**Research Article**

Synthesis and Quantum Chemical Calculations of 2,4-dioxopentanoic Acid Derivatives - Part I

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Abstract

The 2,4-dioxopentanoic acid derivatives (**3a-c**) were obtained from the reaction of 4-acetyl-5-(1-naphthyl)furan-2,3-dione (**1**) with various nitrogenous nucleophiles (**2a-c**). The structures of these newly synthesized compounds (**3a-c**) were determined from the FT-IR, ^{1}H and ^{13}C NMR spectroscopic data and elemental analyses. In addition to experimental analysis, quantum-mechanical calculations of derivatives of 2,4-dioxopentanoic acid (**3a-c**) were carried out by using B3LYP method with basis set of the 6-311G(d,p) in order to find molecular properties. Quantum chemical parameters such as the energy of the highest occupied molecular orbital, the energy of the lowest unoccupied molecular orbital, HOMO–LUMO energy gap, chemical hardness, softness, electronegativity, chemical potential, dipole moment, global electrophilicity, sum of the total negative charge (TNC) and sum of electronic and zero-point energies (SEZPE) were calculated and discussed.
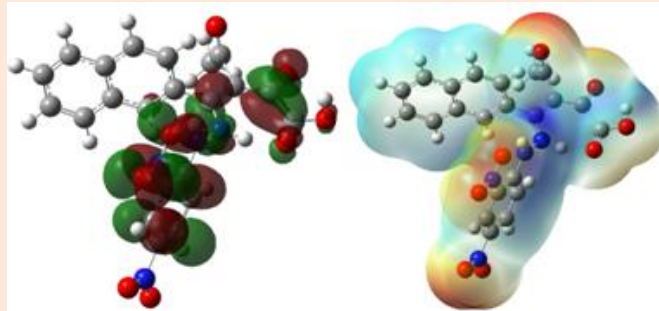
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Introduction

In early studies, 4-acyl-5-alkyl/aryl-2,3-dihydro-2,3-furandiones were obtained from 1,3-dicarbonyl compounds with oxalyl halides [1-4]. Recently, reactions of cyclic oxalyl compounds were reported to give substituted heterocyclic compounds. In addition, the reactions of substituted 2,3-furandiones have been studied with several semi-/thiosemicarbazones, ureas, thioureas, oximes, various hydrazines, some acetanilides and amides under different conditions [5-14]. Most of these obtained compounds in general are well known for their potential biological activities [15-18].

In view of these important properties, we carried out the reactions of 4-acetyl-5-(1-naphthyl)furan-2,3-dione (**1**) with 4-nitrophenylhydrazine, 2,4-dinitrophenylhydrazine and 2-nitrophenyamine (**2a-c**). The compound (**1**) was prepared from 1-(2-naphthyl)butane-1,3-dione with oxalylchloride [19]. The 2,4-dioxopentanoic acid derivatives (**3a-c**) which are α-ketocarboxylic acids were synthesized from the reactions of the various hydrazines and amines (**2a-c**) with 4-acetyl-5-(1-naphthyl)furan-2,3-dione (**1**) (**Scheme 1**).

Computational details

In the section based on DFT calculations of this study, all calculations were carried out using DFT/B3LYP method with 6-311G(d,p) basis sets of Gaussian program [20]. Optimization of synthesized molecules was performed with the help of 6-311G (d,p) basis set, because this basis set is known as one of the basis sets that gives more accurate results in terms of the determination of geometries and electronic properties for a wide range of organic compounds. Quantum chemical parameters such as the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the

lowest unoccupied molecular orbital (E_{LUMO}), HOMO–LUMO energy gap (ΔE), chemical hardness (η), softness (σ), electronegativity (χ), chemical potential (μ), dipole moment (DM), global electrophilicity (ω), sum of the total negative charge (TNC) and sum of electronic and zero-point energies (SEZPE) were calculated and discussed [21].
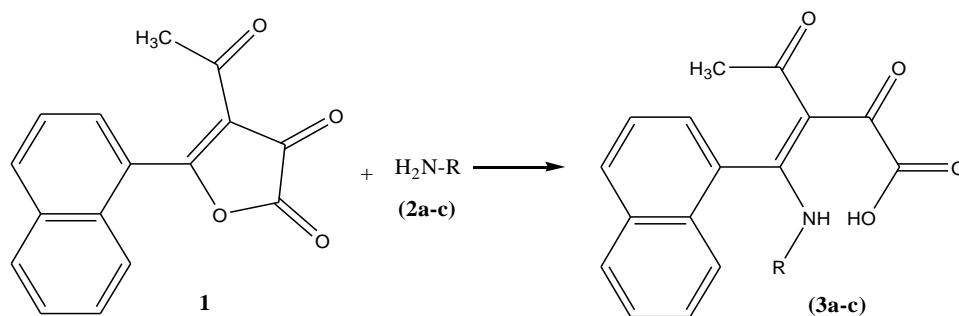
Scheme 1 Short representation of the synthesized molecules (**3a-c**)

Molecular properties, related to the reactivity and selectivity of the compounds were estimated following the Koopmans's theorem relating the energy of the HOMO and the LUMO. Electronegativity is estimated using the following the equation:

$$\chi \cong -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \qquad (1)$$

Chemical hardness (η) measures the resistance of an atom to a charge transfer [22], it is estimated by using the equation:

$$\eta \cong -\frac{1}{2}(E_{HOMO} - E_{LUMO}) \qquad (2)$$

Chemical potential (μ) and electronegativity (χ) can be calculated with the help of the following equations [21].

$$\mu = -\chi \cong \frac{E_{HOMO} + E_{LUMO}}{2} \qquad (3)$$

Electron polarizability, called chemical softness (σ), describes the capacity of an atom or group of atoms to receive electrons [22] and is estimated by using the equation:

$$\sigma = \frac{1}{\eta} \cong -\frac{2}{(E_{HOMO} - E_{LUMO})} \qquad (4)$$

The global electrophilicity (ω) is a useful reactivity descriptor that can be used to compare the electron-donating abilities of molecules [23]. Global electrophilicity index is estimated by using the electronegativity and chemical hardness parameters through the equation:

$$\omega = \frac{\chi^2}{2\eta} \qquad (5)$$

A high value of electrophilicity describes a good electrophile while a small value of elecrophilicity describes a good nucleophile [24].

Experimental

Solvents were dried by refluxing over the appropriate drying agent and distilled before use. Melting points were determined on an Electrothermal 9200 apparatus and were not corrected. Microanalyses were performed on a Carlo Erba elemental analyzer, model 1108. The IR spectra were recorded on a Shimadzu Model 8400 FT IR spectrophotometer. The ^{1}H and ^{13}CNMR spectra were recorded on a Bruker-400 MHz Ultra Shield istrument. The chemical shifts are reported in ppm from tetramethylsilane as an internal standard and are given in δ (ppm). All experiments were followed by TLC using DC Alufolien Kieselgel 60 F_{254} (Merck) and Camag TLC lamp (254/366 nm).

General Procedure for the Preparation of Compounds (3a-c)

To a solution of the compound (**1**) (0.30 g, 0.10 mmol) in benzene (50 mL), 0.173 g (0.10 mmol) *p*-nitrophenylhydrazine (**2a**) for **3a**, 0.22 g (0.10 mmol) 2,4-dinitro phenylhydrazine (**2b**) for **3b** and 0.156 g (0.10 mmol) 2-nitroanilin (**2c**) for **3c** were added dropwise. After the reaction mixture had been stirred at room temperature for 24 h, the precipitate was filtered and recrystallized from toluene and allowed to dry on P_2O_5.

(3Z)-3-{2-Naphthyl[2-(4-nitrophenyl)hydrazino]methylene}-2,4-dioxopentanoic acid (3a)

Yield 0.12 g (36%); m.p.: 195-196 °C; FT-IR ν (cm^{-1})= 3650-3100 (-NH, -OH), 1720, 1650 (C=O), 1340 (Ar-NO$_2$), 750, 820 (mono-substituted benzene C$_6$H$_4$-); ^{1}H NMR (400 MHz, DMSO): δ= 10.45 (t, 3H, C=C-NH, -NH, -OH), 8.03-7.57 (m, 11H, aromatic), 2.65 (s, 3H, <u>CH$_3$</u>CO); ^{13}C NMR (100 MHz, DMSO): δ= 191.32 (CH$_3$<u>CO</u>), 190.45 (C=O), 180.84 (C=O, acide), 154.19-110.11 ppm (aromatic C), 29.07 ppm (CH$_3$-); elemental analysis (%): Found (Calc.): C= 63.26 (63.01), H= 3.95 (4.09), N= 10.30 (12.02).

3(3Z)-3-{[2-(2,4-Dinitrophenyl)hydrazino](2-naphthyl)methylene}-2,4-dioxopentanoic acid (3b)

Yield 0.12 g (57%); m.p.: 179-180 °C; FT-IR ν (cm^{-1})= 3600-3100 (-NH, -OH), 1660, 1580 (C=O), 1340 (Ar-NO$_2$), 820-740 (mono-substituted benzene C$_6$H$_4$-); ^{1}H NMR (400 MHz, DMSO): δ= 11.35 (t, 3H, -NH, C=C-NH, -OH), 8.86-7.40 (m, 10H, aromatic), 2.63 (s, 3H, CH$_3$CO); ^{13}C NMR (100 MHz, DMSO): δ= 191.22 (CH$_3$<u>CO</u>), 190.55 (C=O), 180.94 (C=O, acide), 160.90-110.68 ppm (aromatic C), 29.09 (CH$_3$-); elemental analysis (%): Found (Calc.): C= 57.15 (56.90), H= 3.57 (3.47), N= 11.87 (12.06).

(3Z)-3-{2-Naphthyl[(2-nitrophenyl)amino]methylene}-2,4-dioxopentanoic acid (3c)

Yield 0.12 g (65.8%); m.p.: 170-171 °C; FT-IR ν (cm^{-1})= 3600-3100 (-NH, -OH), 1700, 1640 (C=O), 1400-1300 (Ar-NO$_2$), 820-750 (mono-substituted benzene C$_6$H$_4$-); ^{1}H NMR (400 MHz, DMSO): δ= 12.15 (t, 2H, -NH, -OH), 8.95-7.30 (m, 11H, aromatic), 2.64 (s, 3H, CH$_3$CO); ^{13}C NMR (100 MHz, DMSO): δ= 193.10 (CH$_3$<u>CO</u>), 192.55 (C=O), 179.88 (C=O, acide), 160.17-113.68 (aromatic C), 29.97 (CH$_3$-); elemental analysis (%): Found (Calc.): C= 65.55 (65.34), H= 4.04 (3.99), N= 6.69 (6.93).

Molecular structure

E_{HOMO}, E_{LUMO}, ΔE, DM, MV, TNC, η, σ, μ, χ, ω, SEZPE were calculated for the 2,4-dioxopentanoic acid derivatives (**3a-c**) by using the B3LYP/6-311G(d,p) for gas phase and solvent phase, as shown in **Figures 1** and **2**.

E_{HOMO} and E_{LUMO} are associated with electron donating ability and electron accepting ability of a molecule, respectively. Higher E_{HOMO} is essential for molecular reaction with nucleophiles while lower E_{LUMO} reacts easily with electrophiles [32]. The calculated E_{HOMO} increases in the molecule (**3b**) containing two nitro groups in the ring while E_{LUMO} will decrease. E_{HOMO} values of **3a**, **3b** and **3c** molecules are found for gas phase -6.65, -6.69, -6.47 eV and for solvent phase -6.43, -6.45, -6.38 eV, respectively. According to these results, the electron donating trends for study molecules for gas and solvent phase can be written as: **3b**>**3a**>**3c**. There are two nitro groups at the ortho and para positions of the phenyl group in **3b** molecule and one nitro group at the para position in **3a** molecule and and one nitro

group at the ortho position in **3c** molecule. There is no significant change in the E_{LUMO} values according to the position and number of nitro groups in the ring.
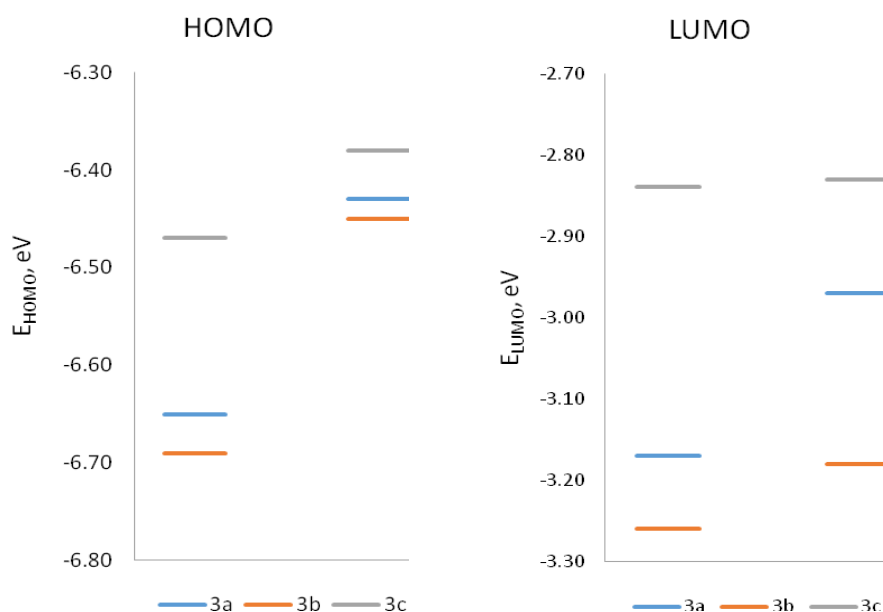

Figure 1 The calculated HOMO and LUMO parameters for neutral molecules for gas and solvent phase using B3LYP/6-311G(d,p) method

HOMO–LUMO energy gap, chemical hardness and softness are closely closely related to chemical properties. HOMO-LUMO gap (ΔE) is smaller when the basis set of atomic orbitals are magnified due to the changing of HOMO, usually to a more negative energy and decreasing in energy of LUMO [33]. More stable molecules have large HOMO–LUMO energy gap and less stable molecules have small HOMO–LUMO energy gap. ΔE values for gas phase of **3a**, **3b** and **3c** molecules were found 3.48, 3.43, 3.63 and 3.46, 3.27, 3.55 eV for solvent phase, respectively. ΔE for **3b** molecule containing two nitro groups in the ring is less than other molecules. **3c** molecule is found more stable than **3a** and **3b** molecules due to the fact that a large HOMO-LUMO gap is observed. The hardness and softness are widely used in chemistry for explaining stability of compounds. According to Maximum Hardness Principle [33], chemical hardness is a measure of the stability of chemical species. The hardness is just half the energy gap between the E_{HOMO} and E_{LUMO} (see eq. 2). If a molecule has a large energy gap, it is called hard and other wise is called soft [34]. Softness is a measure of the polarizability and soft molecules give more easily electrons to an electron acceptor molecule or surface [21]. On the basis of the calculated chemical hardness, softness and energy gap are given in Fig. 2. According to softness values, electron donating trend of studied chemical compounds may be written as: **3b**>**3a**>**3c** for gas and solvent phase.

The average values of the HOMO and LUMO energies have been defined as the chemical potential (μ). The chemical potential was defined as the first derivative of the total energy with respect to the number of electrons. The negative of the chemical potential was known as the electronegativity (χ) (see eq. 3). Chemical potential, electronegativity and hardness are descriptors for the predictions about chemical properties of molecules [35]. Electronegativity that represents the power to attract the electrons of chemical species is a useful quantity in the prediction of inhibitive performance of molecules [21]. The electronegativity value of **3c** is less than those of **3a** and **3b** for gas phase and solvent (see Figure 2).

A typical electron density distribution of Total electronic charge (TNC) values calculated with the 6-311G(d,p) basis set. Total electronic charge values are lower in solvent phase than in gas phase. As can be seen from Fig.2, the negative charge densities are concentrated on oxygen and nitrogen atoms for **3a**, **3b** and **3c** molecules. TNC values for **3a**, **3b** and **3c** molecules are -3.808, -4.385, -4.067 eV for gas phase and -4.046, -4.568, -4.220 eV for solvent phase, respectively.
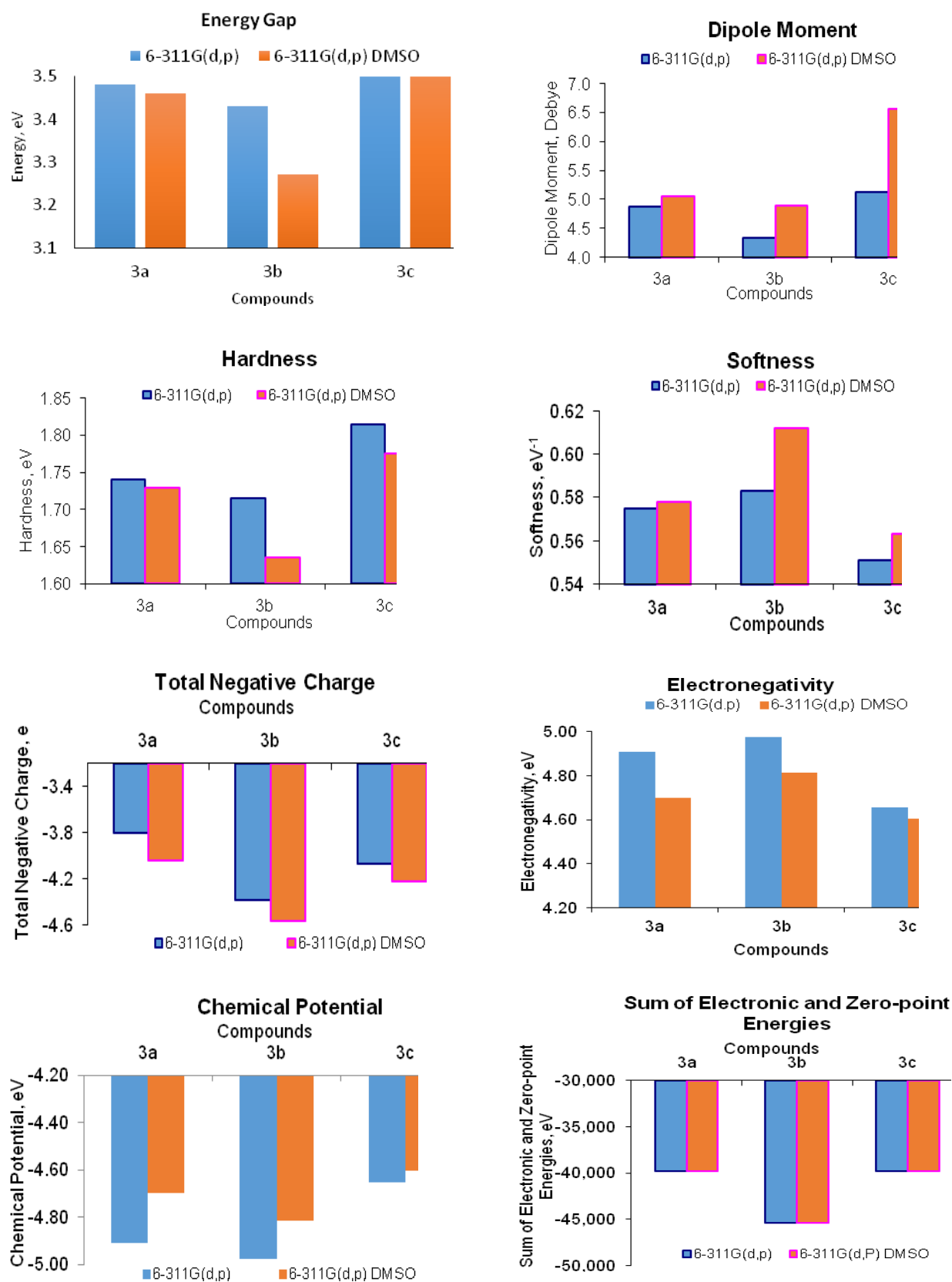
Figure 2 The calculated quantum chemical parameters for the non-protonated for gas and solvent phase compounds using B3LYP/6-311G(d,p) method

Sum of electronic and zero-point energies (SEZPE) for **3b** molecule containing two nitro groups (**3b**) are higher than **3a** and **3c** molecules containing one nitro group (Fig. 2). In Fig. 3 the optimized molecular structures, HOMOs, LUMOs and total electron density are also given. This figure shows that there is much more electron density in the vicinity of oxygen atoms for all studied molecules.
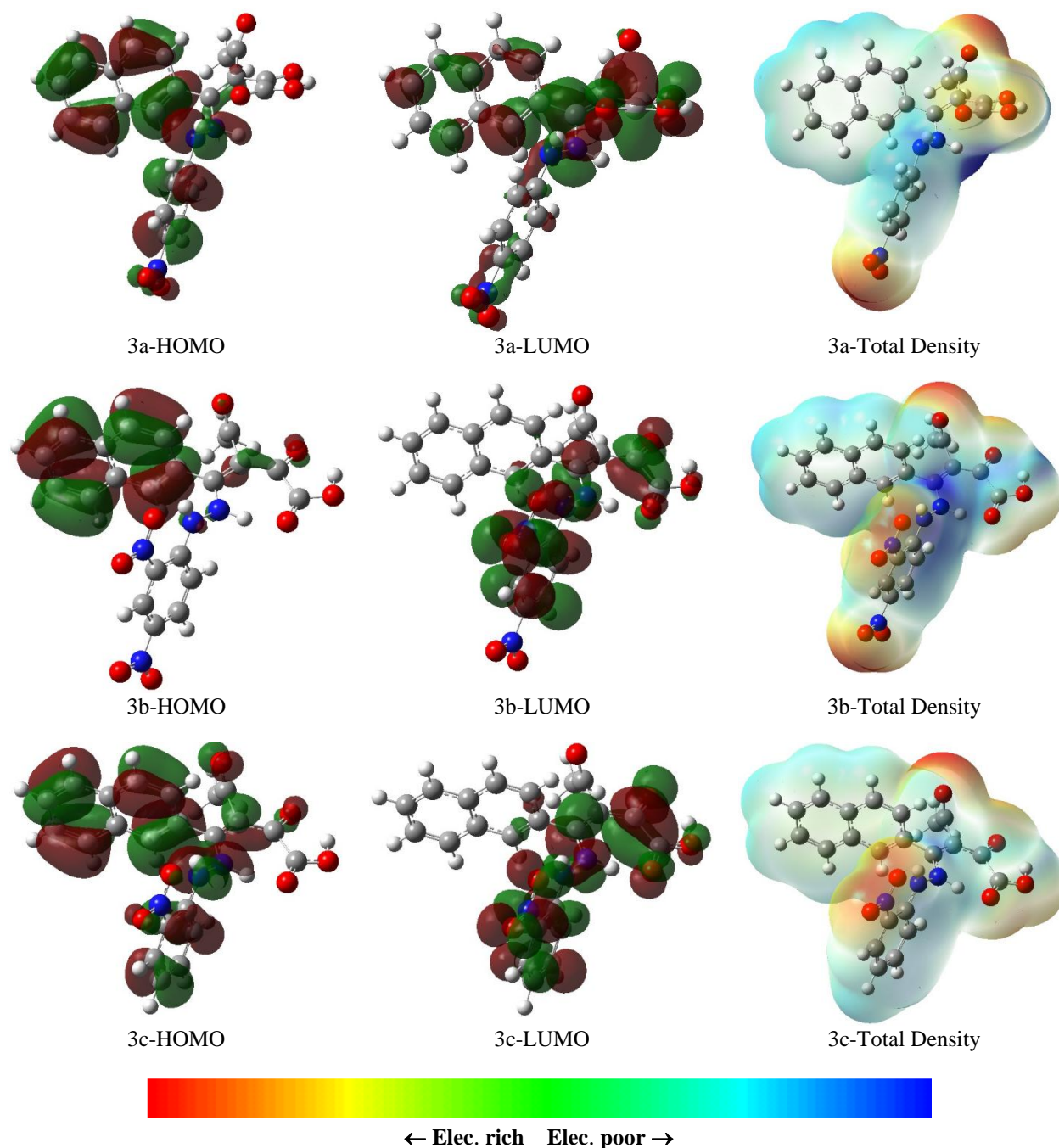

3a-HOMO	3a-LUMO	3a-Total Density
3b-HOMO	3b-LUMO	3b-Total Density
3c-HOMO	3c-LUMO	3c-Total Density

← Elec. rich   Elec. poor →

Figure 3 The optimized molecular structures, HOMOs, LUMOs and total density of the non-protonated inhibitor molecules using DFT/B3LYP/6-311G(d,p).

HOMO and LUMO for **3a**, **3b**, **3c** are shown in Table 1. HOMO and LUMO were calculated with AOmix program [36, 37] after optimization of molecules. HOMO orbitals for **3a**, **3b**, **3c** at non-protonated phase consist of + 5.6% 3PY(N22) + 3.5% 3PY(C26) + 3.3% 4PY(N22) + 3.1% 3PZ(C10) + 3.0% 2PY(N22) - 2.8% 3PZ(C6); - 5.3%

3PX(C3) + 5.3% 3PX(C6) + 4.6% 3PX(C7) - 4.5% 4PX(C3) - 4.5% 3PX(C10) + 4.4% 4PX(C6); + 3.4% 3PY(N22) + 2.5% 3PX(C6) - 2.4% 3PY(C6) + 2.3% 4PY(N22) - 2.3% 3PX(C3) + 2.3% 3PY(C10) and their LUMO consist of + 7.4% 3PZ(C11) + 5.6% 4PZ(C11) - 4.3% 3PX(C15) - 4.2% 4PX(C15) + 3.8% 2PZ(C11) + 3.8% 3PX(O18); + 7.8% 3PY(N48) - 5.5% 3PY(O49) - 5.2% 3PY(O50) - 4.6% 4PY(O49) + 4.5% 2PY(N48) - 4.1% 4PY(O50); - 5.2% 3PZ(C15) - 4.7% 4PZ(C15) - 4.7% 3PY(N45) + 4.5% 3PZ(C11) + 4.0% 3PZ(O18) + 3.4% 4PZ(C11). As seen from **Table 1** and given above HOMO orbitals of **3a**, **3b**, **3c** molecules for gas and solvent phase consist of mainly C3, C6, C10 and N22 atoms.

Table 1 HOMO and LUMO population for molecules using Aomix method after from B3LYP/6-311G method.

Mol.	HOMO
3a	+ 5.6% 3PY(N22) + 3.5% 3PY(C26) + 3.3% 4PY(N22) + 3.1% 3PZ(C10) + 3.0% 2PY(N22) - 2.8% 3PZ(C6)
3b	- 5.3% 3PX(C3) + 5.3% 3PX(C6) + 4.6% 3PX(C7) - 4.5% 4PX(C3) - 4.5% 3PX(C10) + 4.4% 4PX(C6)
3c	+ 3.4% 3PY(N22) + 2.5% 3PX(C6) - 2.4% 3PY(C6) + 2.3% 4PY(N22) - 2.3% 3PX(C3) + 2.3% 3PY(C10)
3a[1]	+ 4.2% 3PY(N22) - 3.5% 3PZ(C6) + 3.5% 3PZ(C10) + 3.3% 3PZ(C3) - 3.0% 3PZ(C7) + 2.9% 4PZ(C3)
3b[1]	+ 5.8% 3PX(C3) - 5.7% 3PX(C6) + 4.9% 4PX(C3) - 4.8% 4PX(C6) - 4.8% 3PX(C7) + 4.7% 3PX(C10)
3c[1]	+ 4.3% 3PX(C3) - 4.2% 3PX(C6) + 3.7% 4PX(C3) - 3.6% 3PX(C7) + 3.5% 3PX(C10) - 3.5% 4PX(C6)

Mol.	LUMO
3a	+ 7.4% 3PZ(C11) + 5.6% 4PZ(C11) - 4.3% 3PX(C15) - 4.2% 4PX(C15) + 3.8% 2PZ(C11) + 3.8% 3PX(O18)
3b	+ 7.8% 3PY(N48) - 5.5% 3PY(O49) - 5.2% 3PY(O50) - 4.6% 4PY(O49) + 4.5% 2PY(N48) - 4.1% 4PY(O50)
3c	- 5.2% 3PZ(C15) - 4.7% 4PZ(C15) - 4.7% 3PY(N45) + 4.5% 3PZ(C11) + 4.0% 3PZ(O18) + 3.4% 4PZ(C11)
3a[1]	+ 7.3% 3PZ(C11) + 5.7% 4PZ(C11) - 3.9% 3PX(C15) - 3.8% 4PX(C15) + 3.8% 2PZ(C11) + 3.2% 3PX(O18)
3b[1]	+ 9.8% 3PY(N48) - 6.5% 3PY(O49) - 6.5% 3PY(O50) + 5.7% 2PY(N48) - 5.6% 4PY(O49) - 5.1% 4PY(O50)
3c[1]	+ 8.0% 3PY(N45) - 5.1% 3PY(O46) - 5.1% 3PY(O47) + 4.7% 2PY(N45) - 4.4% 4PY(O46) - 4.0% 4PY(O47)

[1]in the presence of DMSO

Results and discussion

The cyclocondensation reactions of 1-(2-naphthyl)butane-1,3-dione with oxalyl chloride regiospecifically afforded 4-acetyl-5-(1-naphthyl)furan-2,3-dione (**1**), which exhibits conjugation with double bonds [19].

Herein, we report the synthesis and characterization of 2,4-dioxopentanoic acid derivatives (**3a-c**) (**Scheme 2**). At room temperature in benzene, mixing of 4-acetyl-5-(1-naphthyl)furan-2,3-dione (**1**) and corresponding phenylhydrazines and amines (1:1 mol) for about **24 h** led to the formation of the novel compounds (**3a-c**) in approximately 36-66% yield. In moderate conditions, excellent yields of the reactions can be explained by the chemical behaviour of furandiones similar to the compounds (**2a-c**) towards nucleophiles [6, 25, 26].

Addition of the nucleophiles to the furandiones usually starts with nucleophilic attack at one of the C-2, C-3 and C-5 positions of the furan ring system [27-31]. In this reaction, the formation of 2,4-dioxopentanoic acid derivatives (**3a-c**) may be viewed as occurring *via.* a Michaeal type addition to C-5 atom of (**1**) (**Scheme 3**). The reactions proceeded smoothly at room temperature in benzene for **24 h** and afforded the corresponding acid derivatives (**3a-c**) in yield 36-74%. The new compounds (**3a-c**) can be used as substrate to obtain the new compounds like the pyrrolidione derivatives.

Structures of synthesized compounds were assigned on the basis of analytical as well as spectrocopic data. Product (**3a**) was obtained in 36% yield by treating (**1**) with *p*-nitrophenylhydrazine (**2a**) and stirring in benzene at room temperature for **24 h**. In the IR spectrum of compound (**3a**), the -OH and -NH absorption bands were found to be at 3650-3100 cm^{-1}. The absorption bands of C=O groups were seen at 1720, 1650 cm^{-1}. The ^{1}H NMR signals were found to be at δ= 10.45 ppm (3H, -OH and -NH-NH) and 8.03-7.57 ppm (m, 11H, aromatic) and 2.65 ppm (s, 3H, C$\underline{H_3}$CO). The ^{13}C NMR signals were observed at 191.32 ppm (CH$_3$$\underline{C}$O), 190.45 ppm (C=O), 180.84 ppm (C=O, acide). Finally, the elemental analysis data along with spectroscopic data confirm the structure of **3a**. The reaction pathway from 4-acetyl-5-(1-naphthyl)furan-2,3-dione (**1**) with *p*-nitrophenylhydrazine (**2a**) to (3*Z*)-3-{2-naphthyl[2-(4-nitrophenyl)hydrazino]methylene}-2,4-dioxopentanoic acid (**3a**) is outlined briefly in **Scheme 2**.

Nucleophilic addition of 2-nitroanilin (**2c**) with (**1**) provided (3*Z*)-3-{2-naphthyl[(2-nitrophenyl)amino]methylene}-2,4-dioxopentanoic acid (**3c**) in (66%). At the room temperature in benzene, mixing of furan-2,4-

dione (**1**) and *o*-nitroanilin (**2c**) (1:1 mol) for 24 h. In the IR spectrum of (**3c**) characteristic absorption bands at about 3600-3100 cm^{-1} (-OH, -NH) and 1700, 1640 cm^{-1} (C=O) were observed. The ^{1}H NMR signals were at δ= 12.15 ppm (-OH and NH), 8.95-7.30 ppm (m, 11H, aromatic) and 2.64 ppm (s, 3H, <u>CH$_3$</u>CO). The ^{13}C NMR signals were found to be at 193.10 (CH$_3$<u>CO</u>), 192.55 (C=O), 179.88 (C=O, acide), 160.17-113.68 (aromatic C), 29.97 ppm (CH$_3$-). Other spectral and analytical data of (**3c**) are in full agreement with its proposed structure as well.
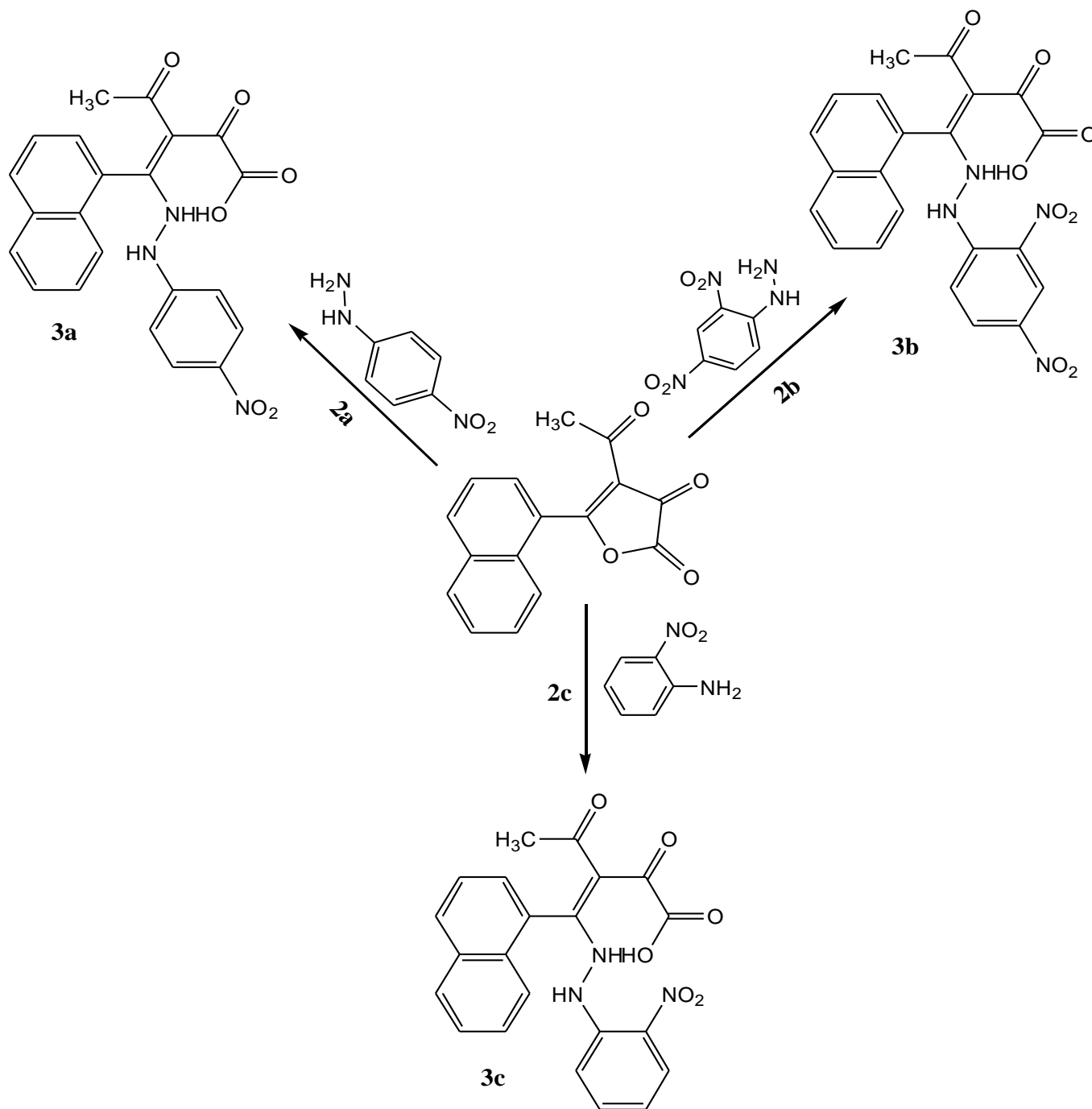
Scheme 2 Synthesis of molecules (**3a-c**)

(1)
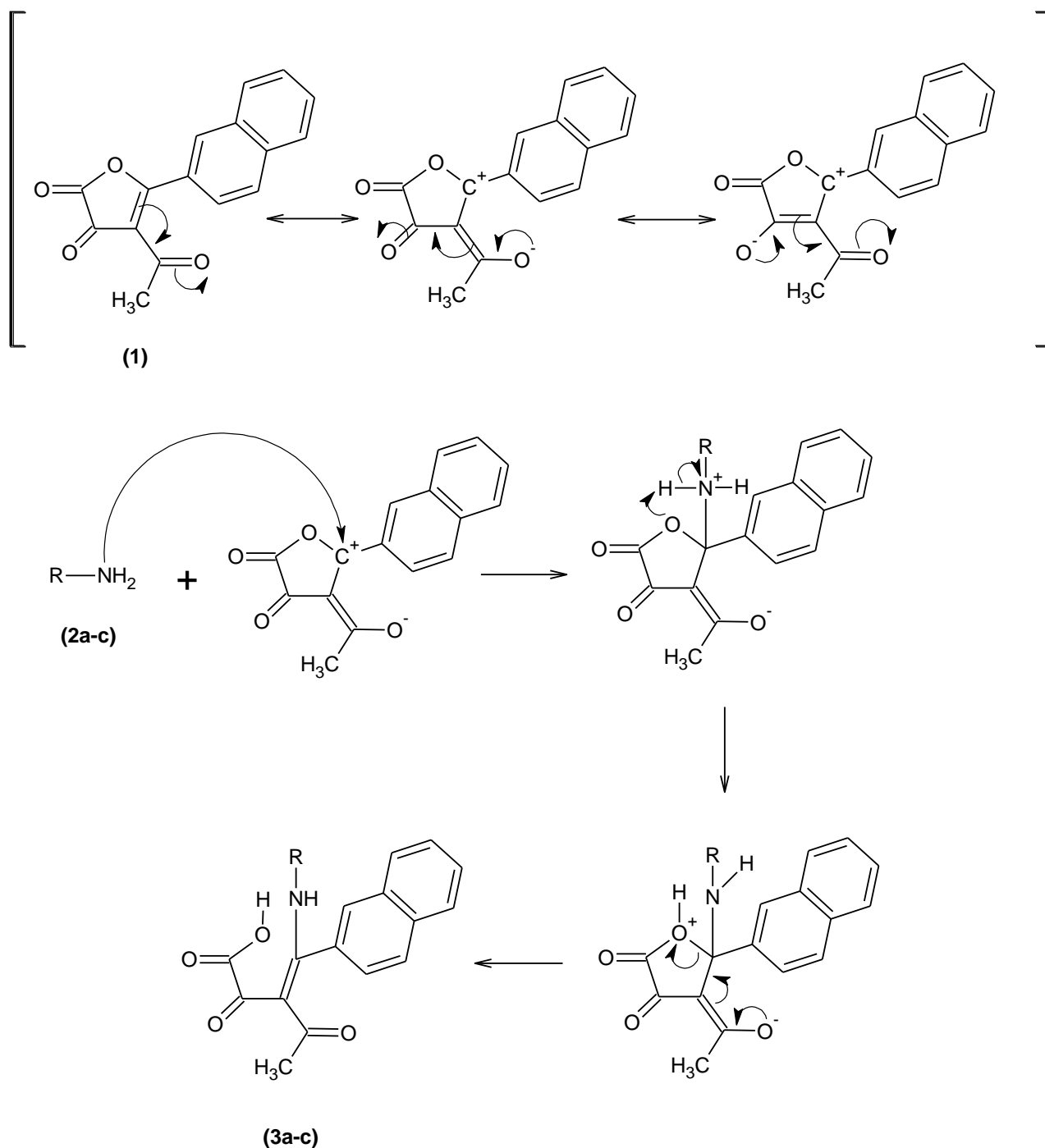
Scheme 3 Mechanizm of reaction (**3a-c**)

Conclusions

In this study, 2,4-dioxopentanoic acid derivatives (**3a-c**) were obtained from the reaction of 4-acetyl-5-(1-naphthyl)furan-2,3-dione (**1**) with various nitrogenous nucleophiles (**2a-c**). The structures of these newly synthesized compounds (**3a-c**) were determined from the FT-IR, ^{1}H and ^{13}C NMR spectroscopic data, elemental analyses and in addition to experimental analysis, we calculated and discussed quantum chemical parameters such as the energy of the highest occupied molecular orbital, the energy of the lowest unoccupied molecular orbital, HOMO–LUMO energy gap, chemical hardness, softness, electronegativity, chemical potential, dipole moment, global electrophilicity, sum of

the total negative charge (TNC) and sum of electronic and zero-point energies (SEZPE) quantum-mechanical calculations by using B3LYP method with basis set of the 6-311G(d,p) in order to find molecular properties.

Acknowledgement

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