

Synthesis and Characterization of Heteromacro cyclic Compounds via cyclization Reactions

Dr. Nagham. Mahmood. Aljamali

Assist. Prof ., Chem. Dept ., College of Education , Univ.Kufa

Abstract :

In the present study , new type of heteromacro cycles [4,5] were synthesized by the reaction between terminal of (amine , thiol) of compounds [1-3] with carbonyl compounds (4 – amino benzoyl chloride ,4-methanal ethyl benzoate , 4-methanal benzaldehyde) by condensation reaction .The synthesized compounds have been investigated using different chemical techniques , such as (Uv–Visible spectra ,FT-IR–spectra ,H.NMR-spectra ,(C.H.N)–analysis , and melting points) .

Introduction :

The importance of this compounds has long been recognized in the synthetic organic chemistry ,which have a wide variety of biological activity such as pharmacological activities ,which include anti fungal^(1,2) ,anti bacterial^(3,4) ,anti tumor ,antibacterial^(5,6) and anti convulsant⁽⁶⁾.

In this article , synthesized heteromacrocyces are result from condensation reaction as the ring – closing step . these compounds are promising candidates for developing new supramolecular structures , they are reported to have antibacterial activity , the structural modification of organic molecule has considerable biological relevance and other uses⁽⁷⁻¹⁰⁾ , which are contain (amide, imine , sulphide , thiazol) groups⁽⁶⁻¹¹⁾ due to activity of these compounds .

These compounds are stable at room temperature and are non hygroscopic , have good yield , from a synthetic point of view , they are containing reactive functional groups are important for the above – listed applications .

Experimental :

All chemical used were supplied from Merck & BDH-chemical company.

All measurements were carried out by :

- Melting points :electro thermal 9300 , melting point engineering LTD , U.K .
- FT-IR spectra : fourrier transform infrared shimadzu (8300) (FT-IR) ,KBr-disc was performed by CO.S.Q. Iraq .
- H-NMR spectra: in centre lab – institute of earth and environmental science , AL – byat university , Jordan .
- Elemental analysis (C.H.N) : EA-017 Mth in centre lab –institute of earth and environmental science , AI-byat university , Jordan .
- Uv–Visible spectra :shimadzu–1700 , double beam with computerized , Japan .

Synthesis of 6-Mercapto-2-(4-amino benzamide)-benzothiazole [1]:

A mixture of (0.05mole , 9.1 gm) of 6-Mercapto -2-(4-amino benzothiazole & (0.05 mole , 7.77 gm)of 4- amino benzoyl chloride were heated under reflux for (2 hrs) , the reaction mixture was cooled , the precipitate was filtered of & recrystallized from ethanol to produce (16.4g) 84% of bill yellow crystal compounds [1].

Synthesis of Bis{6-(mercapto-2-benzamide)-benzothiazol}-4-benzamide methyl imine [2]:

Refluxing mixture of (0.04 mole ,12.04 g) of compounds[1] with (0.02 mole ,3.56 g) of 4-formal- ethyl benzoate were reacted for two hours refluxing until the participitate formed ,after cooling, the precipitate was filtered off & recrystallized to produce(15.2g) 81% of yellow crystal compounds [2] .

Synthesis of Bis{6-(4-aminobenzoyl sulphide-2-benzamide)-benzothiazol}-4-benzamide methyl imine [3]:

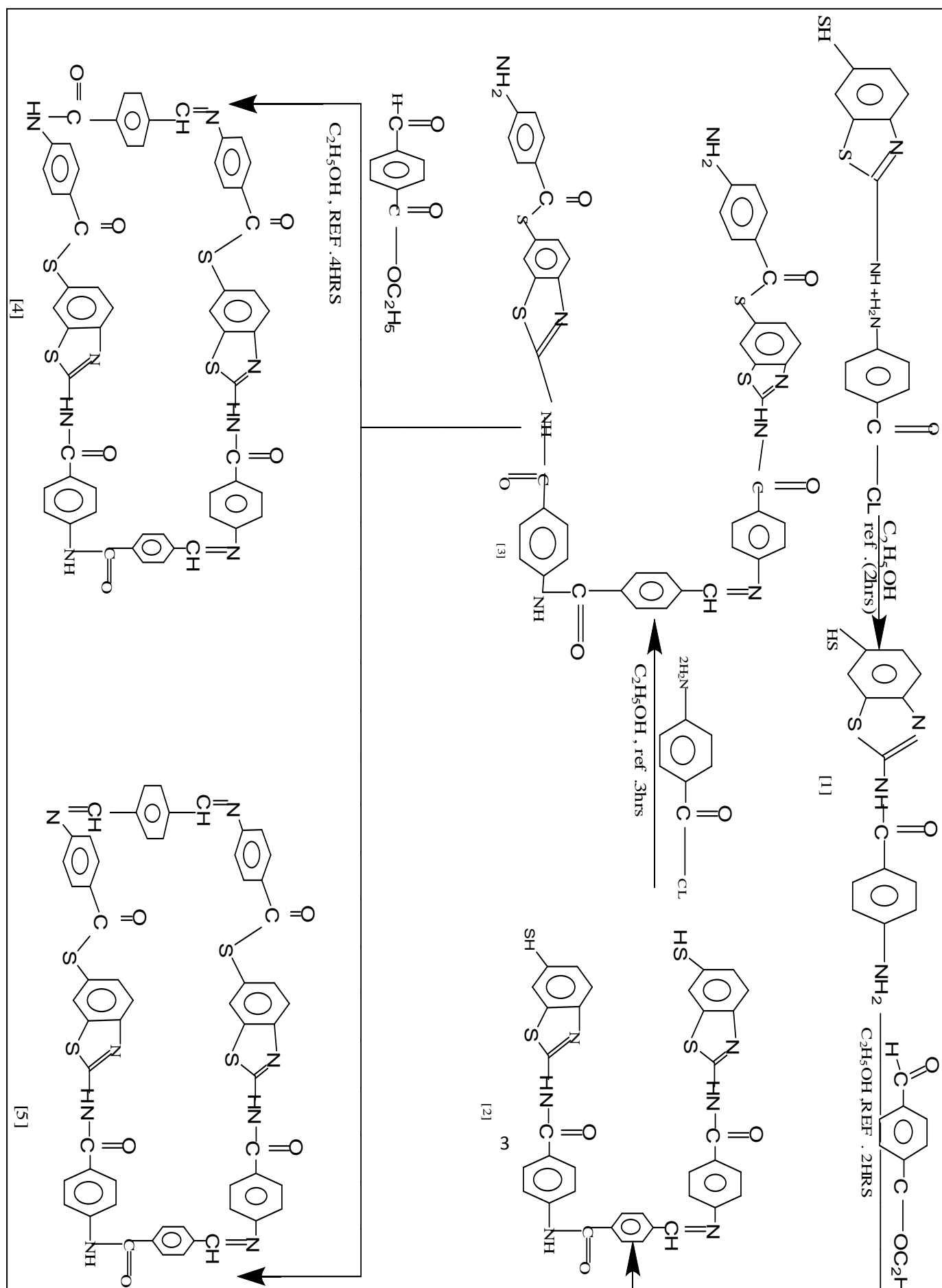
A mixture of (0.04 mole , 28.6g) of compound [2] and (0.08 mole , 12.44 g) of 4-amino benzoyl chloride were reacted by condensation for (3hrs) refluxing until the participitate formed, after cooling , the precipitate was filtered off & recrystallized to produce(45.3g) 83% from bill orange crystal compounds[3].

Synthesis of compounds [4,5]:

(0.02 mole , 19.08 g) of compound [3] was reacted with one of [(0.02 mole , 3.56 gm) of 4-formal–ethyl benzoat , (0.02 mole , 2.68g) of 4-formal benzaldehyde] respectively by reflux for (4hrs) & recrystallized to yield(23.2g ,21.1g) (82% , 80%) from(orange, red) compounds [4,5] respectively :

Compound [4] : Bis – {(6-benzoyl sulphide -2-benzamide) benzothiazol -4-benzamide methyl imine } – hetromacrocycle .

Compound [5]: Bis-{(6-benzoyl sulphide -2-benzamide)-benzothiazol} -4-benzamide – tris (methyl imine) – hetromacrocycle.



Result and Discussion:

All the synthesized compounds[1-5] have been characterized by their melting points and spectroscopic methods , such as (Uv-visible , FT.IR ,H.NMR spectrum, and (C.H.N)-analysis):

FT.IR Spectra:

In FT.IR spectra ,the reaction is followed by disappearance of (-NH₂) absorption band at (3420)cm⁻¹ in compound [1] , and appearance two band :at (1610)cm⁻¹ .(1690)cm⁻¹ due to (HC=N)of azomethine group⁽⁷⁻⁹⁾ and ($\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-$) carbonyl of amide group , respectively in compound [2] . while FT.IR spectra of compound [3] showed disappearance of (S-H) absorption band at (2455) cm⁻¹ and appearance absorption (3455)cm⁻¹ due to (-NH₂) group⁽¹¹⁻¹⁴⁾ .In compound [4] we are observed disappearance of (-NH₂) absorption band and appearance absorption band at (1616)cm⁻¹ due to (HC=N) azomethine group and (1690)cm⁻¹ due to ($\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-$)amide group⁽¹⁵⁻¹⁸⁾ . While FT.IR Spectra of compound [5] showed disappearance of (-NH₂) ,absorption band appearance absorption band at (1631)cm⁻¹ due to (HC=N) azomethine group ,other informative bands⁽¹⁹⁻²¹⁾ are listed in table (1) . The presence these bands consider as indication to formation these compounds .

H.NMR-Spectrum:

H.NMR –spectrum of compounds in figures (4-6) : showed the following characteristics chemical shift were appeared : singlet signal at δ 9.79 for one proton of azomethine^(20,21) group (-CH=N), peak at δ 9.96 for proton of amide group ($\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-$) in compound [2] , signal at δ 8.5 for two proton of amine group (-NH₂) ,signal at δ 9.70 for proton of azomethine group (-CH=N) peak at δ 9.9 for proton of amide group ($\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-$) in compound [3], while the compound [4,5] are disappear the signals at δ 8.5 for protons of amine group (-NH₂) and appear signals at δ 9.71 for proton of imine^(20,21) (-CH=N) and at δ 9.9 for proton of amide group ($-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}$) ,multistate leaning on each other at δ 7.5-7.8 that could be attributed to the protons of benzene ring in these compounds .

This is other evidence to formation of compounds [1-5], and other peaks⁽¹⁸⁻²¹⁾ in figures (4-6).

UV-Visible and (C.H.N)-Analysis:

UV-spectra of compounds [1-5] have electron transition ($n-\pi^*$) due to the heteroatom (S,N) in these compounds beside of transition ($\pi-\pi^*$) of conjugated system, the UV-spectra of these compounds show absorption maxima (315-405) nm due to oxochromic groups ($-\text{NH}_2$, $-\text{SH}$, $-\overset{\text{O}}{\underset{\text{NH}}{\text{C}}}$) with conjugated system of compounds [1-5].

It was found from (C.H.N) –analysis, from compared the calculated data from compounds [1-5] are in good agreement with experimentally, the results were compactable and this is other evidence for formatted compounds, the data of analysis, λ_{max} and melting points are listed in table (2).

Acknowledgment :

I would like to express my thanks to Mr. Muhanad –Abu-Alsoaud in centre Lab-Institute of Earth and Environmental Science –Al-Bayt University H.J.K in Jordan for providing (C.H.N) element analytical, and H.NMR –spectrum.

Table (1) :FT.IR data (cm⁻¹)of compounds[1-5]

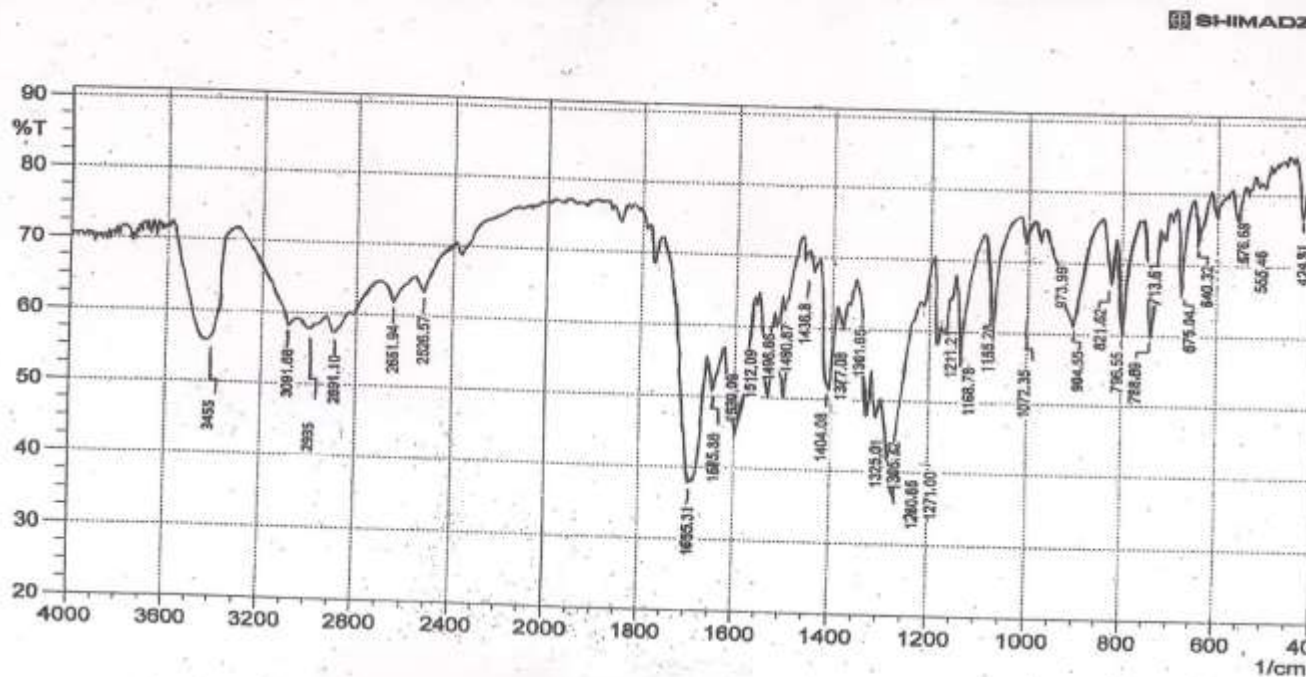
Comp. No.	$\nu(\text{N-H})$	$\nu(\text{S-H})$	$\nu(\text{CH=N})$ Azomthine	$\left(\begin{array}{c} \text{O} \\ \parallel \\ \text{HN}-\text{C}- \end{array} \right)$ carbonyl of amide	(C-S) Sulphide
[1]	3420m	2470w	-----	1685s	-----
[2]	-----	2455w	1610s	1690s	-----
[3]	3455m	-----	1615s	1695s	1325vs , 675s
[4]	-----	-----	1616s	1690s	1315vs , 682s
[5]	-----	-----	1631s	1690s	1323s , 682s

s=strong , m=medium , w=weak , v=very

Table (2):Melting points,M.F , λ_{max} and (C.H.N)-Analysis of compounds[1-5]

Comp . No.	M.F M.Wt _(g/mole)	m.p (c °)	λ_{max} (nm)	Calc / Found C%	H%	N %
[1]	C ₁₄ H ₁₁ N ₃ O S ₂ 301	161	310	55.813 55.609	3.654 3.538	13.953 13.710
[2]	C ₃₆ H ₂₄ N ₆ O ₃ S ₄ 716	182	335	60.335 60.213	3.351 3.274	11.731 11.654
[3]	C ₅₀ H ₃₄ N ₈ O ₅ S ₄ 954	221	360	62.893 62.648	3.563 3.571	11.740 11.599
[4]	C ₅₈ H ₃₆ N ₈ O ₆ S ₄	243	392	65.168	3.370	10.486

	1068			65.096	3.310	10.348
[5]	$C_{58}H_{36}N_8O_5S_4$	247	405	66159	3.422	10.646
	1052			66.145	3.309	10.573



Fig(1) : FT-IR Spectra of compound (3)

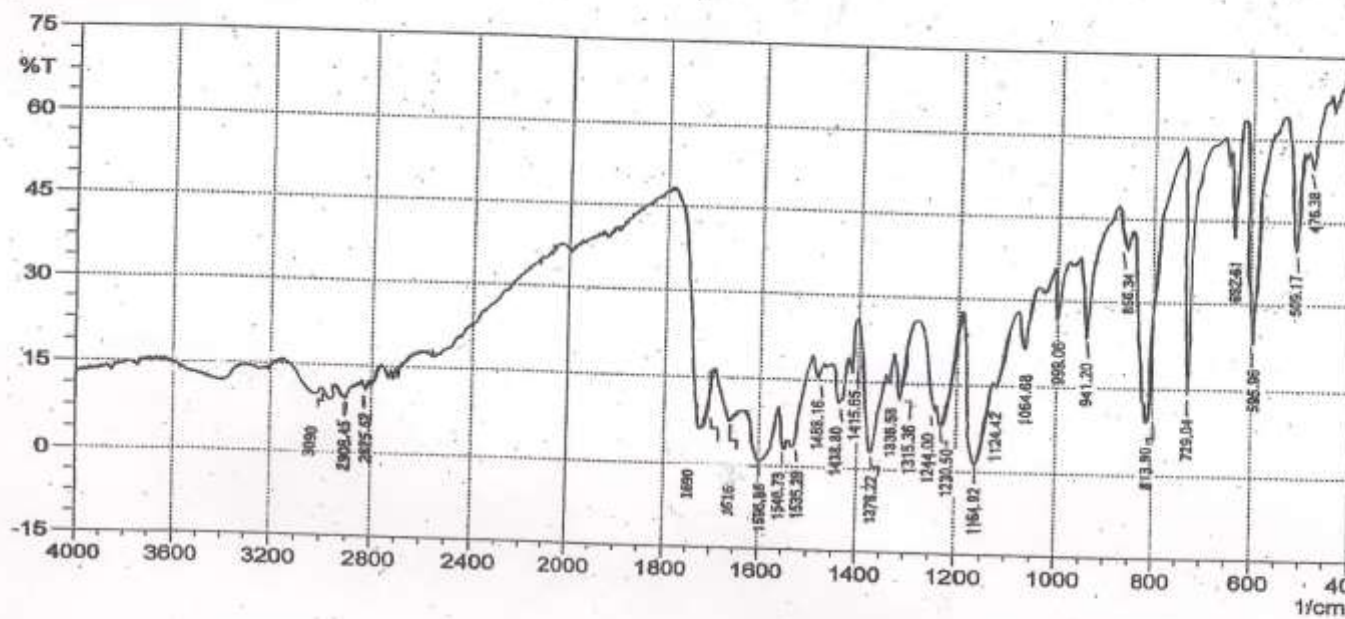


Fig (2): FT-IR Spectra of compound (4)

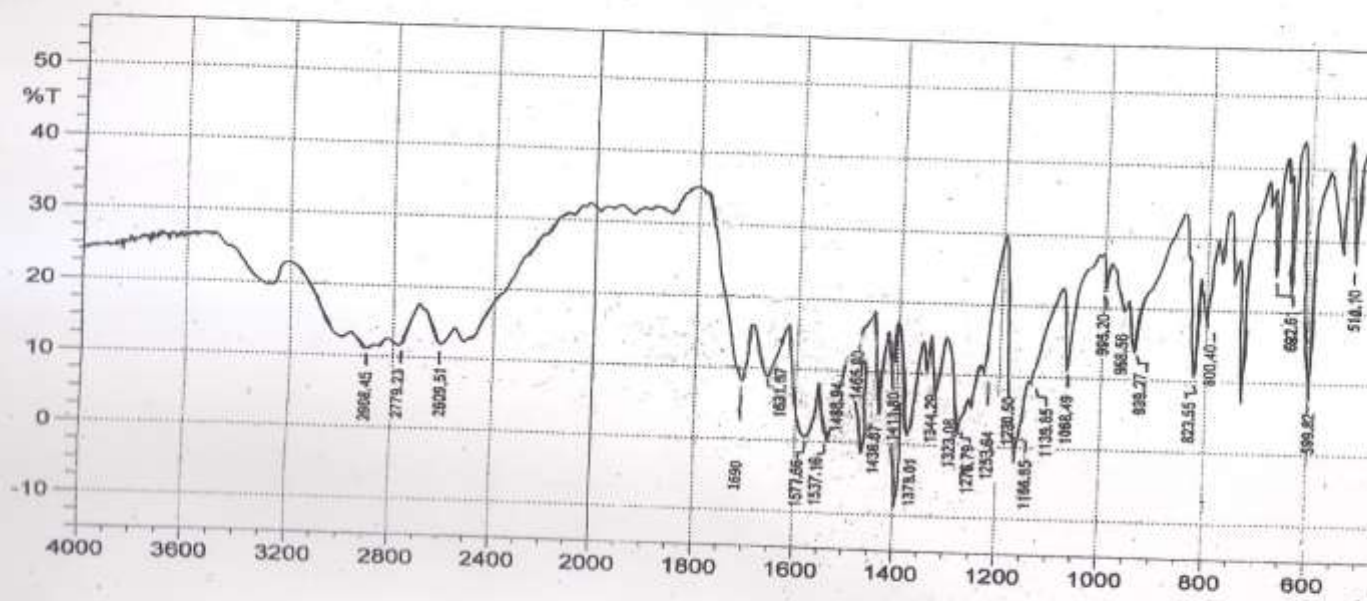
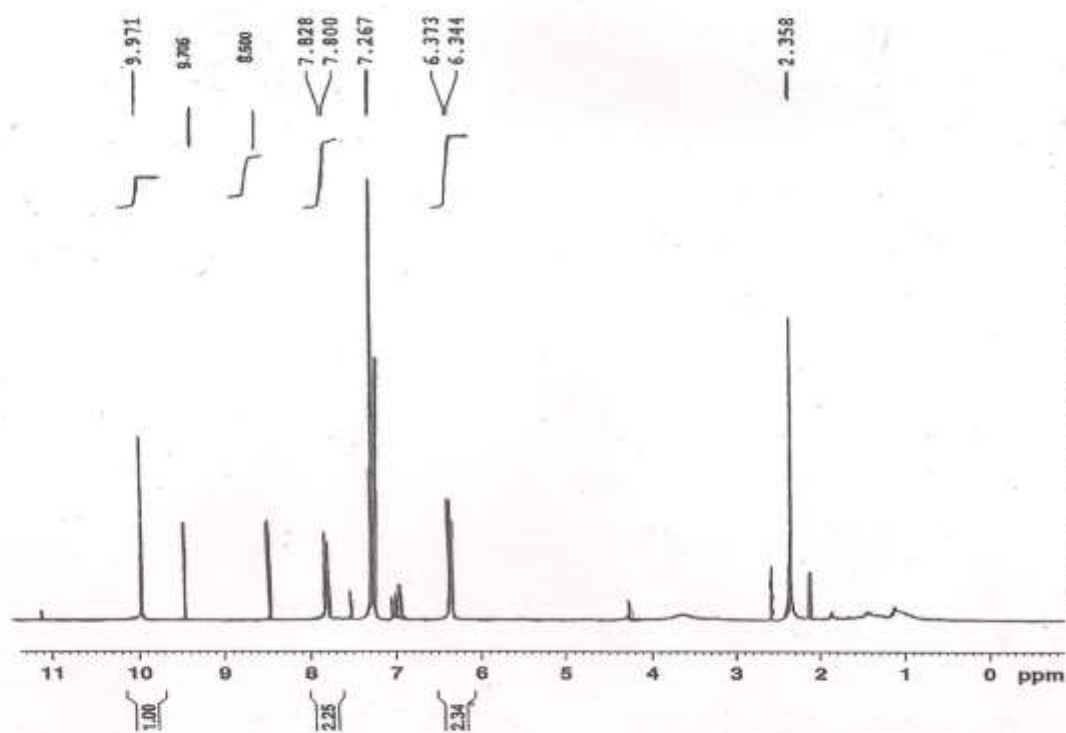
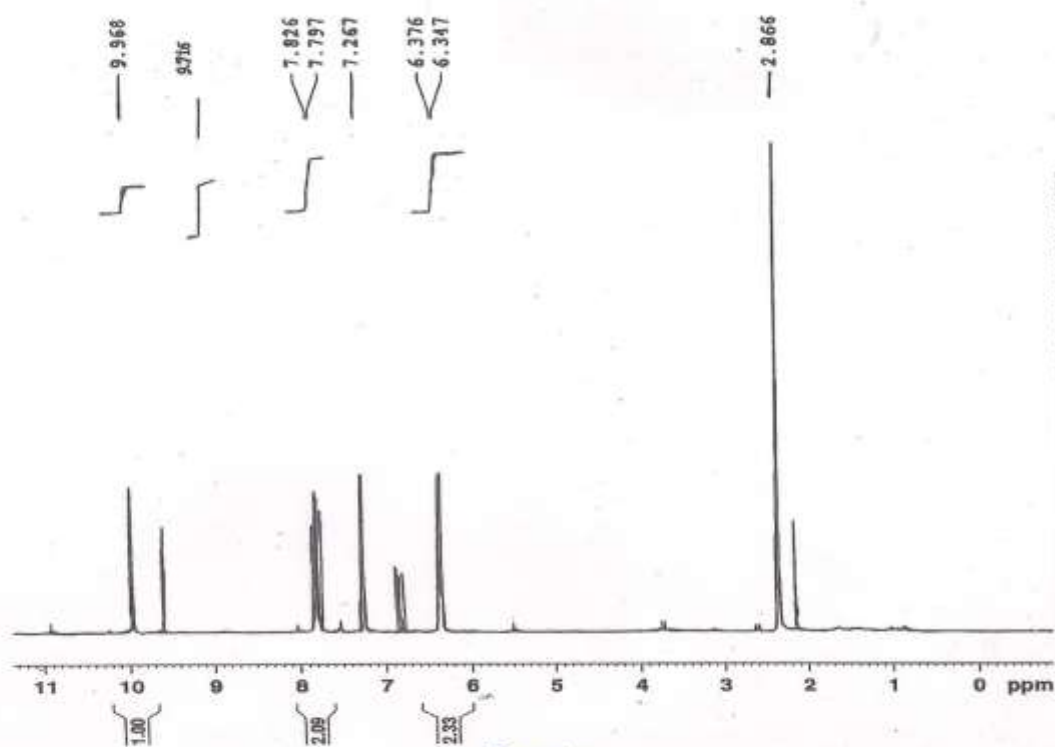


Fig (3) FT-IR Spectrum of compound(5)

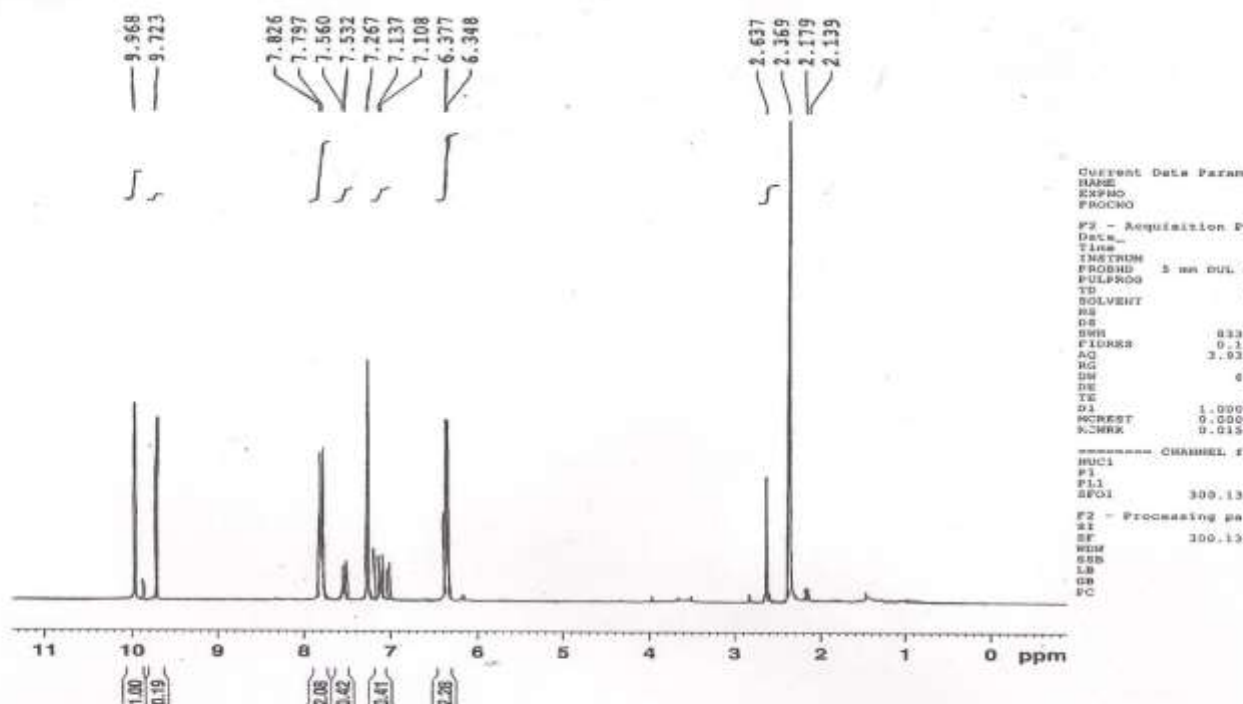


Current Data Parameters
NAME
EXPNO
PROCNO
F2 - Acquisition Parameters
Date_
Time_
INSTRUM
PROBHD 5 mm DUL 1
PULPROG
TD
SOLVENT
NS
DS
SWH 8333
FIDRES
AQ 3.922
RG 181
DN 80
DE
TE
D1 1.0000
MCREST 0.0000
MCKRE 0.0150
===== CHANNEL f1
NUC1
P1
PL1
SFO1 300.131
F2 - Processing parameters
SI 3
SF 300.130
WDW
SSB
LB
GB
PC

Fig (4): ¹H-NMR -Spectra of compound (3)



Fig(5): ¹H-NMR -Spectra of compound (4)



Fig(5) ¹H-NMR -Spectra of compound (5)

Reference :

1. Vinay.V ,Lakshika.K ., (2011) , I.J.R.P.S ,1 ,1, 17-27.
2. Faridbod. F, Ganjali.M, Diarvand. R , (2008) ,Sensors .,8 ,1645– 1703.
3. Beckmann . U and Brooker . S ., (2003) , Coord . Chem. Rev ., 245 , 17 – 29.
4. Amanda .J , Yanalexander .W and Mark. M ., (2005) ,J.Org . Chem. ,70 , 7936–7946.
5. Rajavel .R , Senthil. M and Anitha. C ., (2008),E–Journal of Chemistry ., 5, 3 , 620–626.
6. Leroy.C., (2003) ,Annu.Rep.Porg.Chem.,Sect., A ,99,289-347.
7. Nagham . M . Aljamali ., (2005), J . AlQadisia , 10 ,1 ,131–138.
8. Mustafa.Y,Askin. K and Basaran.D .,(2007) .,J. Serb.Chem .Soc,72 ,3,215–224.
9. Zolfoghar . R , Leili . R . A , Kamellia . N , and Seyed . M ., (2004) ,Acta . Chem . Solv ., 51 , 675 – 686.

10. Harlal . S and Varshney . A . K ., (2007) ,**Bioinorganic Chemistry and Applications** ., 1 –7.
11. Abdullah . M and Khadija . O ., (2007) , **Molecules** , 12 , XC.
12. Andrea.S , Daniel.V , Andre.L , and Lubomir.F., (2001),**Arkivoc** .,(Vi),122–128.
13. Jarrahpour .A , Motamedifar. M and Paskhir., (2004) ,**Molecule** , 9,875, 1420.
14. Canapolot . T ., (2004) ,**Russian . J . Coord . Chem.** , 30 , 87 , 40.
15. Verma . M and Stables . G ., (2004) ,**Molecules**,45 , 46.
16. Pandey . H and Dweiv . R ., (2005) , **Molecules** ,4 , 2 , 88.
17. Sharba . A , Al- Bayati . R , Aouad . M and Rezki . N ., (2005) ,**Molecules** ,10 , 1161–1168.
18. Sharba . A , Al- Bayati . R , Aouad . M and Rezki . N ., (2005),**Molecules**, 10 , 1153 – 1160.
19. Anna . M . , Alessandra . M , Patrizia . D , Paola . B , Antonino . L , Girolama . C and Gaetano . D ., (2001) ,**Arkivoc** , VI , 129 – 142
20. Nagham .Aljamali ., (2010) ,**J .Babylon .Sci** .,4 ,18,1425-1436 .
21. Nagham .Aljamali ., ,(2010) ,**J .Babylon .Sci** .,3 ,18 ,925-942.

تخليق مركبات حلقة كبيرة غير متجانسة عن طريق تفاعلات الحوالة

د.نغم محمود الجمالي

أستاذ مساعد-قسم الكيمياء-كلية التربية للبنات-جامعة الكوفة

الخلاصة :

تم في هذه الدراسة تخليق نوع جديد لمركبات حلقة عيانية غير متجانسة [4,5] من تفاعل مجاميع الثايول و الأمين في مركبات [1-3] مع مركبات الكربونيل (4- أمينو - كلوريد البنزويل , 4- فورمال بنزوات الأثيل , 4- فورمال بنزليدهايد) باستخدام تفاعل التكثيف. شُخصت المركبات المحضرة بمختلف التقنيات الكيميائية تمثلت ب(طيف الاشعة فوق البنفسجية - المرئية , طيف الاشعة تحت الحمراء , طيف الرنين النووي البروتوني المغناطيسي , التحليل الكمي الدقيق للعناصر) ومن ثم قياس درجات أنصهارها.