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Preparation and identification of macrocycles of oxazepine compounds

■ NAGHAM MAHMOOD AL–JAMALI

Author for Correspondence -
NAGHAM MAHMOOD AL-JAMALI
Department of Chemistry, College of Education for Women, Kufa University, Kufa, IRAQ
Email : dr.nagham_mj@yahoo. com

Abstract - A new type of macrocycles of oxazepine compounds have been prepared in this article, the macrocycles [3] has been linked with (maleic anhydride, phthalic anhydride, 3- nitro phthalic anhydride)to produce new type which are macrocycles oxazepine [4-6]. Macrocycles oxazepine [3-6] have been investigated by several techniques ((Uv-Visble), (C.H.N)-analyzer, (FT-IR)-spectra, H-NMR spectra, melting points).

Key words - Macrocycle, Oxazepine

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Oxazepam are class of compounds well known for along time as anesthetic drugs in surgery such as diazepine compounds which were first introduced for the treatment of anxiety.

This report focuses on the development in design and synthesis, macrocycles have played a pivotal role in the development of supra molecular chemistry, these substances have also been used for various applications, such as nano reaction chambers, solubility agents for membrane transport & in the development of chemical sensors[1-5].

Numerous researches have used Schiff- base condensation as the ring–closing step to synthesize macro cycles,often in high yield.

These compounds are intensely colored, but are not luminescent, in the solid state, they appear deep red to brown in color & they absorb very strongly in Uv-Visible region of the spectrum with peaks centred[6-9] at (400 nm).

EXPERIMENTAL METHODOLOGY

– All chemical used were supplied from Merck and 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.
- Micro analysis of elements .
- Ultraviolate–Visible spectra :shimadzu –1700, double beam with computerized, Japan .
- (Magnetic Nuclear Resonance)-spectra .

Synthesis methods:

Synthesis of 4,4–di (4-aniline)-diimine methyl-benzalidine [1] :

Compound [1] prepeared via condensation reaction which considered starting compound to synthesis of macrocyclic compounds in this paper.

A mixture of benzedine (0.07 mole, 12.8 g) and 4-amino benzaldehyde (0.14 mole, 16.9 g) were reacted by condensation in absolute ethanol for (2 hrs) refluxing until the participitate formed, after cooling, the precipitate was

filtered off and recrystallized from ethanol to produce colored crystal (25.5g, 86%) from compound [1].

Synthesis of 4,4–(di(4-aniline benzamide)–di imine methyl) benzalidine [2] :

By reaction of two mole of aroyl chloride with one mole of compound[1] via condensation reaction in ethanol as solvent.

Refluxing mixture of (0.06 mole, 23.4 g) compound [1] with (0.12 mole, 18.6 g) of 4-aminobenzoyl chloride were reacted in presence absolute ethanol with stirrer by condensation for (2 hrs) until the participitate formed, the precipitate was filtered off and recrystallized to produce (36g, 84%) crystal compound [2]

Synthesis of 4,4 – (di(4-phenyl benzamide)-tetra imine methyl) phenyl benzalidine –macrocycle [3] :

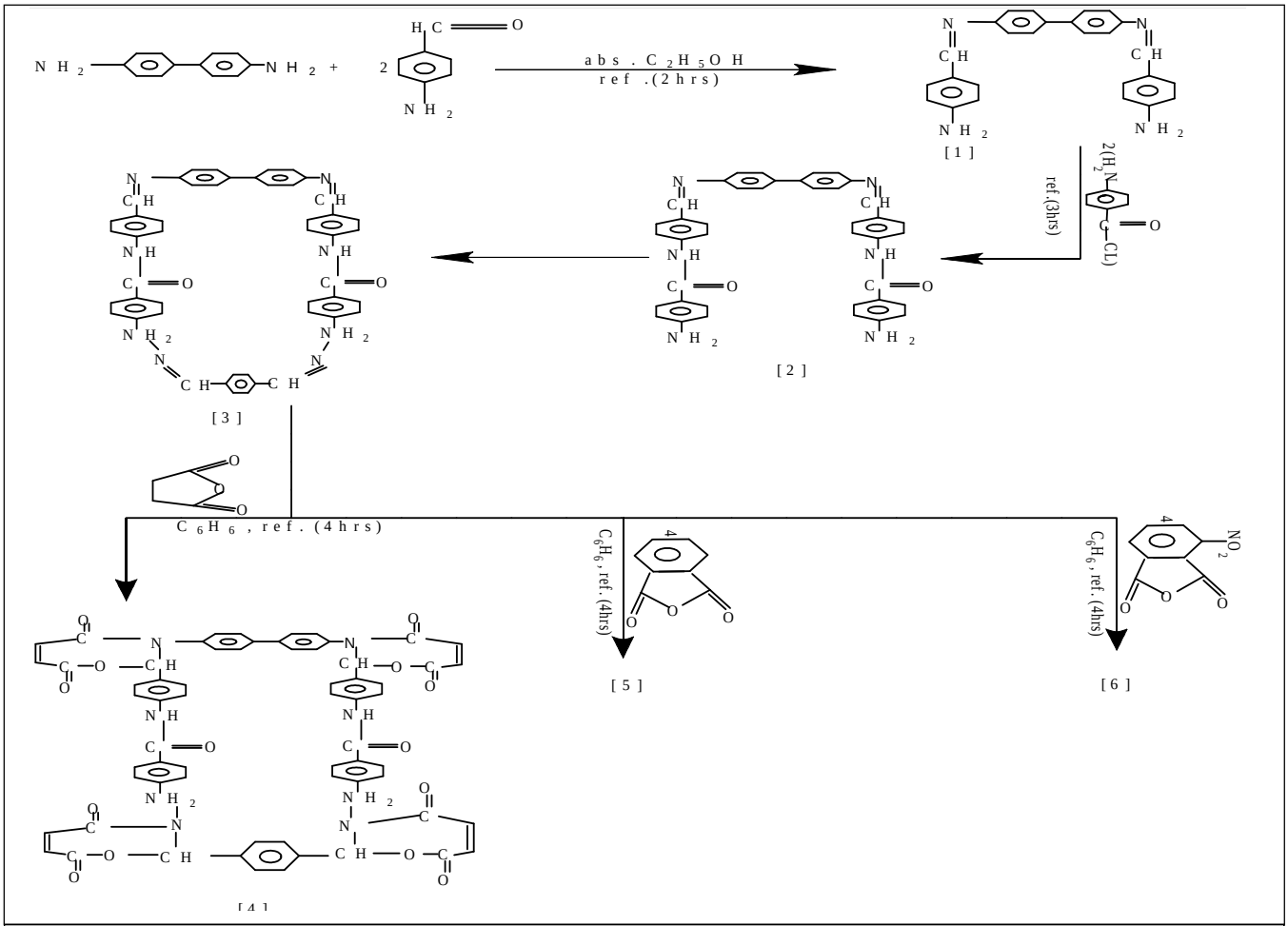
From compound[3], we prepeared macrocycles[4,5,6] by cyclization reaction of compound[2] which containing di amine with di carbonyl compound.

Refluxing ethanolic mixture of (0.03 mole, 18.8g) of compound[2] and (0.03 mole, 5.2 ml) of 4-formal benzaldehyde were reacted in absolute ethanol for (3hrs) the precipitate was filtrated off and recrystallized to give(19g, 82% of macrocycle compound[3].

Synthesis of 4,4-(di (4-phenyl benzamide)-tetra (oxazepine -4,7-dione)phenyl benzalidine. Macrocycles[4-6]:

Targe compounds [4-6] from research were synthised by cyclic addition of anhydride to four imine groups in cyclic compound[3] through break of bond (C=N) imine group and addition of anhydride.

A mixture of (0.01 mole, 7.26 g) of compound [3] with (0.04 mole) of one of anhydrides (maleic anhydride, phthalic anhydride, 3-nitro phthalic anhydride) were refluxed for (4hrs), after cooling, the precipitate was filtered off, and recrystallized to produce macrocycles oxazepines [4,5,6] about {(11.2g, 78%), (12.09, 74%), (13.89, 76%), respectively.



Reaction scheme:

EXPERIMENTAL FINDINGS AND ANALYSIS

Synthesized compounds [1-6] have been characterized by their melting points and spectroscopic techniques (Uv-Visible, FT.IR, H.NMR -spectrum and (C.H.N) – analysis) :

FT.IR- spectra:

FT.IR- showed appearance bands at (1631, 1639, 1611) cm^{-1} due according to reported to imine groups[10,11] (CH=N) of compounds [1,2,3], respectively, while this band is disappear and other bands are appear at (1680-1690) cm^{-1} due to (NH-CO) carbonyl of amid groups[11,12] in oxazepins cycle in compounds [2-6], this is strong evidence to formation macrocycles [4-6] other data of functional groups shown in the following in Table 1 and Fig. 1-4.

H.NMR-Spectrum:

H.NMR – Spectrum of compounds showed : singlet singal at ∫ 9.97 for one proton of azomethine group (-CH=N) [10,11] in compounds [1-3], while this peak is disappear and other peaks are appear in compound[4] such as :signal at 10.3 due to amide in oxazepine(NH-CO), doublet signal at 2.35 due to (CH=CH) alkene of maleic, doublet signal at(6.34, 6.37) due to benzidine, doublet signal at (7.79, 7.82) due to phenyl ring attached to amide, doublet signal at 7.26 due to phenyl ring adjacent o oxazepine ring in compound[4].

While spectra of compounds[5, 6] appeared : singlet two signals at{(10.06, 10.08), (10.44, 10.36)} due to (NH-CO)[10,11] in compounds [5, 6], respectively, singlet signals at {(14.15, 14.17, 14.40), (14.58, 14.72, 14.82)} due to proton of cyclic ester (CH-OOC)lactone in compounds [5, 6], respectively, doublet signal at 6.34, 6.77 and other doublet signal at 6.79, 7.80 due to benzidine, doublet signal at 7.19, 7.21 due to phenyl ring attached to amide group, doublet signal at 7.79, 7.82 due to other phenyl rings, singlet signals at (6.37, 6.80, 7.26, 7.70) due to protons of phthalic in compound[5].

While protons of phenyl group in compound[5] appeared doublet signals at (6.34, 6.37, 7.10, 7.13, 7.53, 7.56) due to (benzidine, phenyl ring attached to amide group, other phenyl rings), respectively, singlet signals at (7.26, 7.71, 7.79, 7.82) due to protons of 3-nitro phthalic in compound [6], all signals in Fig. 5-10.

Uv-Visible–spectra and (C.H.N)- Analysis :

The synthesized compounds have transition (π-π^*) of conjugated system, the Uv-Spectra of compounds [3-6] show absorption maxima (λ_{max} =375-420) nm due to oxochromic groups (amide, $-NO_2$[12], -C=O , - CH=N, ...)with conjugated system[13-16] in these compounds .

(C.H.N)- Analysis, melting point and data of λ_{max} are

Table 1 : FT-IR data (cm^{-1}) of compounds [3-6]

Comp. no	(C=N) Imine group	(C=O)str. Lactam(amide)	(C-O) Lactone	Others
[1]	1631	----	----	($-NH_2$):3317
[2]	1639	----	----	($-NH_2$):3440
[3]	1611	----	----	
[4]	----	1690	1232	
		1665		
[5]	----	1700	1230	
		1675		
[6]	----	1705	1240	($C-NO_2$): 1330,1535
		1670		

Table 2 : Melting points , M.F, $^a{}_{max}$ and (C.H.N) analysis of compounds

Comp. No	M.F	m.p. (c°)	λ_{max} (nm)	Calc. / found C%	H%	N%
1	$C_{26}H_{22}N_4$	152	315			
2	$C_{40}H_{32}N_6O_2$	168	340			
3	$C_{48}H_{34}N_6O_2$	210	375			
4	$C_{64}H_{42}N_6O_{14}$	228	395	68.694	3.756	7.513
				68.608	3.761	7.490
5	$C_{80}H_{50}N_6O_{14}$	235	410	72.837	3.793	6.373
				72.793	3.738	6.384
6	$C_{80}H_{46}N_{10}O_{22}$	248	420	64.085	3.070	9.345
				64.011	3.091	9.314

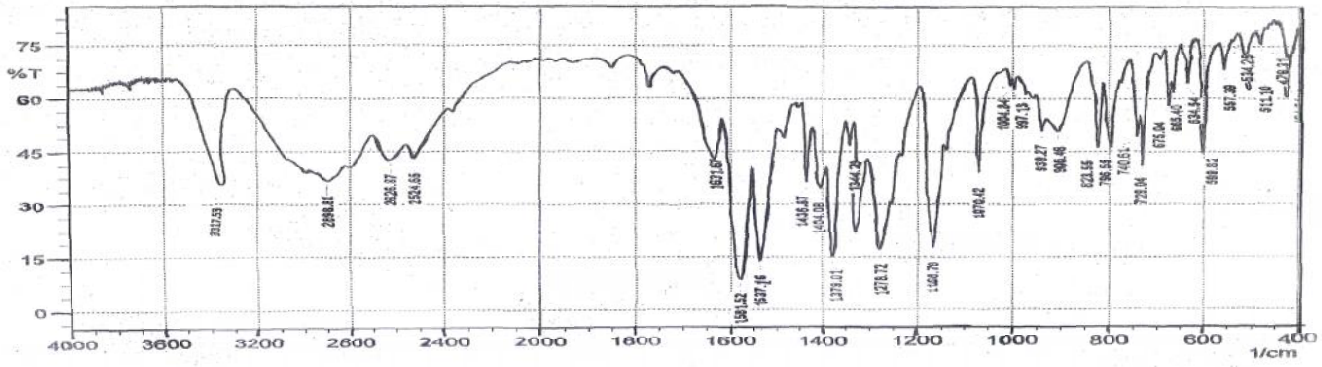


Fig. 1 : FT.IR spectrum of compound [1]

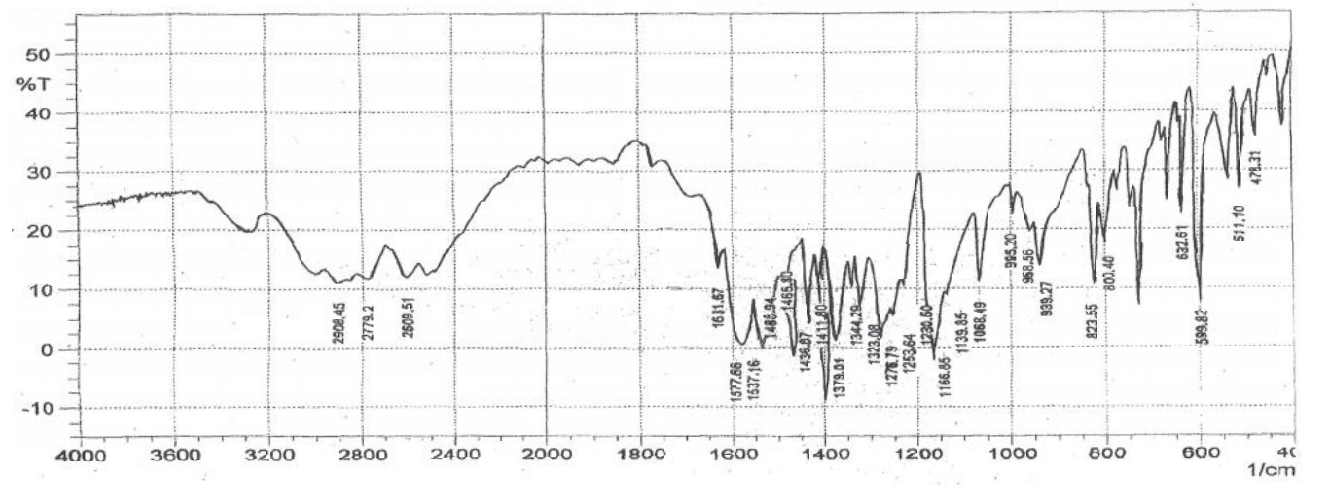


Fig. 3 : FT.IR spectrum of compound [3]

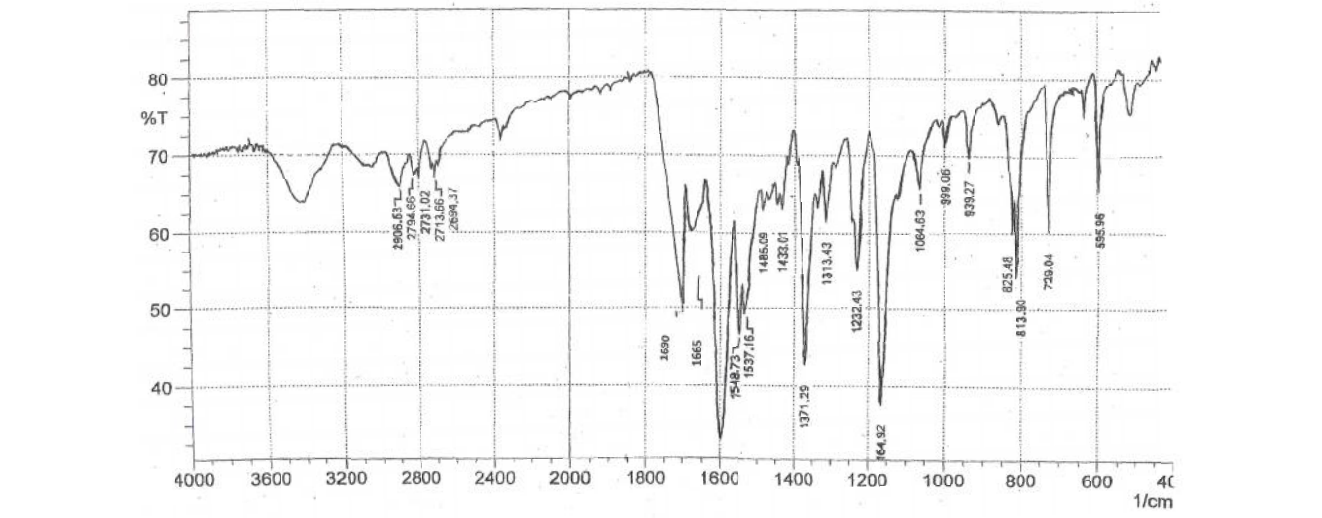


Fig. 4 : FT.IR spectrum of compound [4]

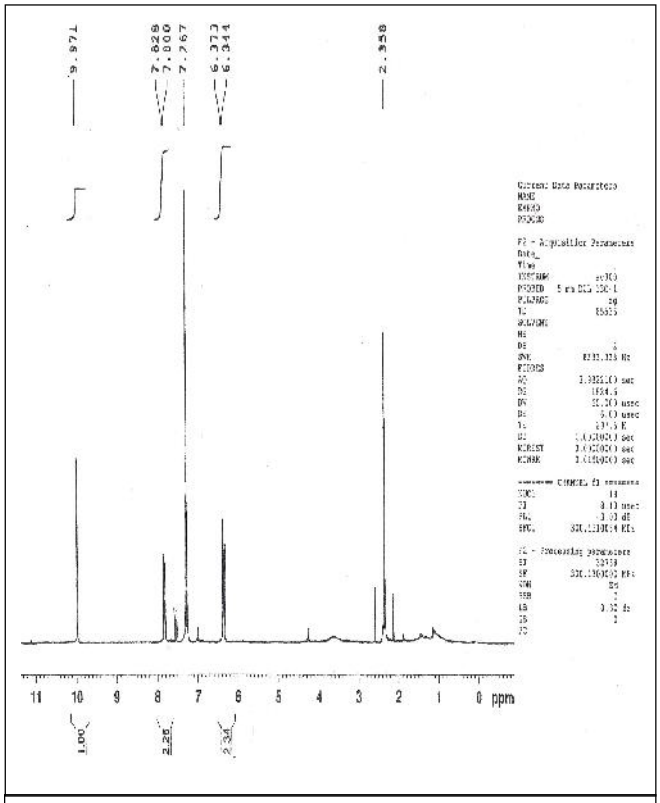


Fig. 5 : H.NMR- spectrum of compound [3]

listed in Table 2.

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