthesis of pyrazoline (indazole).[11]

A solution of cyclohexenone[12] (0.01 mol) in ethanol absolute (25 ml) was treated with hydrazine hydrate 80% and anhydrous sodium acetate (0.01 mol) in 100 ml round-bottomed flask and refluxed for (8 h). The mixture was cooled and then poured over crushed ice the crude products were recrystallized using ethanol as solvent a ford the product. See Table.[1]




X=(1-10)

## RESULTS AND DISCUSSION

The physical properties of the final products (1-10) (melting points, colours) supply an evidence to their formation. The spectral data of (1-10) series support strongly the formation of such compounds. The spectral data of compound number (1) has been discussed as a representative model.

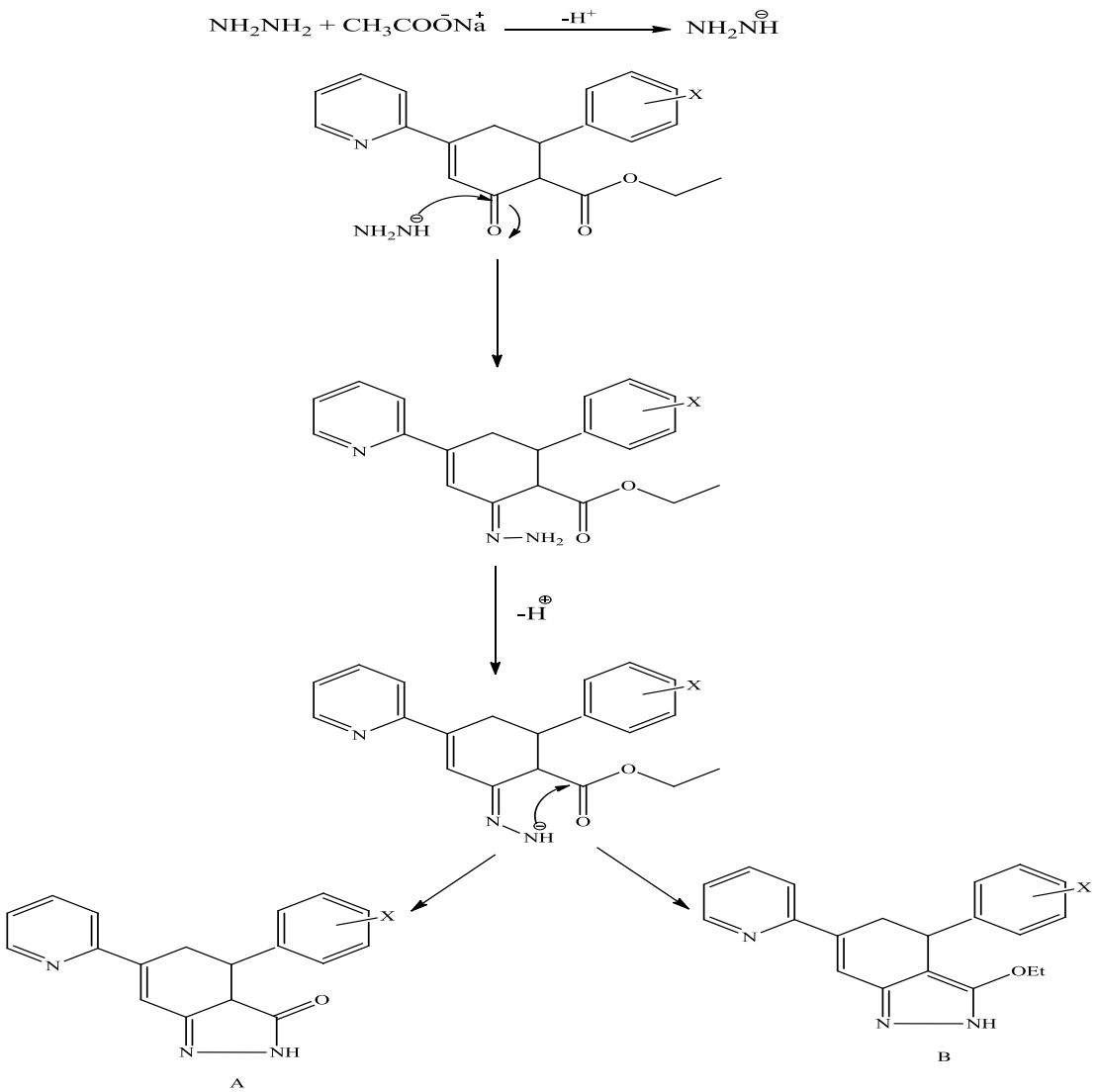
The $^{1}$HNMR spectrum of (1) showed a doublet signal for tow protons (H4) resonate at δ(2) ppm. The benzylic proton (H5) seemed to resonate at δ(3.9) ppm as a quartet signal, but (H6) watched to resonate at δ(3) ppm as a doublet signal. The olefinic proton (H2) looks like a singlet at δ(5.5) ppm, while the aromatic protons (4H from the phenyl & 3H from the pyridyl) reflect a multiplet signal at δ(7-8) ppm. The aromatic proton labeled (H9) on the pyridyl ring resonates at δ(8.5) ppm as a singlet signal and deshielded due to the adjacent nitrogen. The methoxy three protons found clearly as a singlet signal and resonate at δ(3.7) ppm. Finaly the

pyrazoline Proton (H8) found clearly as singlet signal and resonate at (2.6) ppm]. See Table (2).

The IR spectrum[13] of (1) showed many distinguished absorption bands at υ(1736) $cm^{-1}$ related to the pyrazoline carbonyl and υ(1685) $cm^{-1}$ due to the C=N. The olifinic C=C showed a stretching vibration at υ(1509) $cm^{-1}$ whereas the aromatic C… N and C…C displayed on absorption bands at υ(1538) $cm^{-1}$ and υ(1432) $cm^{-1}$ respectively. Finaly showed band at (3100) due to the N-H. See Table (3).

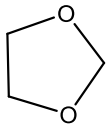
The UV spectrum[14] of (1) exhibited a red shift to a longer wavelength at maximum absorption $\lambda_{max}$ =(232) nm due to the increasing degree of conjugation. See Table (3).

The suggested mechanisms for the reaction of cyclohexenone with hydrazine hydrate may pass through one of two routes.[15]



Finally. It is concluded that the most predominant product is (A)which is in afull agreement with the spectral data.

**Table (1): Physical properties of pyrazolines.**

| No | X | color | Yield% | m.p (°C) |
|---|---|---|---|---|
| 1 | p-$OCH_3$ | 243-241 | 80 | White |
| 2 | m-$OCH_3$ | 215-213 | 94 | White |
| 3 | p-$CH_3$ | 232-235 | 85 | White |
| 4 | p-$NO_2$ | 190-192 | 77 | White |
| 5 | 2,4-DiCL | 207-209 | 75 | White |
| 6 | p-Cl | 205-206 | 81 | White |
| 7 | H | 199-200 | 60 | White |
| 8 |  | 262-264 | 77 | White |
| 9 | 3-4DiCl | 210-212 | 77 | White |
| 10 | N.N-$DiM_e$ | 237-235 | 70 | White |

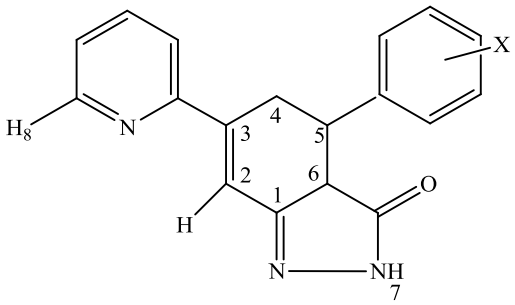



**Table (2): The 1H-NMR spectra data for some of prepared Pyrazoline.[1,5,9,10]**

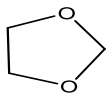
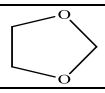
| NO | X | $H^1$-NMR(DMSO);δppm | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **H4** | **H6** | **H5** | **H2** | **H7.** | **Ar-H** | **Pyridyl-H8** | Others |
| 1 | p-$OCH_3$ | 2<br>1H,d | 2.6<br>1H,d | 3.9<br>1H,q | 5.5<br>1H,s | 6.6<br>1H,s | 7.8-6.8<br>7H,m | 8.5<br>1H,s | 3.7<br>3H.S OCH3 |
| 9 | NN-DiMe | 2<br>1H,d | 2.6<br>1H,d | 3.9 | 6.6<br>1H,s | 6.8<br>1H,s | 7.3-8.2<br>7H,m | 8.4<br>1H,s | 2.8<br>CH3-N-CH3<br>3H.s |
| 5 | p-$NO_2$ | 2<br>1H,d | 2.7<br>1H,d | 3.8<br>1H,q | 5.6<br>1H,s | 6.6<br>1H,s | 7-8<br>7H,m | 8.5<br>1H,s | --- |
| 10 |  | 2.5<br>1H,d | 2.8<br>1H,d | 3.5<br>1H,q | 5.6<br>1H,s | 6.5<br>1H,s | 7.3-8.2<br>6H,m | 8.6<br>1H,s | 6<br>O-CH2-O<br>2H.S |

**Table (3): The IR and UV spectral data for Pyrazoline.**

| No. | IR υ $cm^{-1}$ (KBr) | | | | | | Others | UV (CHCl3) $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|---|---|
| | X | C=O | N-H | C=N | C=C |  | | |
| 1 | p-$OCH_3$ | 1736 | 3100 | 1686 | 1509 | 1538<br>1432 | Asy1146 (C-O-C)<br>Sy 1093(C-O-C) | 232 |
| 2 | m-$OCH_3$ | 1650 | 3178 | 1608 | 1485 | 1541<br>1431 | Asy1159 (C-O-C)<br>Sy 1034(C-O-C) | 256 |
| 3 | 3,4-DiO$CH_3$ | 1600 | 3150 | 1591 | 1483 | 1546<br>1434 | Asy1146 (C-O-C)<br>Sy 1028(C-O-C) | 232 |
| 4 | p-$CH_3$ | 1700 | 2998 | 1655 | 1486 | 1587<br>1405 | ---- | 254 |
| 5 | p-$NO_2$ | 1647 | 3100 | 1709 | 1516 | 1583<br>1500 | Asy1402(N---O)<br>Sy 1346(N…O) | 220 |
| 6 | 2,4-DiCl | 1700 | 3011 | 1689 | 1486 | 1587<br>1405 | 789-742 (C-Cl) | 232 |
| 7 | P-Cl | 1666 | 3150 | 1662 | 1577 | 1594<br>1433 | 783(C-Cl) | 248 |
| 8 | H | 1685 | 3000 | 1597 | 1491 | 1585<br>1463 | --- | 254 |
| 9 |  | 1660 | 3178 | 1600 | 1489 | 1543<br>1434 | Asy1147(C-O-C)<br>Sy 1039(C-O-C) | 236 |
| 10 | N,N-DiMe | 1650 | 3135 | 1612 | 1520 | 1591<br>1471 | 1346(C-N) | 254 |

**REFERENCE**


1. Yadav J.S., Rajora J., Srivastava Y.K., Archives of applied Science Research, 2011; 3(2): 192-198.
2. Saha S.K., Banerjee M., Tropical J. pharmaceutical research, 2008; 7: 961-68.
3. Rossela M., Zarin S.K., Dale S., Eur. j. Med. Chem, 2010; 45(12): 6135-38.
4. Won S.J., Liu C.T, Tsao L.T., Lin C.N. Eur. j. Med. ch., 2005; 40: 103-112,
5. Hamdy N.A., EL-Senousy W.M., Acta. Polonia Pharmaceutical. Drug Reaearch, 2013; 1: 99-110.
6. Flora F.B., Hanaa M.H., Adel S.G., Bioorg Med. chem., 2006; 14: 3929.
7. AL—Saadi M.S.M., Saudi pharm. J., 2008; 16: 135-145.
8. Rashad A.E., Shamroukh A.H., Hegab M.I., Awad H.M., Acta. Chem. Solv, 2005; 52: 429-434.
9. Kavitha N.V, Divekav K., Pyriyadarshini B., Gjanen S., Manjunath M., Derpharma chemical, 2011; 3(4): 55-62.
10. Girisha K.S., Balachandra, Eur. J, Med., 2010; 45: 4640-44.

11. Anagarajan V., Thanvsu J., Gopalakrishnan M., Europen Review for Medical and Pharma cologicale Sciences, 2010; 14: 653-660.
12. AL-Hamdany A.J., Farag A.M., World Journal of Pharmacy and Pharmaceutical Sciences, 2017; 6: 9.
13. Williem S. and Fleming "Spectroscopic Methods inorganic. chemistry " 2nd, 1973; 61,
14. Parikh V.M. "Absorption Spectroscopy of organic Molecules" 1985; 95.
15. Rao N.S., Srivastava Y.K. and Kumar R., E-Journal of chemistry Journal, 2008; 5(1): 39-42