RESEARCH ARTICLE

Synthesis, Characterization, and Theoretical Study of New Schiff bases from (*S*)-2-amino-3-(3,4-dihydroxyphenyl)-2-methyl propanoic acid as Initial Material of 1,3-Oxazepine-1,5-dione

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Received: 19th March, 2021; Revised: 14th April, 2021; Accepted: 20th May, 2021; Available Online: 25th June, 2021

ABSTRACT

The present investigation introduced four Schiff bases derived from (S)-2-amino-3-(3,4-dihydroxyphenyl)-2-methylpropanoic acid, featured by the substituted benzaldehyde. These bases were utilized to prepare eight compounds of 1,3-oxazepine by direct condensation with phthalic anhydride and tetrachlorophthalic anhydride. The reactions were watched with thin layer chromatography (TLC) and all structures were characterized utilizing spectroscopy techniques like Fourier-transform infrared spectroscopy (FTIR) and some of them were characterized by Proton nuclear magnetic resonance (^{1}H-NMR), Carbon nuclear magnetic resonance (^{13}C-NMR), and CHN analysis techniques. Theory for the electronic structures was purposed to study the effects of substituted benzaldehyde on the electronic structure of prepared Schiff base by utilizing the Gaussian program. Theoretical outcomes point out that there is the effect of substituted groups on HOMO and LUMO energies of the prepared compounds.

Keywords: 1,3-Oxazepine, DFT, Schiff base, Tetrachlorophthalic anhydride.

International Journal of Drug Delivery Technology (2021); DOI: 10.25258/ijddt.11.2.3

How to cite this article: Al-Naseeri AKA, Saleh HK, Jassim IK. Synthesis, Characterization, and Theoretical Study of New Schiff bases from (S)-2-amino-3-(3,4-dihydroxyphenyl)-2-methyl propanoic acid as Initial Material of 1,3-Oxazepine-1,5-dione. International Journal of Drug Delivery Technology. 2021;11(2):258-264.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

Heterocyclic compounds are considered one of an important type of organic compounds due to their applications in different fields like industrial and biological studies.[1-4] Heterocyclic compounds are cyclic compounds in which One or more of the atoms of the ring are heteroatoms.[5] Schiff base compounds are the most important class containing azomethine group (HC=N-) are known as imine group.[6] The domain of Schiff base has been quickly developed because of the broad possible structures for the products depending upon the active carbonyl compounds and amines considered.[7] Several Schiff bases were reported to own pharmaceutical applications such as antibacterial,[8] antitumor,[9] antifungal,[10] antioxidant,[11] enzymatic activity,[12] anticancer,[13] anti-inflammatory,[14] antihypertensive,[15] anti-glycation,[16] anti-HIV,[17] anti-tubercular,[18] anticonvulsant, and neurotoxicity.[19] In another hand, the coordination chemistry of Schiff bases has been characterized because of the complex's enjoyable and remarkable properties as the ability to bond with toxic and heavy metal atoms[20] and shows up catalytic reduction[21] and photochromism.[22] Schiff bases had applied for industrial aims like catalysts, active transport, pigments, liquid-liquid extraction, polymer stabilizer, and intermediates in organic synthesis.[23] They are helpful in day-to-day life for the imine group's boundless potency and ease in their forming.[24]

Oxazepine has unsaturated seven-member rings, which are non-homologous containing nitrogen and oxygen as two heteroatoms with five carbon atoms.[25] 1,3-oxazepine has been prepared by cycloaddition reaction as one type of pericyclic reaction.[26] Several reports have described the imported Oxazepine derivatives are a great variety of biological activities such as antibacterial,[27] antifungal,[28] antitumor,[29] anti-influenza,[30] antianxiety,[31] antipsychotic,[32] anticonvulsant,[33] anticancer,[34] as well as own them anti-corrosion property.[35]

The novelty of our work here is the preparation and characterization of new1,3-oxazepine by using phthalic anhydride and substituted phthalic anhydride and the studies, supported by Density Function Theory (DFT) calculations of Schiff bases (R_1-R_4) as a source of 1,3-oxazepin. The ground-state properties and bonding characteristics of Schiff bases (R_1-R_4) have performed using (DFT) at the B3LYP/6-311G(d,p) for (R_1-R_4).

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EXPERIMENTAL SECTION: MATERIALS

All chemicals utilized in this study were chemically pure stair. They included 4-hydroxy-3-methoxybenzaldehyde, 4-chlorobenzaldehyde, 2,4-dichlorobenzaldehyde, 4-nitrobenzaldehyde, phthalic anhydride, tetrachlorophthalic anhydride, sodium hydroxide (Sigma-Aldrich chemical Co). solvents (Scharlan and BDH). Standard drug (*S*)-2-amino-3-(3,4-dihydroxyphenyl)-2-methylpropanoic acid was supplied by drug industrials and medical appliances by the state company of drug industrials and medical appliances Samara, Iraq.

Instrumentation

Melting points were registered to utilize electrothermal melting point tool with uncorrected. Infrared spectra detected as KBr disks (Shimadzu FT-IR 8400s spectrophotometer). ^{1}H-NMR spectra by (Bruker Biospin 400MHz spectrometer) by using DMSO-d_6 as a solvent with TMS [$(CH_3)_4Si$] as internal standard. ^{13}C-NMR spectra detection by (Bruker Biospin 400MHz spectrometer) with DMSO-d_6 as a solvent. The micro elemental analysis is implemented by (vario EL-III (CHNS) mode) (Elementar Analyser Systeme GmbH). All the reactions were monitored by thin-layer chromatography (TLC) and spots were visualized utilizing an iodine chamber.

Synthesis Procedures

All compounds (R_1-R_{12}) were synthesized according to Scheme 1, and some of them, compounds (R_1-R_{12}) gave agreeable elemental analysis, FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectra that matched data reported in the borrow references.

*General procedure for synthesis of (imine) sodium**(S,E)**-3-(3,4-dihydroxy phenyl)-2-(substitutedbenzylidene)amino)-2-methyl propanoate[R_1-R_4]*

The imine derivatives under investigation were prepared according to[36] some modifications.

Sodium*(S)*-3-(3,4-dihydroxyphenyl)-2-(4-hydroxy-3-methoxybenzylidene)amino) -2-methyl propanoate [R_1]: Deep green solid, yield 91%, mp 320 ^{o}C Dec., the reflux time of reaction 9hrs, Anal. Found for $C_{18}H_{18}NNaO_6$ (%): C 58.38, H 4.22, N 3.19. Calc. (%): C 58.86, H 4.94, N 3.81. R_f= 0.77 (ethanol:cyclohexane, 8:2). FT-IR (KBr): 3450, 3033, 2941, 2808, 1461, 1402, 1519, 1309, 1612, 1280, 1039, 738, 800, 879, 1120 cm^{-1}.

Sodium(S)-3-(3,4-dihydroxyphenyl)-2-(4-chlorobenzylidene) amino)-2-methyl propanoate [R_2]

Brown solid, yield 82.9%, mp 243-245 ^{o}C, the reflux time of reaction 5.5hrs, Anal. Found for $C_{17}H_{15}ClNNaO_4$ (%): C 57.33, H 4.15, N 3.89. Calc. (%): C 57.40, H 4.25, N 3.94. R_f= 0.82 (ethanol:cyclohexane, 8:2). FT-IR (KBr): 3460, 3095, 2979, 2808, 1527, 1467, 1587, 1317, 1660, 1276, 1039, 709, 831, 1095cm^{-1}.

Sodium(S)-3-(3,4-dihydroxyphenyl)-2-(2,4-dichlorobenzylidene)amino)-2-methyl propanoate [R_3]

Shinning green solid, yield 68.3%, mp 310 ^{o}C Dec., the reflux time of reaction 3hrs, Anal. Found for $C_{17}H_{14}Cl_2NNaO_4$ (%): C 52.29, H 3.61, N 3.56. Calc. (%): C 52.33, H 3.62, N 3.59. R_f= 0.8 (ethanol:cyclohexane, 8:2). FT-IR (KBr): 3445, 3071, 2980, 2825, 1529, 1455, 1571, 1369, 1640, 1241, 1052, 716, 819, 869, 1103cm^{-1}.

Sodium(S)-3-(3,4-dihydroxyphenyl)-2-(4-nitrobenzylidene) amino)-2-methyl propanoate [R_4]

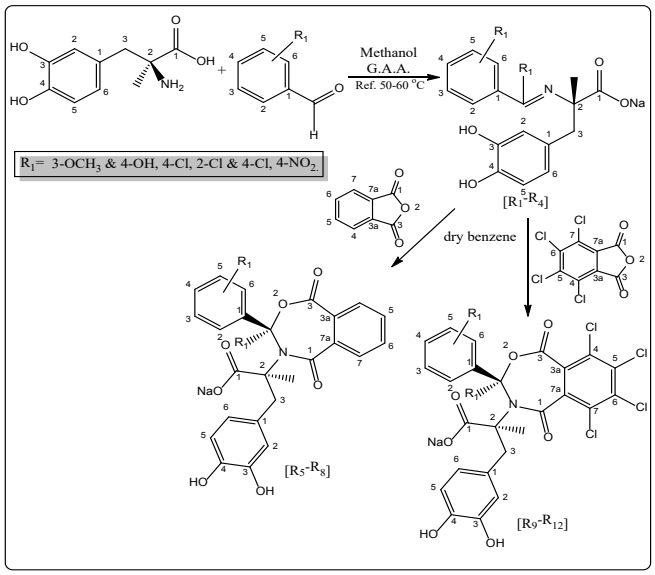
Beige solid, yield 78.5%, mp 117-120 ^{o}C, the reflux time of reaction 6hrs, Anal. Found for $C_{17}H_{15}N_2$ NaO_6 (%): C 55.14, H 3.63, N 6.95. Calc. (%): C 55.74, H 4.13, N 7.65. R_f= 0.87 (ethanol:cyclohexane, 8:2). FT-IR (KBr): 3444, 3093, 2943, 2870, 1515,1480, 1579, 1303, 1606, 1234, 1097, 792, 858, 1346, 1460 cm^{-1}.

General procedure for Synthesis of sodium (S)-3-(3,4-dihydroxyphenyl)-2-((R)-1,5-dioxo-3-substitutedphenyl-1,5-dihydrobenzo[e][1,3]oxazepin-4(3H)-yl)-2-methylpropanoate [R_5-R_8]

The 1,3-oxazepine derivatives under investigation are prepared according to the procedure previously described in literature with some modifications.[37]

Sodium(S)-3-(3,4-dihydroxyphenyl)-2-((R)-1,5-dioxo-3-(4-hydroxy-3-methoxy phenyl)-1,5-dihydrobenzo[e][1,3] oxazepin-4(3H)-yl)-2-methylpropanoate[R_5]

Shining white solid, yield 70%, mp 132 ^{o}C, the reflux time of reaction 8hrs, Anal. Found for $C_{26}H_{22}N$ NaO_9 (%): C 60.09, H 3.83, N 2.49. Calc. (%): C 60.59, H 4.30, N 2.72. R_f= 0.70 (ethylacetate:toluene, 2:1). FT-IR (KBr): 3444, 3093, 2943, 2870, 1505, 1485, 1565, 1305, 1665, 1626, 1243, 1075, 710, 840, 1185cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ_H 1.36 (3H, s, -CH_3), 3.03-3.09 (2H, d, -CH_2-), 3.75(3H, s, -O-CH_3-), 6.58-7.98 (10H, m, Aro. Protons), 7.53 (1H, s, N-CH-O), 8.52 (3H, s, Aro.-O-H). 13C NMR (400 MHz, DMSO-d_6, ppm): δ_C 24.78 (-CH_3), 43.75 (-CH_2-), 58.27 (-O-CH_3), 71.23 (Me-C-N), 85.00 (N-C-O), 148.00 (=C-OMe), 144.54,145.72,147.36 (=C-OH), 168.90 (-O-CO-), 166.03(-N-CO-),179.74(-$CO_{carboxylate}$),116.37,



Scheme 1: Illustration of the synthetic rout for preparation of R_1-R_{12} compounds

118.10, 123.28, 128.79, 125.72, 130.53, 131.98, 133.60, 134.25, 111.15, 114.59, 122.28, 130.99 (C-Ar).

Sodium(S)-3-(3,4-dihydroxyphenyl)-2-((R)-1,5-dioxo-3-(4-chlorophenyl)-1,5-dihydrobenzo[e][1,3] oxazepin-4(3H)-yl)-2-methylpropanoate [R_6]

Beige solid, yield 85%, mp 246 ºC, the reflux time of reaction 6hrs, Anal. Found for $C_{25}H_{19}ClNNaO_7$ (%): C 59.34, H 3.27, N 2.37. Calc. (%): C 59.59, H 3.80, N 2.78. R_f= 0.54 (ethylacetate:toluene, 2:1). FT-IR (KBr): 3448, 3029,2980, 2872, 1573, 1525, 1614, 1315, 1658, 1619, 1238, 1019,702, 829, 1199, 1137cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ_H 1.36 (3H, s, -CH_3), 3.42-3.47 (2H, d, -CH_2-), 6.47-7.94 (11H, m, Aro. Protons), 7.68 (1H, s, N-CH-O), 8.30 (2H, s, Aro.-O-H). 13C NMR (400 MHz, DMSO-d_6, ppm): δ_C 24.78 (-CH_3), 43.75 (-CH_2-), 71.23 (Me-C-N), 86.49 (N-C-O), 136.92(=C-Cl), 144.82,146.03 (=C-OH), 170.78(-O-CO-), 168.90(-N-CO-), 179.74(-$CO_{carboxylate}$), 126.75, 129.26, 130.94, 131.98, 132.76, 134.25, 116.37, 118.10, 123.28, 128.79, 127.37, 130.53, 139.73 (C-Ar).

Sodium(S)-3-(3,4-dihydroxyphenyl)-2-((R)-1,5-dioxo-3-(2,4-dichlorophenyl)-1,5-dihydrobenzo[e][1,3]oxazepin-4(3H) -yl)-2-methylpropanoate [R_7]

Off white solid, yield 78%, mp 242 ºC, the reflux time of reaction 6hrs, Anal. Found for $C_{25}H_{18}Cl_2NNaO_7$ (%): C 56.55, H 3.84, N 3.31. Calc. (%): C 55.78, H 3.37, N 2.60. R_f= 0.52 (ethylacetate:toluene, 2:1). FT-IR (KBr): 3541, 3030, 2924, 2845, 1575, 1534, 1601, 1313, 1772, 1648, 1243, 1108, 773, 831, 1140,1199 cm^{-1}.^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ_H 1.36 (3H, s, -CH_3), 3.05-3.16 (2H, d, -CH_2-), 6.48-7.74 (10H, m, Aro. Protons), 7.89 (1H, s, N-CH-O), 8.77 (2H, s, Aro.-O-H).13C NMR (400 MHz, DMSO-d_6, ppm): δ_C 23.29 (-CH_3), 41.60 (-CH_2-), 71.30 (Me-C-N), 84.03 (N-C-O), 133.25, 133.69(=C-Cl), 144.59,145.05 (=C-OH), 164.70(-O-CO-), 167.89 (-N-CO-), 175.44(-$CO_{carboxylate}$),115.49, 116.16, 122.05, 128.68, 126.67, 128.91, 130.16, 131.50, 132.99, 136.41, 128.07, 129.76, 131.64, 134.03 (C-Ar).

Sodium(S)-3-(3,4-dihydroxyphenyl)-2-((R)-1,5-dioxo-3-(4-nitrophenyl)-1,5-dihydrobenzo[e][1,3] oxazepin-4(3H)-yl)-2-methylpropanoate [R_8]

Beige solid, yield 90%, mp 260 ºC, the reflux time of reaction 6hrs, Anal. Found for $C_{25}H_{19}N_2NaO_9$ (%): C 59.121, H 4.21, N 5.87. Calc. (%): C 58.37, H 3.72, N 5.45. R_f= 0.61 (ethylacetate:toluene, 2:1). FT-IR (KBr): 3441, 3077,2995, 2854, 1581, 1516, 1601, 1399, 1760, 1695, 1251,1072,740, 802, 1463,1316,1195 cm^{-1}.^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ_H 1.37 (3H, s, -CH_3), 3.07-3.19 (2H, d, -CH_2-), 6.45-7.85 (11H, m, Aro. Protons), 7.37 (1H, s, N-CH-O), 8.54 (2H, s, Aro.-O-H).^{13}C NMR (400 MHz, DMSO-d_6, ppm): δ_C 20.27 (-CH_3), 57.37 (-CH_2-), 59.46 (Me-C-N), 85.27 (N-C-O),147.36(=C-NO_2), 144.60,145.17(=C-OH),168.93(-O-CO-), 174.51(-N-CO-), 176.21(-$CO_{carboxylate}$), 115.60, 116.37, 122.28, 128.79,126.75, 129.22, 130.53, 130.94, 132.76, 134.25, 124.14, 127.70, 140.75 (C-Ar).

General procedure for Synthesis of sodium (R)-3-(3,4-dihydroxyphenyl)-2-methyl-2-((R)-6,7,8,9-tetrachloro-1,5-dioxo-3-substitutedphenyl-1,5-dihydro benzo[e][1,3] oxazepin-4(3H)-yl) propanoate

The tetrachloro-1,3-oxazepine derivatives under investigation are prepared according to the procedure previously described in the literature with some modifications.[38]

Sodium(R)-3-(3,4-dihydroxyphenyl)-2-methyl-2-((R)-6,7,8,9-tetrachloro-1,5-dioxo-3-(4-hydroxy-3-methoxyphenyl)-1,5-dihydrobenzo[e][1,3]oxazepin-4(3H)-yl) propanoate [R_9]

Beige solid, yield 65%, mp 210 ºC, Anal. Found for $C_{26}H_{18}Cl_4NNaO_9$ (%): C 49.09, H 3.35, N 1.56. Calc. (%): C 47.81, H 2.78, N 2.14. R_f=0.84 (benzene:methanol, 7:2). FT-IR (KBr): 3541, 3073, 2936, 2813,1531,1493,1610,1375,1775,1648,1255,1128,737,823,1080,1290 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ_H 1.38 (3H, s, -CH_3), 2.73-2.95 (2H, d, -CH_2-),3.54 (3H,s,-O-CH_3), 6.38-6.67 (6H, m, Aro. Protons), 7.64 (1H, s, N-CH-O), 8.17 (3H, s, Aro -O-H).^{13}C NMR (400 MHz, DMSO-d_6, ppm): δ_C 21.23 (-CH_3), 42.15 (-CH_2-), 56.51(-O-CH_3),70.97 (Me-C-N), 86.82(N-C-O),144.51(=C-OCH_3),145.24,148.72 (=C-OH),164.30(-O-CO-), 166.39(-N-CO-), 173.45(-$CO_{carboxylate}$),111.94,115.40, 116.11,116.91,123.47 ,127.28,129.49, 129.58, 129.80, 135.83, 121.64, 128.79, 132.93, 135.20 (C-Ar).

Sodium (R)-3-(3,4-dihydroxyphenyl)-2-methyl-2-((R)-6,7,8,9-tetrachloro-1,5-dioxo-3-(4-chlorophenyl)-1,5-dihydro benzo[e][1,3]oxazepin-4(3H)-yl)propanoate [R_{10}]

Off white solid, yield 70%, mp 254 ºC, Anal. Found for $C_{25}H_{15}Cl_5NNaO_7$ (%): C 46.54, H 2.12, N 1.98. Calc. (%): C 46.80, H 2.36, N 2.18. R_f=0.65 (benzene:methanol, 7:2). FT-IR (KBr): 3548, 3048, 2984, 2855, 1576, 1532, 1600, 1301, 1770, 1648, 1234, 1133, 737, 831, 1092, 1315 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ_H 1.51 (3H, s, -CH_3), 2.93-3.18 (2H, d, -CH_2-), 6.54-7.50 (7H, m, Aro. Protons), 7.54 (1H, s, N-CH-O), 8.80 (2H, s, Aro -O-H).^{13}C NMR (400 MHz, DMSO-d_6, ppm): δ_C 25.30(-CH_3), 43.23(-CH_2-), 71.30(Me-C-N), 86.65(N-C-O), 134.08 (=C-Cl), 144.5, 145.24 (=C-OH), 164.30 (-O-CO-), 166.57 (-N-CO-), 176.66 (-$CO_{carboxylate}$), 129.49, 129.58, 131.98, 132.93, 133.02, 135.20, 116.11, 117.35, 123.47, 128.79, 128.95, 129.80, 134.08, 135.20 (C-Ar).

Sodium (R)-3-(3,4-dihydroxyphenyl)-2-methyl-2-((R)-6,7,8,9-tetrachloro-1,5-dioxo-3-(2,4-dichlorophenyl)-1,5-dihydro benzo[e][1,3]oxazepin-4(3H)-yl)propanoate [R_{11}]

Light yellow solid, yield 81 %, mp 224 ºC, Anal. Found for $C_{25}H_{14}Cl_6NNaO_7$ (%) : C 43.83, H 2.42, N 1.84. Calc. (%): C 44.41, H 2.09, N 2.07R_f=0.70 (benzene:methanol, 7:2). FT-IR (KBr): 3489, 3043,2989, 2891, 1579, 1527, 1608, 1375, 1775, 1650, 1228, 1186, 875, 730, 1053, 1286cm^{-1}.^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ_H 1.36 (3H, s, -CH_3), 2.74-2.96 (2H, d, -CH_2-), 6.47-6.79 (6H, m, Aro. Protons), 7.66 (1H, s, N-CH-O), 8.16 (2H, s, Aro -O-H).^{13}C NMR (400 MHz, DMSO-d_6, ppm): δ_C 20.41(-CH_3),40.56(-CH_2-),71.60(Me-C-N), 84.02(N-C-O), 134.20 (=C-Cl), 144.38, 145.23 (=C-OH), 164.36 (-O-CO-),

166.77 (-N-CO-), 173.32 (-$CO_{carboxylate}$), 115.50, 116.13, 121.60, 128.47, 128.91, 129.76, 132.52, 133.26, 135.99, 136.28, 127.79, 131.10, 131.26, 137.15 (C-Ar).

Sodium (R)-3-(3,4-dihydroxyphenyl)-2-methyl-2-((R)-6,7,8,9-tetrachloro-1,5-dioxo-3-(4-nitrophenyl)-1,5-dihydrobenzo [e][1,3]oxazepin-4(3H)-yl)propanoate [R_{12}]

Light yellow solid, yield 86 %, mp 262 ºC, Anal. Found for $C_{25}H_{15}Cl_4N_2NaO_9$ (%) : C 45.61, H 1.79, N 3.92. Calc. (%) : C 46.04, H 2.32, N 4.32. R_f=0.72 (benzene:methanol, 7:2). FT-IR (KBr): 3442, 3054, 2987, 2849, 1549, 1446, 1610, 1325, 1714, 1648, 1239, 1146,731, 838, 1450, 1349, 1064 cm^{-1}.^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ_H 1.53 (3H, s, -CH_3), 2.94-3.18 (2H, d, -CH_2-), 6.44-7.50 (7H, m, Aro. Protons), 7.56 (1H, s, N-CH-O), 8.73 (2H, s, Aro -O-H).^{13}C NMR (400 MHz, DMSO-d_6, ppm): δ_C 25.38(-CH_3),43.46(-CH_2-),72.33(Me-C-N), 85.94(N-C-O), 147.90 (=C-NO_2), 144.38, 145.68 (=C-OH), 165.26 (-O-CO-), 167.38 (-N-CO-), 175.73 (-$CO_{carboxylate}$), 116.13, 117.83, 122.02, 128.28, 128.94, 129.76, 131.10, 133.09, 134.55,136.31, 124.11, 144.56, 128.28 (C-Ar).

Computation Details and Methodology

In this work, we try to scout about the optimized geometric boundary (bond lengths and bond angles), and some electronic properties of the ground state for the Schiff bases [R_1-R_4].

In all calculations, Density Functional Theory and Schiff bases [R_1-R_4] modeling theoretical were carried out on Gaussian 09W package,[39] at DFT level of theory. The molecular geometry for the Schiff bases [R_1-R_4] was totally optimized utilizing DFT based on (B3LYP) level,[40] 6-311G,[41] as a basis set for the Schiff bases [R_1-R_4].

RESULTS AND DISCUSSION

A new Schiff base has prepared from condensation of (*S*)-2-amino-3-(3,4-dihydroxyphenyl)-2-methylpropanoic acid and substituted aldehyde, and the products of this interaction have utilized as starting materials for prepared seven-membered heterocyclic ring by their reaction with phthalic and substituted phthalic anhydride. the elemental analysis results for Schiff bases [R_1-R_4] were in good approved with the calculated values that corroborate its molecular formula (Scheme 1). Synthesized structures were depicted by FT-IR, ^{1}H NMR, ^{13}C NMR and Elemental Analysis and the outcomes are in approval with the proposed structures. The FT-IR spectrum has a remarkable role in identifying the functional groups and displaying important evidence for the reaction between the

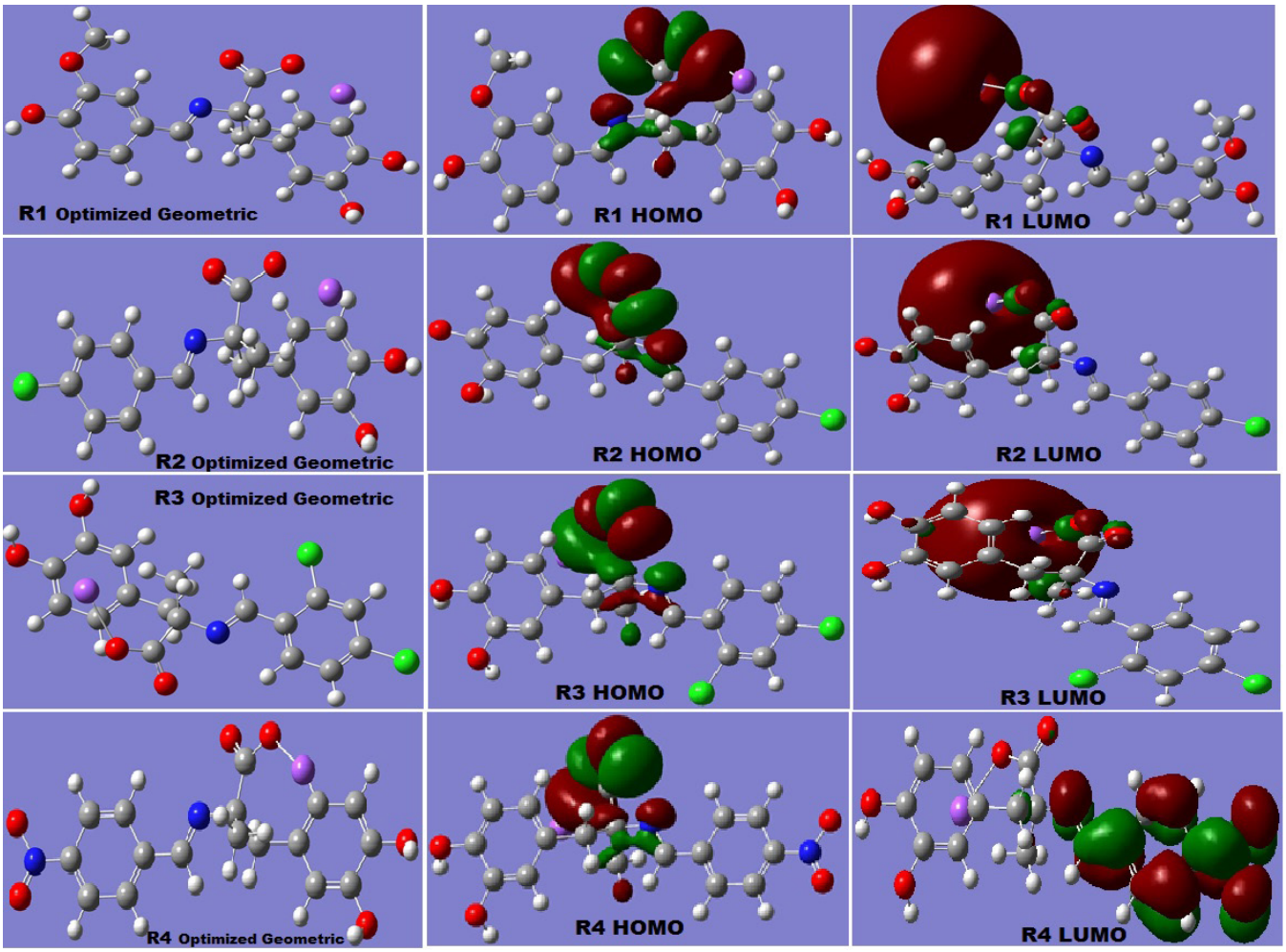


Figure 1: Illustration of the optimized geometric, HOMO and LUMO orbitals for the Schiff bases [R_1-R_4].

Table 1: The HOMO-LUMO energies and E_g, Mulliken Charge, point group, degree of freedom and stoichiometry

				Mulliken Charge					
				Azomethine group		*Sub. Group*	*Point*	*Deg. of*	
Code No.	E_{HOMO}	E_{LUMO}	ΔE	*N*	*C*	*Carbonyl Com.*	*group*	*freedom*	*Stoichiometry*
R_1	-0.19146	-0.03812	0.15334	-0.408607	0.111803	(O-CH_3) -0.5176849 (O-H) -0.546426	C1	126	$C_{18}H_{18}NNaO_6$
R_2	-0.21528	-0.04163	0.17365	-0.395990	0.111281	(4-Cl) -0.027381	C1	111	$C_{17}H_{15}ClNNaO_4$
R_3	-0.21876	-0.04824	0.17052	-0.395247	0.112708	(2-Cl) -0.010361 (4-Cl) -0.012574	C1	111	$C_{17}H_{14}Cl_2NNaO_4$
R_4	-0.2236	-0.08685	0.13675	-0.387746	0.111440	(N) 0.384492	C1	117	$C_{17}H_{15}N_2NaO_6$

Table 2: The quantum chemical parameters of Schiff bases [R_1-R_4]

Code No.	*X*	*η*	*σ*	P_i	*Δ*	*ω*	ΔN_{max}	E_A	I_P	*D.M. (μ) (Debye)*
R_1	0.11479	0.0767	13.04291	-0.11479	6.52145	0.08593	1.49719	0.03812	0.1914	4.639051
R_2	0.128456	0.0868	11.51742	-0.12845	5.758710	0.095022672	1.479470199	0.04163	0.21528	6.693915
R_3	0.1335	0.0853	11.72883	-0.1335	5.864415	0.104517065	1.565798733	0.04824	0.21876	6.633422
R_4	0.155225	0.0684	14.62523	-0.15522	7.312614	0.176195978	2.270201097	0.0885	0.22360	10.245707

first materials to give the Schiff base. The FT-IR spectra for Schiff bases show the manifestation of aromatic (C-H) with range of (3095.54–3033.82 cm^{-1}), imine groups (C=N) within range of (1660.6–1606.59 cm^{-1}), double bond aromatic ring within (1461.94–1529.09 cm^{-1}) and (1402.15–1480.33cm^{-1}) and other absorption bands of FT-IR data for [R_1-R_4]. The FT-IR spectra for 1,3-oxazepine displayed aromatic (C-H) within range of (3029.96–30.93.61 cm^{-1}), the stretching vibrations of ($C=O_{Lactone}$), ($C=O_{Lactam}$) groups assured by frequency range (1723.5–1691.46cm^{-1}) and (1658.11-1642.7 cm^{-1}) respectively, as strong absorption bands,[42] with other absorption frequency bands for [R_5-R_8].

^{1}H-NMR spectra for 1,3-oxazepine appeared singlet signal in the extent of (δ= 7.89-7.53 ppm) appoint to (N-CH-O) in heterocyclic, whilst the signal for aromatic protons monitored as multiplet-signal.[42] ^{13}C-NMR spectra of 1,3-oxazepine show the existence of aromatic carbons signals in extent (δ=111.94-147.39 ppm), ($C=O_{Lactone}$) in extent (δ = 170.78–164.30 ppm), ($C=O_{Lactame}$) in extent (δ =174.51-166.39 ppm), and (N-CH-O) in the heterocyclic ring in extent (δ = 86.82–84.02 ppm).[39]

Geometric Optimization of the Schiff bases [R_1-R_4]

The 3D geometric structure of gas-phase for Schiff bases was shown in Figure 1, and DFT calculation was carried out by (B3LYP/6-311G (d,p)) basis set utilized Gaussian 09W program. Likewise, the bond lengths and bond angles were registered in the Table not shown. From DFT, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were obtained. The calculated energy gap E_g (E_{LUMO}-E_{HOMO}) is a substantial stability index that assists in characterizing the chemical reactivity and kinetic stability of the molecule.[41] Molecule with great energy gap E_g is typically stable and unreactive, while the little gap is reactive and the higher E_{HOMO}, the easier for HOMO to donate electrons, the lower the E_{LUMO}, the easier for LUMO to accept electrons.[43] The HOMO-LUMO energies and the differences between the orbital energies, Mulliken Charge, point group, degree of freedom and stoichiometry were displayed in Table 1.

The theoretical study exhibited a few effects of prepared Schiff bases [R1-R4] by substituting the aromatic ring. R_1 has largest value of LUMO energy level for that the molecule becomes more stable from other compounds. This conduct can be expounded to the substitute group's low electronegativity and electrophilicity; results are given in Table 1 and Figure 1. LUMO and HOMO orbitals and their energy gap for [R_1-R_4] compounds moreover, the computed quantum chemical parameters of Schiff bases were given in Table 2. Extra parameters like absolute electronegativities (χ), absolute hardness (η), chemical potentials (P_i), absolute softness (σ), global electrophilicity (ω), global softness (ϑ), electronic charge (ΔN_{max}), electron affinity (E_A), ionization potential (I_P) and dipole moment (μ) were calculated by the equations mentioned in the literature.[44-47]

CONCLUSION

From present results, the 1,3-oxazepines were successfully prepared, this has been evidenced by spectral analysis. Theoretical study of HOMO energies orbitals positive indicates that Schiff bases [R_1-R_4] are stable compounds, hardness results signal that Schiff base [R_2] has more aromatic character compared to other Schiff base [R_1, R_3, R_4].

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