Indones. J. Chem., 2017, 17 (2), 330 - 335

Synthesis, Characterization and DFT Study of 4,4′-Oxydianiline Imines as Precursors of Tetrahalo-1,3-oxazepine-1,5-dione

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Received February 25, 2017; Accepted May 14, 2017

ABSTRACT

This work presents four Schiff bases derived from 4,4'-Oxydianiline, distinguished by the para substituted halogen of benzaldehyde. These bases were used to synthesize eight compounds of di-1,3-oxazepine by direct condensation with tetrachloro phthalic anhydride and tetrabromo phthalic anhydride. The reactions were monitored with TLC and all structures were characterized using spectroscopic techniques such as FT-IR, ^{1}H-NMR, ^{13}C-NMR and C, H, N techniques. On the other hand, a theoretical study by Density Functional Theory (DFT) for the electronic structures was intended to study the effects of para-substituted halogen of benzaldehyde on the electronic structure of synthesized Schiff bases by using the Gaussian program. Theoretical results indicate that there is no effect of halogen atoms except for bromine on HOMO and LUMO energies of the synthesized compounds.

Keywords: *Schiff bases; 1,3-Oxazepine; tetrachloro phthalic anhydride; DFT tetrabromo phthalic anhydride*

ABSTRAK

Penelitian ini menyajikan empat basa Schiff yang berasal dari 4,4'-Oksidianilina, yang dibedakan oleh subistitusi para halogen pada benzaldehida. Basa Schiff ini digunakan untuk mensintesis delapan senyawa di-1,3-oksazepin melalui kondensasi langsung dengan anhidrida tetrakloro ftalat dan anhidrida tetrabromo fthalat. Reaksi dipantau dengan KLT dan semua struktur dikarakterisasi dengan teknik spektroskopi seperti FT-IR, ^{1}H-NMR, ^{13}C-NMR dan C, H, N. Studi teoritis menggunakan Density Functional Theory (DFT) untuk struktur elektronik juga telah dilakukan untuk mempelajari efek subsitusi para halogen pada benzaldehida terhadap struktur elektronik basa Schiff yang disintesis dengan menggunakan program Gaussian. Hasil teoritis menunjukkan bahwa tidak ada efek dari atom halogen kecuali bromin pada energi HOMO dan LUMO dari senyawa yang disintesis.

Kata Kunci: *Basa Schiff; 1,3-Oxazepine; anhidrida tetrakloroftalat; DFT, anhidrida tetrabromoftalat*

INTRODUCTION

Oxazepam is non-homologous seven member ring contain two heteroatoms (oxygen and nitrogen) [1]. Oxazepine was synthesized by cycloaddition reaction which is a type of pericyclic reaction [2].The importance of 1,3-oxazepine is ascribed to their applications as anticonvulsant [3-7], antidepressant [8], skeletal muscle relaxants [9], neuroleptic [10], antitumor agent [11], antibacterial [12], anti-corrosion [13], anti-anxiety [14]. Many researchers were reported the synthesis of 1,3-oxazepine by either maleic anhydride or phthalic anhydride [15-17].The novelty of the present paper is the synthesis two core 1,3-oxazepine in same molecule by using substitute phthalic anhydrides and DFT Study of 4,4′-oxydianiline Imines as precursors of tetrahalo-1,3-oxazepine to calculate the energies of the HOMO and LUMO orbitals used to predict some physical properties of Schiff bases M1-M4, such as hardness, electron affinity *A,* Ionization potential *I*, absolute electronegativity *μ*, absolute hardness *η*, and electrophilicity w, stability and aromaticity.

EXPERIMENTAL SECTION

Materials

Benzaldehyde, 4-Fluoro benzaldehyde, 4-Chloro benzaldehyde, 4-Bromo benzaldehyde, tetrachloro phthalic anhydride, tetrabromo phthalic anhydride, 4,4′-Oxydianiline were supplied from Sigma-Aldrich Chemical Co. used directly without further purification, Solvents were supplied from Scharlau.

Instrumentation

Infrared spectra were recorded as KBr pellets on Bruker-Tensor 27 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker-300 MHz spectrometer using DMSO-d_6 as a solvent and TMS

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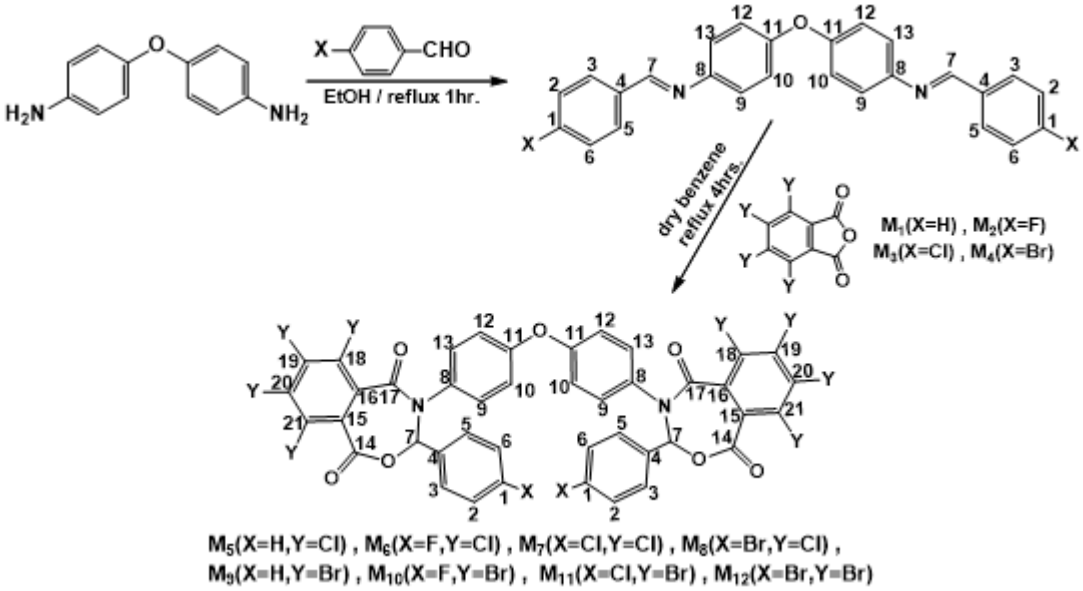
DOI: 10.22146/ijc.22437



Scheme 1. Synthetic route for synthesis of M_1-M_{12} compounds

(tetramethylsilane $(CH_3)_4Si$) as internal standard. The micro elemental analysis was performed using EURO-EA, UV/visible Jenway spectrophotometer Model 6800 was used to record UV-Vis spectra, TLC eluent (benzene:ethanol) (9:1) and developed by iodine.

Procedure

Routes formation of all compounds M_1-M_{12} and atoms number were depicted in Scheme 1.

General procedure for synthesis of (Imines) 4,4'-oxybis(N-(4- halobenzylidene) aniline) M_1-M_4

A solution of 4,4′-Oxydianiline (0.01 mol) in EtOH (20 mL) was added to 100 mL two neck round bottom flask containing appropriate aldehyde (0.02 mol) and EtOH (25 mL). The mixture was refluxed for 0.5 h and the obtained precipitate was filtered, washed with EtOH (20 mL) and recrystallized from EtOH.

Characterization of 4,4'-oxybis(N-benzylideneaniline) [M_1]. White solid, yield 82%; mp 169 °C. ^{1}H-NMR spectrum (δ, ppm) : 7.52-7.54 (t, *J*=6 Hz, $H_{1,2,6}$), 7.93-7.96 (m, *J*=3 Hz, $H_{3,5}$), 7.35-7.38 (d, *J*=9 Hz, $H_{13,9}$), 7.11-7.08 (d, *J*=9 Hz, $H_{12,10}$) and 8.67 (s, H_7). IR (KBr, v cm^{-1}): 3052 (C-H aromatic), 1617 (C=N), 1579, 1487 (C=C aromatic), 1243 (C-O). UV/visible (THF) nm: 252 π→π*(rings), 326 π→π*(C=N). TLC: R_f =0.81 (benzene:methanol)(9:1).

Characterization of 4,4'-oxybis(N-(4-fluorobenzylidene)aniline) [M_2]. White solid, yield 80%; mp 199 °C. ^{1}H-NMR spectrum (δ, ppm): 7.08-7.11 (d, *J*=8.5 Hz, $H_{12,10}$), 7.34-7.40 (t, *J*=8.7 Hz, $H_{2,6}$), 7.34-7.40 (t, *J*=9 Hz, $H_{13,9}$), 7.98-8.03 (m, *J*=6 Hz, $H_{3,5}$) and 8.67 (s, H_7). IR (KBr) (v cm^{-1}): 3064 (C-H aromatic), 1624 (C=N), 1590, 1492 (C=C aromatic), 1237 (C-O), 1099 (Ph-F). UV/visible (THF) nm : 252 π→π*(rings), 320 π→π*(C=N). TLC: R_f =0.80 (benzene:methanol)(9:1).

Characterization of 4,4'-oxybis(N-(4-chlorobenzylidene)aniline) [M_3]. White solid, yield 82%; mp 231 °C. ^{1}H-NMR spectrum (δ, ppm): 7.09-7.12 (d, *J*=8.9 Hz, $H_{12,10}$), 7.36-7.39 (d, *J*=8.9 Hz, $H_{13,9}$), 7.59-7.61 (d, *J*=8.3 Hz, $H_{2,6}$), 7.94-7.97 (d, *J*=8.5 Hz, $H_{3,5}$) and 8.69 (s, H_7). IR (KBr, v cm^{-1}): 3035 (C-H aromatic), 1620 (C=N), 1585, 1489 (C=C aromatic), 1249 (C-O), 1086 (Ph-Cl). UV/visible (THF, nm): 252 π→π*(rings), 322 π→π*(C=N). TLC: R_f = 0.73 (benzene:methanol)(9:1).

Characterization of 4,4'-oxybis(N-(4-bromobenzylidene)aniline) [M_4]. White solid, yield 89%; mp 249 °C. ^{1}H-NMR spectrum (δ, ppm): 7.09-7.12 (d, *J*=8.5 Hz, $H_{12,10}$), 7.37-7.40 (d, *J*=8.3 Hz, $H_{13,9}$), 7.73-7.76 (d, *J*=8.4 Hz, $H_{2,6}$), 7.88-7.90 (d, *J*=5.8 Hz, $H_{3,5}$) and 8.68 (s, H_7). IR (KBr, v cm^{-1}): 3034 (C-H aromatic), 1619 (C=N), 1582, 1488 (C=C aromatic), 1248 (C-O), 1063 (Ph-Br). UV/visible (THF, nm): 252 π→π*(rings), 316 π→π*(C=N). TLC: R_f = 0.72 (benzene:methanol)(9:1).

General procedure for synthesis of 4,4'-(4,4'-oxybis(4,1-phenylene))bis(6,7,8,9-tetrahalo-3-(4-halophenyl)-3,4-dihydrobenzo[1,3]oxazepine-1,5-dione) M_5-M_{12}

A solution of appropriate imine **M_1-M_4** (0.01 mol) in dry benzene (30 mL) was added to 250 mL two neck round bottom flask containing a mixture of appropriate anhydride (0.02 mol) and dry benzene (30 mL). The mixture was refluxed for 4 h then cooled and stirred at r.t. overnight. The obtained precipitate was filtered, washed with $NaHCO_3$ solution (10 mL) then distilled water (20 mL), dried and recrystallized from benzene to give the desired product.

Characterization of M_5-M_{12} compounds

The yields, elemental analytical, FT-IR, ^{1}H and ^{13}C NMR data for compounds ***M_5-M_{12}*** are summarized as follows:

M_5. Pale yellow solid, yield 71%; mp 281 °C dec., Anal. Found for $C_{42}H_{20}Cl_8N_2O_7.C_6H_6$ (%): C 50.07, H 2.31, N 2.96. Calc. (%) C 49.15, H 1.96, N 2.72. ^{1}H-NMR spectrum (δ, ppm): 10.85 (s, H_7), 6.5–7.95 (complex, $H_{aromatic}$). IR (KBr, ν cm^{-1}): 3061 (C-$H_{aromatic}$), 1725 (C=$O_{lactone}$), 1671 (C=O_{lactam}), 1607, 1547 (C=$C_{aromatic}$), 1499 (CO)-N, 1335 (CO)-O. UV/visible (THF, nm): 252 π→π*(rings). TLC : R_f = 0.69 (benzene:methanol)(7:3).

M_6. Pale yellow solid, yield 70%; mp 283 °C dec. Anal. Found for $C_{42}H_{18}Cl_8F_2N_2O_7.C_6H_6$ (%): C 47.23, H 1.41, N 3.04. Calc. (%) C 47.48, H 1.70, N 2.63. ^{1}H-NMR spectrum (δ, ppm): 10.84 (s, H_7), 6.64–7.62 (complex, $H_{aromatic}$). ^{13}C-NMR spectrum (δ, ppm): 116.18 (C_7), 161.49 (C_{17}), 165.38 (C_{14}), 116.48–158.90 ($C_{aromatic}$). IR (KBr, ν cm^{-1}): 3066 (C-$H_{aromatic}$), 1724 (C=$O_{lactone}$), 1669 (C=O_{lactam}), 1604, 1547 (C=$C_{aromatic}$), 1499 (CO)-N, 1336 (CO)-O. UV/visible (THF, nm): 252 π→π*(rings). TLC : R_f = 0.62 (benzene:methanol)(7:3).

M_7. Pale yellow solid, yield 69%; mp 241 °C dec., Anal. Found for $C_{42}H_{18}Cl_{10}N_2O_7.C_6H_6$ (%): C 45.28, H 2.12, N 2.83. Calc. (%) C 46.05, H 1.65, N 2.55. ^{1}H-NMR spectrum (δ, ppm): 10.84 (s, H_7), 6.64–7.63 (complex, $H_{aromatic}$). ^{13}C NMR spectrum (δ, ppm): 116.67 (C_7), 161.49 (C_{17}), 165.36 (C_{14}), 117.13–159.01 ($C_{aromatic}$). IR (KBr, ν cm^{-1}): 3059 (C-$H_{aromatic}$), 1723 (C=$O_{lactone}$), 1667 (C=O_{lactam}), 1609, 1539 (C=$C_{aromatic}$), 1503 (CO)-N, 1334 (CO)-O. UV/visible (THF, nm): 252 π→π*(rings). TLC : R_f = 0.45 (benzene:methanol)(7:3).

M_8. Pale yellow solid, yield 70%; mp 249 °C dec., Anal. Found for $C_{42}H_{18}Br_2Cl_8N_2O_7$ (%): C 46.36, H 2.13, N 2.95. Calc. (%) C 45.61, H 1.64, N 2.53. ^{1}H-NMR spectrum (δ, ppm): 10.85 (s, H_7), 6.66–7.89 (complex, $H_{aromatic}$). ^{13}C-NMR spectrum (δ, ppm): 116.94 (C_7), 161.50 (C_{17}), 165.28 (C_{14}), 118.01–159.04 ($C_{aromatic}$). IR (KBr, ν cm^{-1}): 3062 (C-$H_{aromatic}$), 1722 (C=$O_{lactone}$), 1666 (C=O_{lactam}), 1609, 1545 (C=$C_{aromatic}$), 1501 (CO)-N, 1336 (CO)-O. UV/visible (THF) nm : 252 π→π*(rings),. TLC : R_f =0.84 (benzene:methanol)(7:3).

M_9. Pale yellow solid, yield 56%; mp 271 °C dec., Anal. Found for $C_{42}H_{20}Br_8N_2O_7.C_6H_6$ (%): C 35.95, H 1.75, N 2.74. Calc. (%) C 36.50, H 1.45, N 2.02. ^{1}H-NMR spectrum (δ, ppm): 10.75 (s, H_7), 6.76–7.93 (complex, $H_{aromatic}$). IR (KBr, ν cm^{-1}): 3059 (C-$H_{aromatic}$), 1722 (C=$O_{lactone}$), 1671 (C=O_{lactam}) 1605, 1542 (C=$C_{aromatic}$), 1500 (CO)-N, 1310 (CO)-O. UV/visible (THF, nm): 242 π→π*(rings). TLC : R_f = 0.58 (benzene:methanol)(7:3).

M_{10}. Pale yellow solid, yield 58%; mp 279 °C dec., Anal. Found for $C_{42}H_{18}Br_8F_2N_2O_7.C_6H_6$ (%): C 33.45, H 1.78, N 2.45. Calc. (%) C 33.71, H 1.21, N 1.87. ^{1}H-NMR spectrum (δ, ppm): 10.76 (s, H_7), 6.61-8.02 (complex, $H_{aromatic}$). ^{13}C-NMR spectrum (δ, ppm): 116.20 (C_7), 162.96 (C_{17}), 166.44 (C_{14}), 116.49–158.91 ($C_{aromatic}$). IR (KBr, ν cm^{-1}): 3066 (C-$H_{aromatic}$), 1723 (C=$O_{lactone}$), 1671 (C=O_{lactam}) 1603, 1543 (C=$C_{aromatic}$), 1502 (CO)-N, 1310 (CO)-O. UV/visible (THF, nm): 240 π→π*(rings). TLC : R_f = 0.75 (benzene:methanol)(7:3).

M_{11}. Pale yellow solid, yield 58%; mp 261 °C dec., Anal. Found for $C_{42}H_{18}Br_8Cl_2N_2O_7$ (%): C 36.49, H 1.95, N 2.58. Calc. (%) C 36.74, H 1.32, N 2.04. ^{1}H-NMR spectrum (δ, ppm): 10.76 (s, H_7), 6.68–7.96 (complex, $H_{aromatic}$). ^{13}C-NMR spectrum (δ, ppm): 116.03 (C_7), 162.93 (C_{17}), 166.34 (C_{14}), 117.77–158.93 ($C_{aromatic}$). IR (KBr, ν cm^{-1}): 3060 (C-$H_{aromatic}$), 1722 (C=$O_{lactone}$), 1670 (C=O_{lactam}), 1599, 1538 (C=$C_{aromatic}$), 1500 (CO)-N, 1310 (CO)-O. UV/visible (THF, nm): 248 π→π*(rings). TLC : R_f = 0.76 (benzene:methanol)(7:3).

M_{12}. Pale yellow solid, yield 59%; mp 199 °C dec., Anal. Found for $C_{42}H_{18}Br_{10}N_2O_7.C_6H_6$ (%): C 32.16, H 1.48, N 2.62. Calc. (%) C 32.76, H 1.17, N 1.81. ^{1}H-NMR spectrum (δ, ppm): 10.62 (s, H_7), 6.57–7.74 (complex, $H_{aromatic}$). ^{13}C-NMR spectrum (δ, ppm): 115.63 (C_7), 162.99 (C_{17}), 166.48 (C_{14}), 115.87-158.54 ($C_{aromatic}$). IR (KBr, ν cm^{-1}): 3049 (C-$H_{aromatic}$), 1722 (C=$O_{lactone}$), 1672 (C=O_{lactam}), 1616, 1540 (C=$C_{aromatic}$), 1500 (CO)-N, 1310 (CO)-O. UV/visible (THF, nm): 260 π→π*(rings). TLC : R_f = 0.78 (benzene:methanol)(7:3).

RESULT AND DISCUSSION

Characterization of M_1-M_4 by FTIR and ^{1}H-NMR

Schiff bases were synthesized by direct condensation of primary amine and aldehyde. They were used as starting materials for the synthesis of seven member heterocyclic ring by their reaction with a cyclic anhydride.

FTIR Spectra for Schiff bases showed the appearance of aromatic C–H within range of 3034–3064 cm^{-1}, azomethine groups (C=N) within range of 1617-1624 cm^{-1}, ν C=C for aromatic ring within range (1579-1590 cm^{-1}) and (1487-1492 cm^{-1}), while Ph-x absorption bands appear within range (1063–1099 cm^{-1}) [15]. FTIR data for M1-M4 are tabulated in Table 1.

^{1}H-NMR for Schiff bases spectra exhibited pure singlet signal within range of δ= 8.67–8.69 ppm attributed to protons for azomethine group and set of signals within range of δ =7.09–8.2 ppm attributed for aromatic protons [16-17]. ^{1}H-NMR data are detailed in Table 2.

Characterization of M_5-M_{12} by FTIR and ^{1}H, ^{13}C-NMR

FTIR spectra for 1,3-Oxazepine showed aromatic C–H within range of 3049–3066 cm^{-1}, the stretching vibrations of the C=$O_{lactone}$, C=O_{lactam} groups confirmed

Table 1. FTIR spectral data (cm^{-1}) for synthesized M_1-M_4 compound

Comp.	v C-H $_{arom.}$	v C=N	v C=C $_{ring}$		v C-O	Ph-X
M_1	3052	1617	1579	1487	1243	-
M_2	3064	1624	1590	1492	1237	1099
M_3	3035	1620	1585	1489	1249	1086
M_4	3034	1619	1582	1488	1248	1063

Table 2. ^{1}H-NMR chemical shift (ppm) for synthesized M_1-M_4 compounds

	Compounds Symb.			
	M_1	M_2	M_3	M_4
H_1	7.54-7.52 (t, *J*=6 Hz)	-	-	-
$H_{2,6}$	7.54-7.52 (t, *J*=6 Hz)	7.40-7.34 (t, *J*=8.7 Hz)	7.61-7.59 (d, *J*=8.3 Hz)	7.76-7.73 (d, *J*=8.4 Hz)
$H_{3,5}$	7.96-7.93 (m, *J*=3 Hz)	8.03-7.98 (m, *J*=6 Hz)	7.97-7.94 (d, *J*=8.5 Hz)	7.90-7.88 (d, *J*=5.8 Hz)
$H_{13,9}$	7.38-7.35 (d, *J*=9 Hz)	7.40-7.34 (t, *J*=9 Hz)	7.39-7.36 (d, *J*=8.9 Hz)	7.40-7.37 (d, *J*=8.3 Hz)
$H_{12,10}$	7.11-7.08 (d, *J*=9 Hz)	7.11-7.08 (d, *J*=8.5 Hz)	7.12-7.09 (d, *J*=8.9 Hz)	7.12-7.09 (d, *J*=8.5 Hz)
H_7	8.67(s)	8.67(s)	8.69(s)	8.68(s)

Table 3. FTIR spectral data (cm^{-1}) for synthesized M_5-M_{12} compounds

Comp.	v C-H $_{arom.}$	v C=O $_{lactone}$	v C=O $_{lactam}$	v C=C $_{ring}$	(CO)-N	(CO)-O
M_5	3061	1725	1671	1607, 1547	1499	1335
M_6	3066	1724	1669	1604, 1547	1499	1336
M_7	3059	1723	1667	1609, 1539	1503	1334
M_8	3062	1722	1666	1609, 1545	1501	1336
M_9	3059	1722	1671	1605, 1542	1500	1310
M_{10}	3066	1723	1671	1603, 1543	1502	1310
M_{11}	3060	1722	1670	1599, 1538	1500	1310
M_{12}	3049	1722	1672	1616, 1540	1500	1310

Table 4. ^{1}H-NMR chemical shift (ppm) for synthesized M_5-M_{12} compounds

Comp.	H_7	$H_{aromatic\ rings}$
M_5	10.85 s	6.5–7.95 complex
M_6	10.84 s	6.64–7.62 complex
M_7	10.84 s	6.64–7.63 complex
M_8	10.85 s	6.66–7.89 complex
M_9	10.75 s	6.76–7.93 complex
M_{10}	10.76 s	6.61–8.02 complex
M_{11}	10.76 s	6.68–7.96 complex
M_{12}	10.62 s	6.57–7.74 complex

Table 5. ^{13}C-NMR chemical shift (ppm) for selected synthesized compounds

Comp.	C_7	C_{17}	C_{14}	$C_{aromatic\ rings}$
M_6	116.18	161.49	165.38	116.48–158.90
M_7	116.67	161.49	165.36	117.13–159.01
M_8	116.94	161.50	165.28	118.01–159.04
M_{10}	116.20	162.96	166.44	116.49–158.91
M_{11}	116.03	162.93	166.34	117.77–158.93
M_{12}	115.63	162.99	166.48	115.87–158.54

by strong absorption bands within frequency range 1722–1725, 1666–1672 cm^{-1}, respectively, v C=C for aromatic ring observed within range (1599–1616 cm^{-1}) and (1538–1547 cm^{-1}), and v (CO)-N, v (CO)-O observed within range of 1499–1503, 1310–1337 cm^{-1}, respectively [18]. FTIR data are illustrated in Table 3.

^{1}H-NMR spectra for 1,3-Oxazepine showed singlet signal within the range of δ 10.62–10.85 ppm assign to H_7 protons, while the signal for aromatic protons observed as multiplet-signal [17]. ^{1}H-NMR data are presented in Table 4.

Moreover, the structures of the title compounds are further substantiated by ^{13}C-NMR. The ^{13}C-NMR spectra of 1,3-Oxazepine indicate the presence of aromatic carbons signals within range δ = 118.01–158.54 ppm, $C14_{(C=O\ lactone)}$ within range δ = 165.28–166.48 ppm, $C17_{(C=O\ lactam)}$ within range δ = 161.49–162.99 ppm and C7 within range δ = 116.03–116.94 ppm [16]. ^{13}C-NMR data are presented in Table 5.

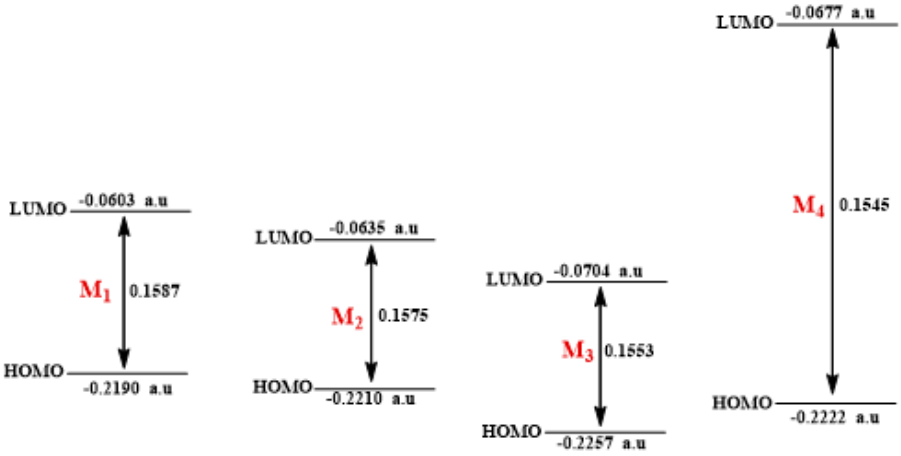


Fig 1. HOMO and LUMO orbitals and their energy gap for M_1-M_4 compounds

Table 6. HOMO, LUMO, and Mulliken charge for M_1-M_4 synthesized compounds (a.u.)

Comp.	HOMO	LUMO	LUMO – HOMO	Mulliken charge		X
				X	N	
M_1	-0.2190	-0.0603	0.1587	0.191602	-0.567040	H
M_2	-0.2210	-0.0635	0.1575	-0.288833	-0.568794	F
M_3	-0.2257	-0.0704	0.1553	0.163581	-0.566420	Cl
M_4	-0.2222	-0.0677	0.1545	0.209521	-0.566931	Br

Table 7. Some electronic properties for synthesized M_1-M_4 compounds

Comp.	μ	ω	η	*I*	A	D.M. Debye	Point group
M_1	0.13973	0.0002498	0.07935	0.21909	0.06038	1.457	C_1
M_2	0.14233	0.0002441	0.07875	0.22108	0.06358	2.385	C_1
M_3	0.14812	0.0002341	0.07765	0.22577	0.07047	3.221	C_1
M_4	0.14499	0.0002309	0.07729	0.22229	0.06770	2.500	C_1

[μ= Electronegativity, ω= Electrophilicity, η= Hardness, *I*= Ionization potential, *A*= Electron affinity]

Table 8. The arrangement results for calculating property

Property	Results of arrangement
LUMO – HOMO gap	$M_1 > M_2 > M_3 > M_4$
$A=(-E_{LUMO})$	$M_3 > M_4 > M_2 > M_1$
$I=(-E_{HOMO})$	$M_3 > M_4 > M_2 > M_1$
$\eta = 1/2(I-A)$	$M_1 > M_2 > M_3 > M_4$
$\omega = \mu^2/2\eta$	$M_1 > M_2 > M_3 > M_4$
$\mu = 1/2(I+A)$	$M_3 > M_4 > M_2 > M_1$
Dipole moment (D.M)	$M_3 > M_4 > M_2 > M_1$

Computational Study

Molecular properties related to synthesized M_1-M_4 compounds such as dipole moment, HOMO, LUMO, HOMO-LUMO gap and some electronic properties were performed by using density functional theory (DFT), (B3LYP) and the 6-31G as a basis set using the Gaussian 09W package.

Density Functional Theory Calculations

Molecule with large HOMO-LUMO gaps is generally stable and unreactive, while with small gaps is reactive and the higher the HOMO energies, the easier for HOMO to donate electrons, the lower the LUMO energies, the easier for LUMO to accept electrons [19].

Theoretical study showed a little effect of synthesized Schiff bases M_1-M_4 by substitution of halogen except for M_4 increasing the LUMO energy level and the molecule becomes more stable compared to other compounds. This behaviour can be explained to the low electronegativity of bromine atom, results are given in Table 6, Fig. 1. HOMO and LUMO orbitals and their energy gap for M_1-M_4 compounds.

The electronic properties such as electron affinity *A,* Ionization potential *I*, absolute electronegativity *μ*, absolute hardness *η*, and electrophilicity *ω* were calculated by the following equations [19], results are given in Table 7.

$$A = (-E_{LUMO})$$

$$I = (-E_{HUMO})$$

$$\mu = \frac{1}{2}(I + A)$$

$$\eta = \frac{1}{2}(I - A)$$

$$\omega = \frac{\mu^2}{2\eta}$$

The arrangement for electronic properties summarized in Table 8.

CONCLUSION

In this paper, the 1,3-oxazepines were successfully synthesized, and this has been proved by spectral analyses. The study of energies of the HOMO and LUMO orbitals negative indicates that compounds M_1-M_4 are stable compounds, Hardness results indicate that compound M_1 has more aromatic character compared to other compounds.

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