

Synthesis and Characterization of Heteromacro cyclic Compounds via cyclization Reactions

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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).

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Keyword: macro cycle, sulphur, heterocycle.

Introduction:

The importance of these 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, antitubercular^(5,6) and anti convulsant⁽⁶⁾.

In this article, synthesized heteromacrocycles 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: fourier transform infrared shimadzu (8300) (FT-IR), KBr-disc was performed by CO.S.Q. Iraq.

-H-NMR spectra: in DMSO as solvent.

-Elemental analysis (C.H.N): EA-017 Mth.

-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 off & 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 precipitate 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]:

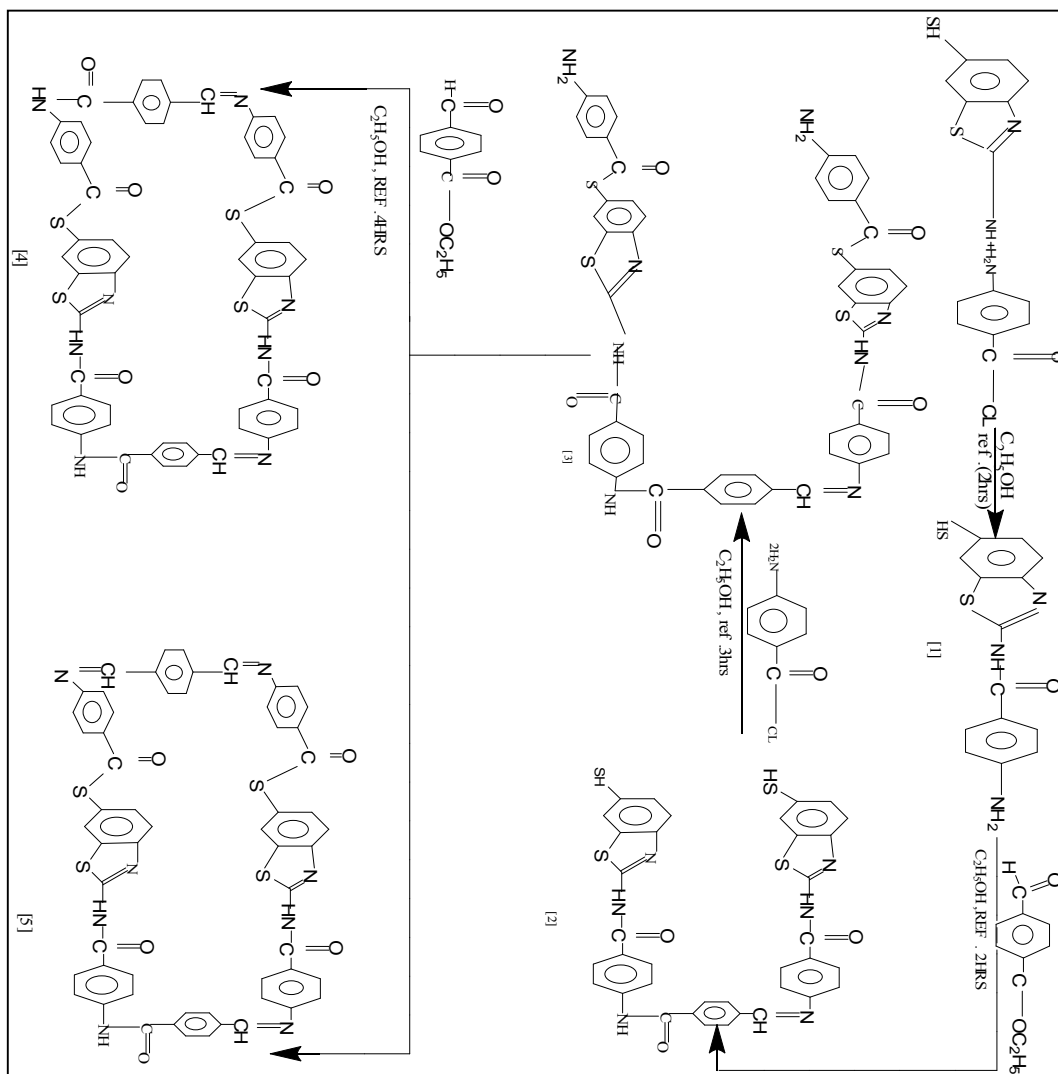
A mixture of (0.04 mole, 28.6g) of compound [2] and (0.08 mole, 12.44 g) of 4-amino benzoyl chloride were reacted by condensation for (3hrs) refluxing until the precipitate formed, after cooling, the precipitate was filtered off & recrystallized to produce (45.3g) 83% from bill orange crystal compounds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

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



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 (NH-CO) 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 ((NH-CO) 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 ((NH-CO) 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 δ9.9 for proton of amide

group (NH-CO) 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 (NH-CO), 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- π^*) due to the hetroatom (S,N) in these compounds beside of transition (π - π^*) of conjugated system, the UV-spectra of these compounds show

absorption maxima (315-405) nm due to oxochromic groups (-NH₂, -SH, NH-CO) 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.Audai for providing (C.H.N) element analytical, and H.NMR -spectrum.

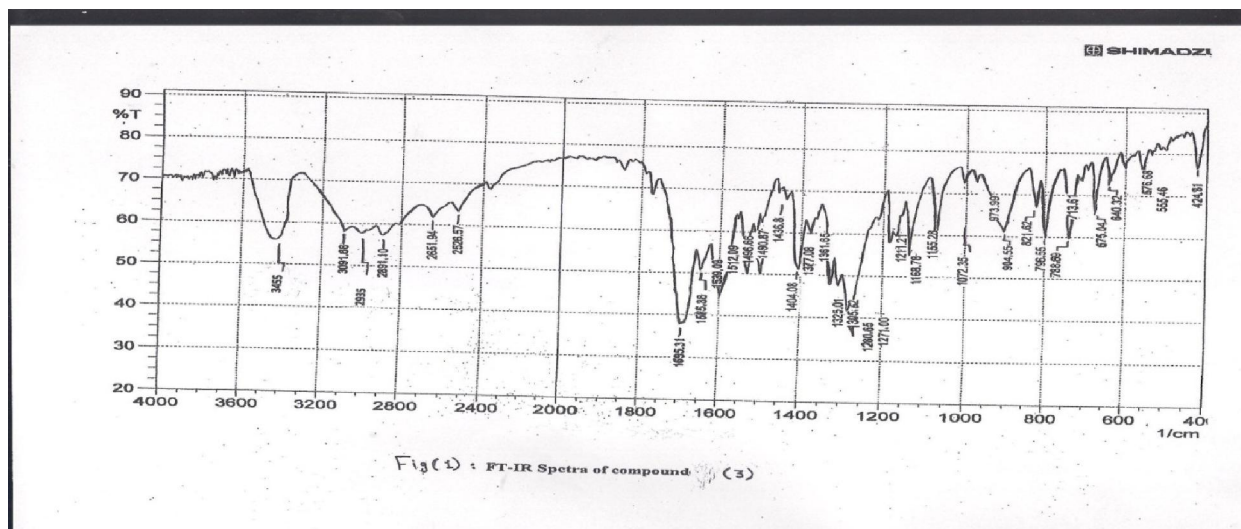
Table (1):FT.IR data (cm⁻¹)of compounds[1-5]

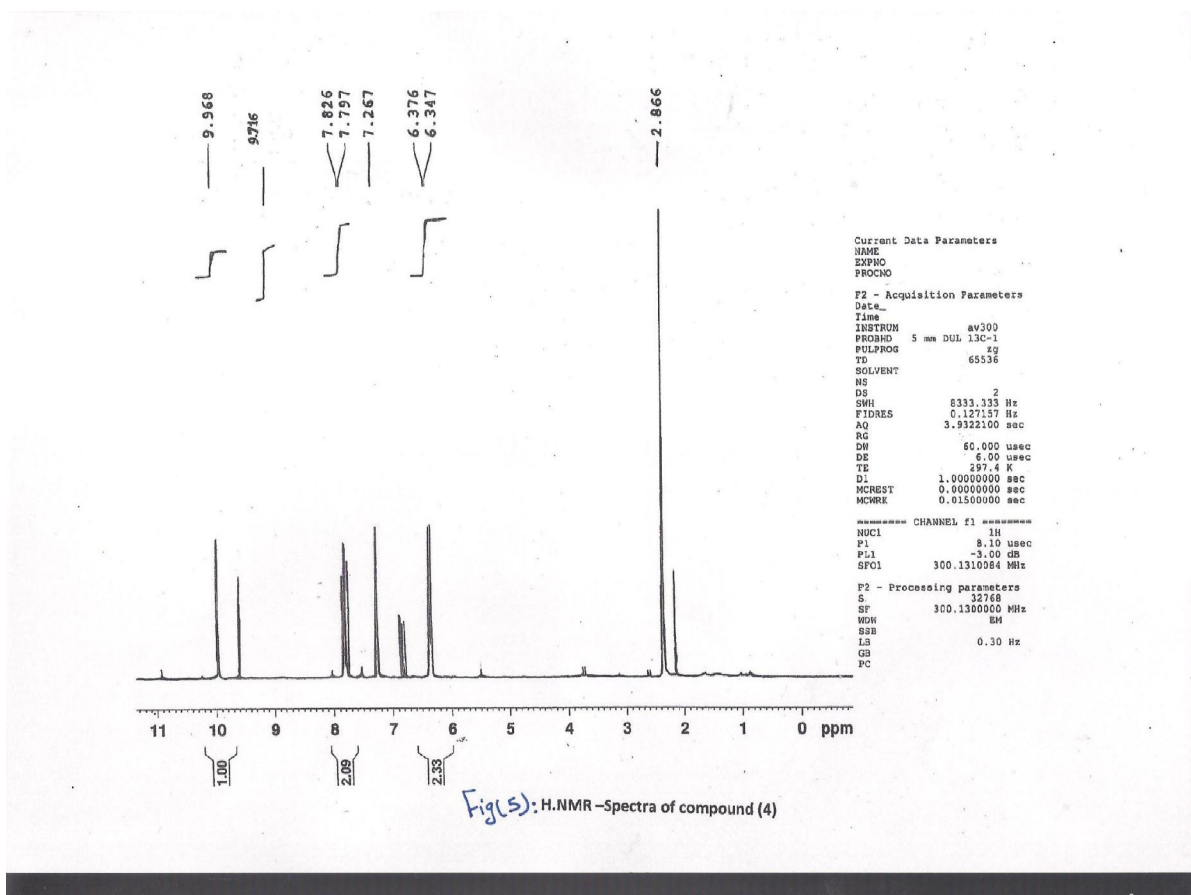
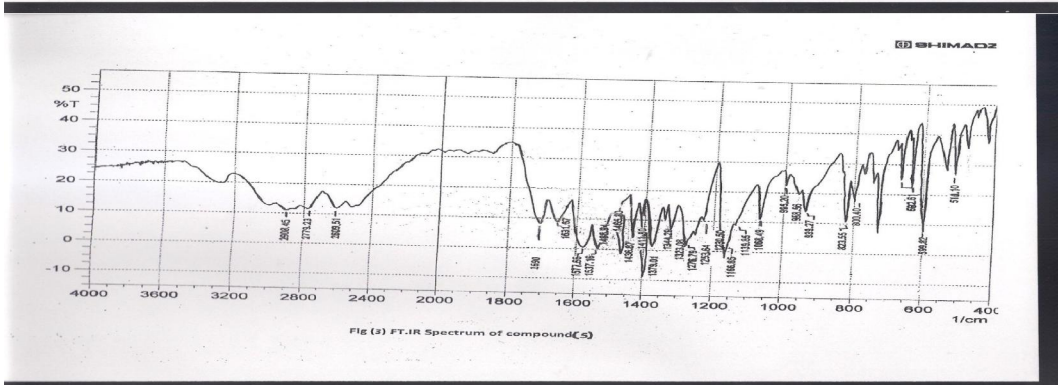
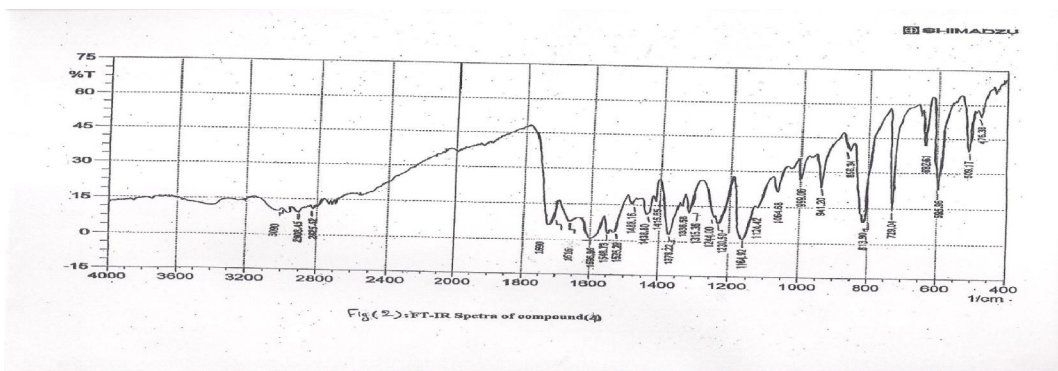
Comp. No.	ν (N-H)	ν (S-H)	ν (CH=N) Azomthine	(NH-CO) carbonyl of amide	(C-S) Sulphide
[1]	3420m	2470w	-----	1685s	-----
[2]	-----	2455w	1610s	1690s	-----
[3]	3455m	-----	1615s	1695s	1325vs, 675s
[4]	-----	-----	1616s	1690s	1315vs, 682s
[5]	-----	-----	1631s	1690s	1323s, 682s

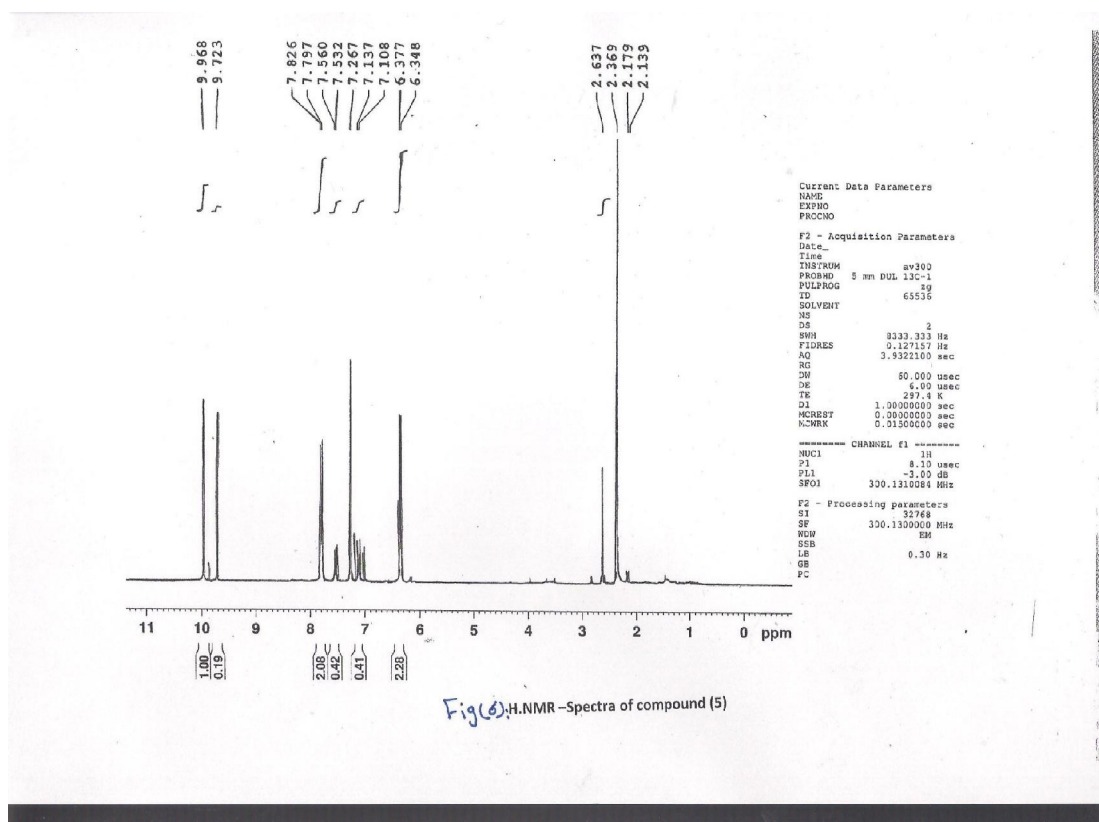
s=strong, m=medium, w=weak, v=very

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 ₂ 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 1068	243	392	65.168 65.096	3.370 3.310	10.486 10.348
[5]	C ₅₈ H ₃₆ N ₈ O ₅ S ₄ 1052	247	405	66.159 66.145	3.422 3.309	10.646 10.573







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