

Research Article

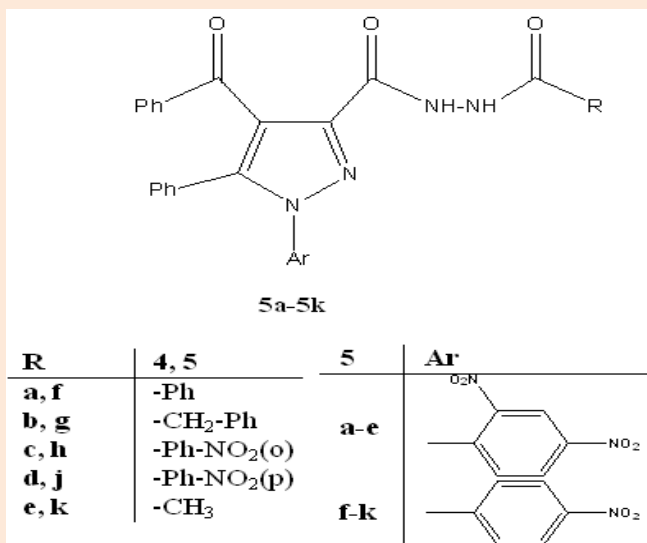
The Reactions and Quantum Chemical Calculations of Some Pyrazole-3-Carboxylic Acid Chlorides with Various Hydrazides

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Abstract

The 1*H*-pyrazole-3-carboxylic acids **2a-b** were converted via reactions of acid chlorides **3a-b** with various hydrazide derivatives **4a-k** into the corresponding novel 1*H*-pyrazole-3-carbohydrazides **5a-k**, in good yields (60-90%). It was demonstrated that with the variation in reaction conditions, the reaction changes leading to different products. All the newly synthesized compounds were characterized by elemental analyses, IR, ¹H and ¹³C NMR spectroscopic data. All compounds were compared with their previous analogues. The highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap between E_{HOMO} and E_{LUMO}, dipole moment (DM), sum of the total negative charge (TNC), global hardness (η), softness (σ), chemical potential (μ), and electronegativity (χ) values and Fukui functions were calculated.

Keywords: Furan-2,3-dione, Pyrazole-3-carboxylic acid, Pyrazole-3-carboxylic acid chlorides, Hydrazide, Quantum chemical calculations



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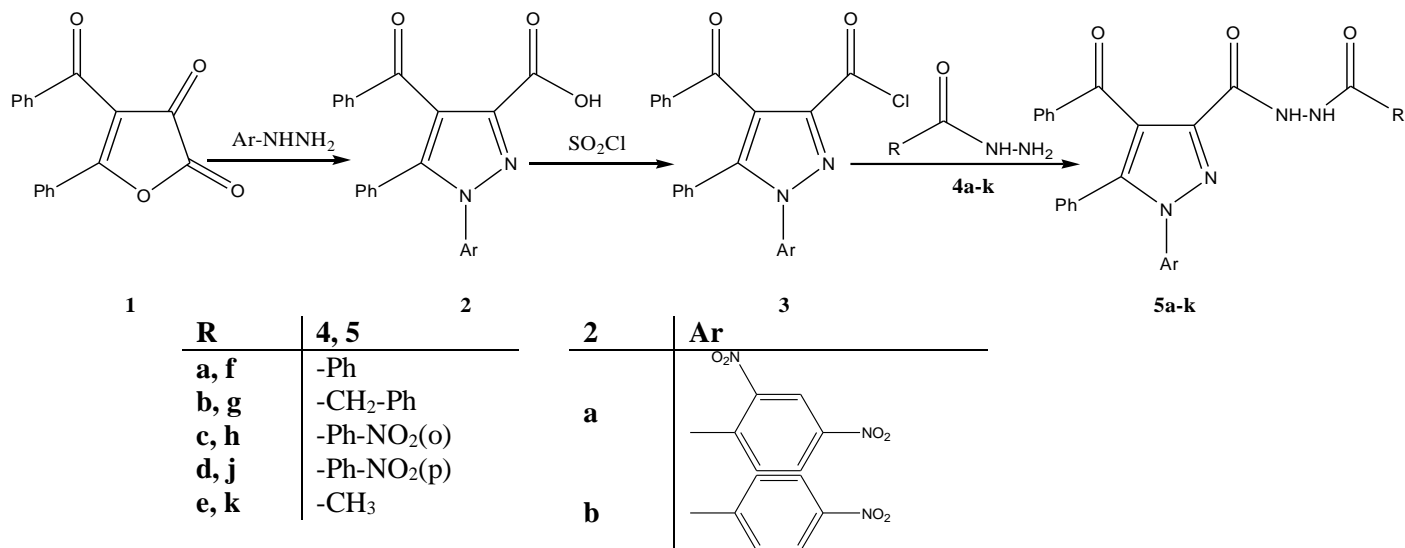
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Introduction

The cyclocondensation reaction of 1,3-dicarbonyl compounds with oxalyl chloride represents a convenient synthesis of furan-2,3-dione systems [1-3] which constitute an important group of oxygen-containing heterocyclic starting materials that have been widely explored during the last few decades [4-7]. A convenient method for their synthesis and the mechanism of the reactions, as well as semi-empirical (AM1 and PM3) and ab initio calculations on the interaction of 4-benzoyl-5-phenyl-2,3-dihydro-2,3-furandione **1** with several semicarbazones, ureas, thioureas and oximes, have been reported recently [8-13]. The reaction of the furan-2,3-dione **1** with various hydrazones and hydrazines results in new pyrazole-3-carboxylic acids, pyrazolopyridazinones, and some of their derivatives [14-16].

Pyrazole derivatives in general are well-known nitrogen-containing heterocyclic compounds and various procedures have been developed for their syntheses [17-21]. The chemistry of pyrazole derivatives has the subject of much research due to their importance in various applications and their widespread potential biological and pharmacological activities. These include the following: antiinflammatory, antipyretic, analgesic, antimicrobial, antiviral, antitumor, antifungal, pesticidal, anticonvulsant, CNS regulants, antihistaminic, antibiotics and antidepressant activities [22-32]. In view of these important properties, we attempted both to prove the reproducibility of the reaction of 4-benzoyl-1-(2,4-dinitrophenyl)-5-phenyl-1*H*-pyrazole-3-carboxylic acid chloride **3a** and 4-benzoyl-1-(4-nitrophenyl)-5-phenyl-1*H*-pyrazole-3-carboxylic acid chloride **3b** with some hydrazine derivatives **4a-k** and to extend

our investigations so as to prepare new heterocycles, which include the pyrazole ring in their structure. We here in report the reaction mechanism, synthesis and characterization of novel 1*H*-pyrazole-3-carbohydrazides **5a-k** by the reaction of pyrazole-3-carboxylic acid chlorides **3** with the corresponding hydrazine derivatives such as benzoic hydrazide **4a**, 4-nitro benzoic hydrazide **4b**, phenyl acetyl hydrazide **4c**, 2-nitro benzoic hydrazide **4d** and acetic hydrazide **4e** (see **Scheme 1**). The quantum chemical calculations of the molecules under study were carried out by using B3LYP/6-31G(d,p).



Scheme 1 Synthesis of the pyrazole-3-carboxylate derivatives **5a-k**

Experimental

Melting points (m.p.) were determined on an Electrothermal 9200 apparatus and are uncorrected. Microanalyses were performed on a Carlo Erba elemental analyzer, model 1108. A Shimadzu FT-IR-8400 model spectrophotometer was used for IR spectra (in the range of 400-4000 cm⁻¹ region), using ATR techniques. The ¹H and ¹³C NMR spectra were measured with a Bruker Avance III 400 MHz spectrometer and the chemical shifts were recorded in ppm units. After completion of the reactions, solvents were evaporated with a rotary evaporator (Buchi RE model 111). The reactions were followed by TLC using a DC Alufolien Kieselgel 60 F254 (Merck) and a Camag TLC lamp (254/366 nm). Solvents and all other chemical reagents were purchased from commercial suppliers and were of reagent grade quality. Solvents were dried by refluxing with the appropriate drying agents and distilled before use.

4-Benzoyl-5-phenyl-1-[2,4-dinitrophenyl]-N'-(phenylcarbonyl)-1*H*-pyrazole-3-carbohydrazide (**5a**)

0.20 g of **3a** was dissolved in 20 mL of benzene. To this solution, 0.06 g of benzoic hydrazide **4a** dissolved in benzene was added dropwise and the reaction mixture was refluxed for 3 h. Evaporation of the solvent gives the crude **5a** which is recrystallized by ethanol to yield 0.23 g (90%); C₃₀H₂₀N₆O₇, 576.52 g/mol, m.p. 170 °C; IR (ν_{max}, cm⁻¹): 3342, 3172 (-NH-NH-); 3051 (aromatic, C-H); 1722, 1647, 1606 (C=O); 1533-1468 (C≡C, C≡N); 1453-1340 (N=O); ¹H NMR (CDCl₃, δ): 9.62 and 9.03 (d, -NH-NH-), 8.15-7.16 ppm (m, 18H, aromatic H); ¹³C NMR (CDCl₃, δ): 191.55 ppm (C=O, benzoyl), 165.01 and 158.46 (C=O, hydrazides), 148.21 and 147.80 (C-NO₂), 138.41-120.95 (m, 24C, aromatic C); Elemental analysis (%): found (calcd.) C: 62.32 (62.50); H: 3.62 (3.50); N: 14.20 (14.58).

4-Benzoyl-5-phenyl-1-[2,4-dinitrophenyl]-N'-(phenylacetylcarbonyl)-1*H*-pyrazole-3-carbohydrazide (**5b**)

0.20 g of **3a** was dissolved in 20 mL of toluene. To this solution, 0.06 g of phenyl acetic hydrazide **4b** dissolved in benzene was added dropwise and the reaction mixture was refluxed for 2 h. Evaporation of the solvent gives the crude **5b** which is recrystallized by ethanol to yield 0.22 g (85%); C₃₁H₂₂N₆O₇, 590.54 g/mol, m.p. 225 °C; IR (ν_{max}, cm⁻¹): 3290, 3122 (-NH-NH-); 3022 (aromatic, C-H); 2944 (aliphatic, C-H); 1668, 1643, 1581 (C=O); 1537-1479 (C≡C, C≡N); 1453-1344 (N=O); ¹H NMR (CDCl₃, δ): 3.77 ppm (s, 2H, -CH₂-); 10.48 and 10.40 (d, -NH-NH-), 7.77-7.13

ppm (m, 18 H, aromatic H); ^{13}C NMR (CDCl_3 , δ): 191.10 ppm (C=O, benzoyl), 151.51 and 147.62 (C=O, hydrazides), 136.60-121.10 (m, 24 C, aromatic C), 40.30 ($-\text{CH}_2-$); Elemental analysis (%): found (calcd.) C: 62.99 (63.05); H: 3.60 (3.75); N: 14.52 (14.23).

4-Benzoyl-5-phenyl-1-[2,4-dinitrophenyl]-N'-(2-nitrophenylcarbonyl)-1H-pyrazole-3-carbohydrazide (5c)

0.20 g of **3a** was dissolved in 20 mL of benzene. To this solution, 0.08 g of 2-nitro benzoic hydrazide **4c** dissolved in benzene was added dropwise and the reaction mixture was refluxed for 3 h. Evaporation of the solvent gives the crude **5c** which is recrystallized by ethanol to yield 0.20 g (76%); $\text{C}_{30}\text{H}_{19}\text{N}_7\text{O}_9$, 621.51 g/mol, m.p. 185 $^\circ\text{C}$; IR (ν_{max} , cm^{-1}): 3268, 3175 ($-\text{NH}-\text{NH}-$); 3072 (aromatic, C-H); 1684, 1653, 1606 (C=O); 1529-1446 ($\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$); 1425-1348 (N=O); ^1H NMR ($\text{DMSO}-d_6$, δ): 11.36 and 11.25 (d, $-\text{NH}-\text{NH}-$), 8.49-7.13 ppm (m, 17 H, aromatic H); ^{13}C NMR ($\text{DMSO}-D_6$, δ): 190.37 ppm (C=O, benzoyl), 169.33 and 159.32 (C=O, hydrazides), 147.84 and 145.10 (C- NO_2), 138.43-121.09 (m, 24 C, aromatic C); Elemental analysis (%): found (calcd.) C: 58.42 (57.97); H: 3.42 (3.08); N: 15.55 (15.78).

4-Benzoyl-5-phenyl-1-[2,4-dinitrophenyl]-N'-(4-nitrophenylcarbonyl)-1H-pyrazole-3-carbohydrazide (5d)

0.20 g of **3a** was dissolved in 20 mL of benzene. To this solution, 0.08 g of 4-nitro benzoic hydrazide **4d** dissolved in benzene was added dropwise and the reaction mixture was refluxed for 2 h. Evaporation of the solvent gives the crude **5d** which is recrystallized by ethanol to yield 0.22 g (80 %); $\text{C}_{30}\text{H}_{19}\text{N}_7\text{O}_9$, 621.51 g/mol, m.p. 216 $^\circ\text{C}$; IR (ν_{max} , cm^{-1}): 3300, 3188 ($-\text{NH}-\text{NH}-$); 3088 (aromatic, C-H); 1684, 1652, 1606 (C=O); 1522-1456 ($\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$); ^1H NMR ($\text{DMSO}-d_6$, δ): 11.27 and 11.07 (d, $-\text{NH}-\text{NH}-$), 7.98-7.16 ppm (m, 17 H, aromatic H); ^{13}C NMR ($\text{DMSO}-d_6$, δ): 192.39 ppm (C=O, benzoyl), 162.44 and 159.39 (C=O, hydrazides), 147.86 and 145.15 (C- NO_2), 136.20-115.22 (m, 24 C, aromatic C); Elemental analysis (%): found (calcd.) C: 57.66 (57.97); H: 3.54 (3.08); N: 15.68 (15.78).

N'-(acetylcarbonyl)-4-benzoyl-5-phenyl-1-[2,4-dinitrophenyl]-1H-pyrazole-3-carbohydrazide (5e)

0.20 g of **3a** was dissolved in 20 mL of benzene. To this solution, 0.03 g of acetic hydrazide **4e** dissolved in benzene was added dropwise and the reaction mixture was refluxed for 3 h. Evaporation of the solvent gives the crude **5e** which is recrystallized by ethanol to yield 0.15 g (65%); $\text{C}_{25}\text{H}_{18}\text{N}_6\text{O}_7$, 514.45 g/mol, m.p. 268 $^\circ\text{C}$; IR (ν_{max} , cm^{-1}): 3219, 3114 ($-\text{NH}-\text{NH}-$); 3002 (aromatic, C-H); 2920 (aliphatic, C-H); 1660, 1645, 1607 (C=O); 1598-1446 ($\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$); 1425-1341 (N=O); ^1H NMR ($\text{DMSO}-d_6$, δ): 2.66 ppm (s, 3H, $-\text{CH}_3$); 12.43 and 12.38 (d, $-\text{NH}-\text{NH}-$), 8.47-6.92 ppm (m, 13 H, aromatic H); ^{13}C NMR ($\text{DMSO}-d_6$, δ): 189.30 ppm (C=O, benzoyl), 153.36 and 150.12 (C=O, hydrazides), 147.53 and 144.26 (C- NO_2), 136.03-118.89 (m, 18 C, aromatic C), 19.00 ($-\text{CH}_3$); Elemental analysis (%): found (calcd.) C: 58.22 (58.37); H: 3.38 (3.53); N: 16.59 (16.34).

4-Benzoyl-5-phenyl-1-[4-nitrophenyl]-N'-(phenylcarbonyl)-1H-pyrazole-3-carbohydrazide (5f)

0.20 g of **3b** was dissolved in 20 mL of benzene. To this solution, 0.06 g of benzoic hydrazide **4f** dissolved in benzene was added dropwise and the reaction mixture was refluxed for 4 h. Evaporation of the solvent gives the crude **5f** which is recrystallized by ethanol to yield 0.22 g (84%); $\text{C}_{30}\text{H}_{21}\text{N}_5\text{O}_5$, 531.52 g/mol, m.p. 230 $^\circ\text{C}$; IR (ν_{max} , cm^{-1}): 3253, 3122 ($-\text{NH}-\text{NH}-$); 3066 (aromatic, C-H); 1693, 1680, 1606 (C=O); 1591-1439 ($\text{C}\equiv\text{C}$) and ($\text{C}\equiv\text{N}$); 1417-1331 (N=O); ^1H NMR ($\text{DMSO}-d_6$, δ): 10.98 and 10.53 (d, $-\text{NH}-\text{NH}-$), 8.43-7.14 ppm (m, 19 H, aromatic H); ^{13}C NMR ($\text{DMSO}-d_6$, δ): 190.64 ppm (C=O, benzoyl), 170.89 and 159.79 (C=O, hydrazides), 147.30 (C- NO_2), 131.70-115.64 (m, 24 C, aromatic C); Elemental analysis (%): found (calcd.) C: 68.02 (67.79); H: 4.19 (3.95); N: 13.46 (13.18).

4-Benzoyl-5-phenyl-1-[4-nitrophenyl]-N'-(phenylacetylcarbonyl)-1H-pyrazole-3-carbohydrazide (5g)

0.20 g of **3b** was dissolved in 20 mL of toluene. To this solution, 0.07 g of phenyl acetic hydrazide **4g** dissolved in benzene was added dropwise and the reaction mixture was refluxed for 3 h. Evaporation of the solvent gives the crude **5g** which is recrystallized by ethanol to yield 0.24 g (87%); $\text{C}_{31}\text{H}_{23}\text{N}_5\text{O}_5$, 545.54 g/mol, m.p. 237 $^\circ\text{C}$; IR (ν_{max} , cm^{-1}): 3190, 3116 ($-\text{NH}-\text{NH}-$); 3038 (aromatic, C-H); 2960 (aliphatic, C-H); 1657, 1610, 1588 (C=O); 1516-1447 ($\text{C}\equiv\text{C}$) and ($\text{C}\equiv\text{N}$); 1420-1256 (N=O); ^1H NMR ($\text{DMSO}-d_6$, δ): 3.76 ppm (s, 2H, $-\text{CH}_2-$); 10.18 and 9.79 (d, $-\text{NH}-\text{NH}-$), 8.42-7.14 ppm (m, 19 H, aromatic H); ^{13}C NMR ($\text{DMSO}-d_6$, δ): 189.89 ppm (C=O, benzoyl), 174.79 and 169.38 (C=O,

hydrazides), 153.27 (C-NO₂), 136.17-124.44 (m, 24 C, aromatic C), 39.31 (-CH₂-); Elemental analysis (%): found (calcd.) C: 67.99 (68.25); H: 4.53 (4.25); N: 12.56 (12.84).

4-Benzoyl-5-phenyl-1-[4-nitrophenyl]-N'-(2-nitrophenylcarbonyl)-1H-pyrazole-3-carbohydrazide (5h)

0.20 g of **3b** was dissolved in 20 mL of benzene. To this solution, 0.08 g of 2-nitro benzoic hydrazide **4h** dissolved in toluene was added dropwise and the reaction mixture was refluxed for 4 h. Evaporation of the solvent gives the crude **5h** which is recrystallized by ethanol to yield 0.20 g (70%); C₃₀H₂₀N₆O₇, 576.52 g/mol, m.p. 234 °C; IR (ν_{max}, cm⁻¹): 3233, 3161 (-NH-NH-); 3072 (aromatic, C-H); 1730, 1616, 1610 (C=O); 1526-1447 (C≡C) and (C≡N); 1413-1342 (N=O); ¹H NMR ((DMSO-d₆, δ): 11.78 and 11.47 (d, -NH-NH-), 8.53-7.34 ppm (m, 18 H, aromatic H); ¹³C NMR (DMSO-d₆, δ): 191.90 ppm (C=O, benzoyl), 159.50 and 149.89 (C=O, hydrazides), 147.49 and 144.78 (C-NO₂), 137.61-124.06 (m, 24 C, aromatic C); Elemental analysis (%): found (calcd.) C: 62.76 (62.50); H: 3.71 (3.50); N: 14.26 (14.58).

4-Benzoyl-5-phenyl-1-[4-nitrophenyl]-N'-(4-nitrophenylcarbonyl)-1H-pyrazole-3-carbohydrazide (5j)

0.20 g of **3b** was dissolved in 20 mL of benzene. To this solution, 0.08 g of 4-nitro benzoic hydrazide **4j** dissolved in benzene was added dropwise and the reaction mixture was refluxed for 3 h. Evaporation of the solvent gives the crude **5j** which is recrystallized by ethanol to yield 0.17 g (60%); C₃₀H₂₀N₆O₇, 576.52 g/mol, m.p. 214 °C; IR (ν_{max}, cm⁻¹): 3263, 3151 (-NH-NH-); 3101 (aromatic, C-H); 1701, 1664, 1599 (C=O); 1518-1475 (C≡C) and (C≡N); 1435-1347 (N=O); ¹H NMR (DMSO-d₆, δ): 11.36 and 11.07 (d, -NH-NH-), 8.33-7.09 ppm (m, 18 H, aromatic H); ¹³C NMR (DMSO-d₆, δ): 190.89 ppm (C=O, benzoyl), 159.50 and 146.95 (C=O, hydrazides), 131.03-125.05 (m, 24 C, aromatic C); Elemental analysis (%): found (calcd.) C: 62.72 (62.50); H: 3.68 (3.50); N: 14.63 (14.58).

N'-(acetylcarbonyl)-4-benzoyl-5-phenyl-1-[4-nitrophenyl]-1H-pyrazole-3-carbohydrazide (5k)

0.20 g of **3b** was dissolved in 20 mL of benzene. To this solution, 0.03 g of acetic hydrazide **4k** dissolved in benzene was added dropwise and the reaction mixture was refluxed for 3 h. Evaporation of the solvent gives the crude **5k** which is recrystallized by ethanol to yield 0.17 g (75%); C₂₅H₁₉N₅O₅, 469.45 g/mol, m.p. 230 °C; IR (ν_{max}, cm⁻¹): 3300, 3214 (-NH-NH-); 3080 (aromatic, C-H); 2981 (aliphatic, C-H); 1694, 1680, 1638 (C=O); 1516-1439 (C≡C) and (C≡N); 1415-1348 (N=O); ¹H NMR (DMSO-d₆, δ): 1.86 ppm (s, 3 H, -CH₃); 10.55 and 10.35 (d, -NH-NH-), 8.42-7.00 ppm (m, 14 H, aromatic H); ¹³C NMR (DMSO-d₆, δ): 190.97 ppm (C=O, benzoyl), 162.53 and 152.62 (C=O, hydrazides), 146.13 (C-NO₂), 137.92-115.73 (m, 24 C, aromatic C), 22.16 (-CH₃); Elemental analysis (%): found (calcd.) C: 63.74 (63.96); H: 4.29 (4.08); N: 14.63 (14.92).

Computational details

Quantum chemical calculations were carried out by using B3LYP which uses Becke's three parameter functional (B3) and includes a mixture of HF with DFT Exchange terms associated with the gradient corrected correlation functional of Lee, Yang and Parr (LYP) [33], a version of DFT. All the quantum chemical calculations on the compounds under study were performed with full geometrical optimizations with the B3LYP/6-31G(d,p) level of theory in the gas phase by using the standard Gaussian 09 software package [34]. The theoretical parameters were calculated in the gas and solvent phase. Fukui functions, which are common descriptors of site reactivity, were calculated by the AOMix program [35, 36].

Results

Our approach to obtain the particular heterocyclic systems uses the synthesis of the 1H-pyrazole-3-carboxylic acid **2a-b** from 4-benzoyl-5-phenyl-2,3-dihydro-2,3-furandione and 4-nitrophenylhydrazine and 2,4-dinitrophenyl-hydrazine, respectively. The compounds **2a-b** can easily be transformed into the corresponding 1H-pyrazole-3-carboxylic acid chlorides **3a-b** by the usual chemical procedures. The substituted 2,3-furandione, acid **2** and acid chlorides **3a-b**, which are used as important materials in the synthesis of the target heterocycles, were prepared using the literature procedures [1, 4, 30, 31].

In the present study, the reaction of the pyrazole nucleus **3** with hydrazide acyl hydrazide, namely hydrazides, was investigated. The preparation of substituted hydrazides **4a-k** was achieved by refluxing equimolar amounts of the pyrazole **3** and hydrazides in dry benzene or toluene for 2-4 hours, without opening the pyrazole ring. The products of the reactions were easily obtained in good yields (60-90%) from nucleophilic addition of **5a-k** to **3** (Scheme 1). In order to make the reaction selective, we had to determine the parameters, in other words the reaction pathways, leading to such results. The excellent yield of the reaction can be explained by the chemical behavior of compound **3** towards H-active nucleophiles, such as hydroxylamines and carbazates. It should start with a nucleophilic attack of the nitrogen and/or oxygen atoms' lone pair electrons of the hydroxylamine on the antibonding (π^*) orbital of the carbonyl carbon at the C-3 position of the pyrazole ring. The new products obtained, **5a-k**, arise followed by the elimination of hydrogen chloride. The by products formed in this way are removed when the raw products are treated with diethyl ether. The treatment of compounds **3a-b** with various hydrazide derivatives **4** in boiling benzene or toluene gave the corresponding 1H-pyrazole-3-carbohydrazides **5** as the main product.

The progress of the reactions was monitored by thin-layer chromatography until complete consumption of the starting materials. The compounds **5a-k** were obtained in moderate yields (60-90%) after evaporation of the organic solvents and recrystallization from proper solvents (like ethanol, see Scheme 1). The structures of the synthesized compounds were assigned on the basis of analytical as well as spectroscopic data. Product **5a** was obtained in 90% yield by treating **3a** with benzoic hydrazide and refluxing in boiling ethanol for 3 h.

The theoretical values, calculated with B3LYP/6-31G(d,p) denoting a density functional calculation done with the Becke 1988 exchange functional and the Lee-Yang-Parr correlation functional, with the KS orbitals expended in a B3LYP/6-31G(d,p) basis set [34, 35], and the experimental wavenumbers as well as the approximated assignments for **5a** are listed in Table 1.

Table 1 Experimental and theoretical vibrational assignments of **5a** carried out with B3LYP/6-31G(d,p) method

Experimental Frequency	B3LYP/6-31G(d,p)		
Frequency	Frequency ^a	Intensity	Assignments
3342	3582	83	v(N ₂₄ H)
3169	3451	335	v(N ₂₃ H)
3051	3263	22	v(C ₃₁ H)
	3252	6	v(C ₂₈ H), v(C ₂₉ H)
	3230	0.3	v(C ₂₈ H), v(C ₂₉ H)
	3223	6	v(C ₄₂ H), v(C ₄₃ H)
	3221	6	v(CH) _{ring 3}
	3218	5	v(C ₁₁ H), v(C ₁₃ H), v(C ₁₄ H), v(C ₁₅ H)
	3215	12	v(CH) _{ring 4}
	3209	19	v(CH) _{ring 2}
	3208	11	v(C ₁₈ H), v(C ₁₉ H), v(C ₂₁ H), v(C ₂₂ H)
	3206	20	v(CH) _{ring 3}

	3201	8	$\nu(\text{C}_{18}\text{H}), \nu(\text{C}_{20}\text{H}), \nu(\text{C}_{22}\text{H})$
	3199	27	$\nu(\text{CH})_{\text{ring } 2}$
	3197	9	$\nu(\text{C}_{11}\text{H}), \nu(\text{C}_{12}\text{H}), \nu(\text{C}_{14}\text{H}), \nu(\text{C}_{15}\text{H})$
	3194	2	$\nu(\text{C}_{18}\text{H}), \nu(\text{C}_{19}\text{H}), \nu(\text{C}_{21}\text{H}), \nu(\text{C}_{22}\text{H})$
	3191	6	$\nu(\text{CH})_{\text{ring } 2}$
	3187	1	$\nu(\text{CH})_{\text{ring } 4}$
	3186	1	$\nu(\text{CH})_{\text{ring } 3}$
	3182	1	$\nu(\text{CH})_{\text{ring } 2}$
1722	1768	8	$\nu(\text{C}_{25}=\text{O}_{27}), \nu(\text{C}_6=\text{O}_7), \delta(\text{N}_{23}\text{H}), \delta(\text{N}_{24}\text{H})$
	1726	482	$\nu(\text{C}_{25}=\text{O}_{27}), \nu(\text{C}_6=\text{O}_7), \nu(\text{C}_9=\text{O}_8), \delta(\text{N}_{23}\text{H}), \delta(\text{N}_{24}\text{H})$
1647	1709	147	$\nu(\text{C}_{25}=\text{O}_{27}), \nu(\text{C}_6=\text{O}_7), \nu(\text{C}_9=\text{O}_8), \delta(\text{N}_{23}\text{H})$
1606	1677	224	$\nu(\text{CC})_{\text{ring } 5}, \nu(\text{NO}_2),$
1533	1670	193	$\nu(\text{CC})_{\text{ring } 5}, \delta(\text{CH})_{\text{ring } 5}, \nu(\text{NO}_2),$
1498	1653	37	$\nu(\text{CC})_{\text{ring } 3}, \delta(\text{C}_{11}\text{H}), \delta(\text{C}_{12}\text{H}), \delta(\text{C}_{14}\text{H}), \delta(\text{C}_{15}\text{H})$
1488	1638	49	$\nu(\text{CC})_{\text{ring } 5}, \delta(\text{CH})_{\text{ring } 5}, \nu(\text{NO}_2),$
	1636	10	$\nu(\text{CC})_{\text{ring } 2}, \delta(\text{CH})_{\text{ring } 2}$
	1633	7	$\nu(\text{CC})_{\text{ring } 3}, \delta(\text{CH})_{\text{ring } 3}$
	1632	15	$\nu(\text{CC})_{\text{ring } 4}, \delta(\text{CH})_{\text{ring } 4}$
1440	1623	76	$\nu(\text{CC})_{\text{ring } 5}, \delta(\text{CH})_{\text{ring } 5}, \nu(\text{NO}_2),$
	1605	39	$\delta(\text{N}_{23}\text{H}), \delta(\text{N}_{24}\text{H})$
	1575	29	$\nu(\text{CC})_{\text{ring } 4}, \nu(\text{C}_2\text{C}_3)_{\text{ring } 1}, \delta(\text{C}_{18}\text{H}), \delta(\text{C}_{19}\text{H}), \delta(\text{C}_{21}\text{H}), \delta(\text{C}_{22}\text{H})$
	1542	24	$\delta(\text{N}_{24}\text{H}), \delta(\text{CH})_{\text{ring } 5}, \delta(\text{C}_{19}\text{H}), \delta(\text{C}_{22}\text{H}), \delta(\text{C}_{39}\text{H}), \delta(\text{C}_{40}\text{H}), \delta(\text{C}_{42}\text{H}), \delta(\text{C}_{43}\text{H})$
	1537	62	$\delta(\text{CH})_{\text{ring } 5}, \delta(\text{C}_{39}\text{H}), \delta(\text{C}_{40}\text{H}), \delta(\text{C}_{42}\text{H}), \delta(\text{C}_{43}\text{H})$
	1532	7	$\delta(\text{C}_{11}\text{H}), \delta(\text{C}_{12}\text{H}), \delta(\text{C}_{14}\text{H}), \delta(\text{C}_{15}\text{H}), \delta(\text{C}_{19}\text{H}), \delta(\text{C}_{22}\text{H})$
1340	1499	620	$\delta(\text{N}_{23}\text{H}), \delta(\text{N}_{24}\text{H}), \delta(\text{C}_{13}\text{H}), \delta(\text{C}_{14}\text{H}), \delta(\text{C}_{19}\text{H}), \delta(\text{C}_{20}\text{H}), \delta(\text{C}_{22}\text{H}), \delta(\text{C}_{28}\text{H}),$ $\delta(\text{C}_{40}\text{H}), \delta(\text{C}_{41}\text{H}), \delta(\text{C}_{43}\text{H})$
	1490	23	$\delta(\text{C}_{12}\text{H}), \delta(\text{C}_{13}\text{H}), \delta(\text{C}_{14}\text{H}), \delta(\text{C}_{40}\text{H}), \delta(\text{C}_{41}\text{H}), \delta(\text{C}_{42}\text{H})$
	1488	10	$\delta(\text{C}_{12}\text{H}), \delta(\text{C}_{13}\text{H}), \delta(\text{C}_{14}\text{H}), \delta(\text{C}_{19}\text{H}), \delta(\text{C}_{20}\text{H}), \delta(\text{C}_{21}\text{H}), \delta(\text{C}_{40}\text{H}), \delta(\text{C}_{41}\text{H}),$ $\delta(\text{C}_{42}\text{H})$
1258	1485	95	$\delta(\text{N}_{24}\text{H}), \delta(\text{C}_{13}\text{H}), \delta(\text{C}_{18}\text{H}), \delta(\text{C}_{19}\text{H}), \delta(\text{C}_{20}\text{H}), \delta(\text{C}_{21}\text{H}), \delta(\text{C}_{40}\text{H}), \delta(\text{C}_{41}\text{H}),$ $\delta(\text{C}_{42}\text{H})$
1250	1461	334	$\nu(\text{C}_1\text{N}_5), \nu(\text{C}_3\text{N}_4), \delta(\text{CH})_{\text{ring } 5}, \delta(\text{N}_{23}\text{H}), \delta(\text{N}_{24}\text{H}), \delta(\text{C}_{19}\text{H}), \delta(\text{C}_{22}\text{H})$

^aunscaled

Harmonic vibrational frequencies were computed using and B3LYP methods with the 6-31G(d) basis sets. The anharmonicity of the fundamental frequencies is most often taken into account by scaling the calculated harmonic frequencies, The HF and B3LYP calculated vibrational frequencies have been scaled by a single factor of 0.88 and 0.96 for all molecules to correct the well-known systematic 10–12% frequency overestimation [37]. Theoretical values of IR were given as unscaled.

The bands located in the high frequency region of the spectra of **3a** and **3b** are easy to identify and concentrate CH, CH₂ and CH₃ stretching. The stretching vibrations of the aromatic C-H of the studied molecules give rise to bands in the region of 3100-3035 cm⁻¹. B3LYP/6-31G(d,p) calculations show that these vibrations are located in the range of 3090-3050 cm⁻¹. Methyl group stretching vibrations absorb in the region of 2930-2920 cm⁻¹. The experimental bands at 3342 and 3169 cm⁻¹ correspond to the stretching $\nu(\text{N}_{16}\text{-H}), \nu(\text{N}_{24}\text{-H})$ and $\nu(\text{N}_{23}\text{-h})$ vibrations of the **5a** molecule, respectively. These bands are assigned at 3582 and 3451 cm⁻¹ with the level of B3LYP/6-31G(d,p).

The stretching vibrations of the aromatic C-H of **5a** observed in the region of 3091-3025 cm⁻¹ as experimental are calculated with the B3LYP/6-31G(d,p) method in the range of 3263-3182 cm⁻¹. In the FT IR spectra of compound **5a**, the C=O absorptions seen at 1722, 1647, 1606 cm⁻¹ were calculated at 1768, 1726, 1709 cm⁻¹ as theoretically nitro group in *p*-nitrophenyl and the *p*-nitrobenzoyl derivatives of *o,o'*-alkylene dithiophosphate show a strong absorption band at 1550-1520 cm⁻¹ [36]. The N-O bonds of the nitro groups are observable, one in the 1550-1500 cm⁻¹ region and another in the 1360-1290 cm⁻¹ region due to the coupled stretches of the two N-O bonds in each molecule. One coupling

interaction is asymmetric and the other is symmetric. The absorption bands of the nitro group in **5a** assigned at 1533 and 1525 cm^{-1} were calculated at 1677 and 1670 cm^{-1} .

NMR-Study

The ^1H NMR signals were observed at 9.62 and 9.03 (d, -NH-NH-), and at 8.15-7.16 ppm (m, 18H, aromatic H). The ^{13}C NMR signals were found at 191.55 ppm (C=O, benzoyl), 165.01 and 158.46 (C=O, hydrazides), 148.21 and 147.80 (C-NO₂), and at 138.41-120.95 (m, 24C, aromatic C) the elemental analysis data confirm the structure of **5a**.

Theoretical Calculations and Results

The optimized molecular structures for **5a** and the electron density from the total SCF density of the molecules (**5a-k**) using B3LYP/6-31G(d,p) are given in **Figure 1**. The red regions show low energy (negative region) near O and the blue regions show high energy (positive region) in the electron density figure from the total SCF density of the molecules (**5a-k**). The HOMO and LUMO orbitals for (**5a-k**) using B3LYP/6-31G(d,p) are given in **Figure 1** and the fragment contributions (in the MPA framework) to the HOMO and the LUMO calculated by the AOMix method after the B3LYP/6-31G method are given in **Table 2**. The HOMO is localized only on nitrogen atoms for **5a** and **5f** and consists of + 11.8% 2pz (N23) - 11.2% 2pz(N24) + 7.4% 3pz(N23) - 7.3% 2py(N24) + 7.0% 2py(N23) - 6.8% 3pz(N24) and + 10.5% 2pz(N23) - 10.1% 2pz(N24) + 8.4% 2py(N24) - 8.3% 2py(N23) + 6.6% 3pz(N23) - 6.1% 3pz(N24). The HOMO is localized on nitrogen and oxygen atoms for **5b-5d** and **5g-5j** molecules and for example the HOMO of **5b** and **5g** consists of + 17.3% 2pz(N23) - 16.6% 2pz(N24) - 10.2% 3pz(N24) + 10.1% 3pz(N23) + 8.3% 2pz(O26) - 5.5% 2pz(O7), and + 17.5% 2pz(N23) - 16.6% 2pz(N24) + 10.2% 3pz(N23) - 10.2% 3pz(N24) + 8.4% 2pz(O26) + 5.2% 3pz(O26) respectively. In contrast, the LUMO is delocalized over the entire molecule for the studied molecules.

The highest occupied and the lowest unoccupied molecular orbital energies (E_{HOMO} and E_{LUMO}), the five molecular orbital energies, the energy gap between E_{HOMO} and E_{LUMO} , dipole moment (μ), sum of the total negative charge (TNC), global hardness (η), softness (σ), chemical potential (μ), and electronegativity (χ) values were calculated with B3LYP/6-31G(d,p) and are shown in **Table 3**. HOMO energy is the ability to donate an electron to an appropriate acceptor with empty molecular orbitals.

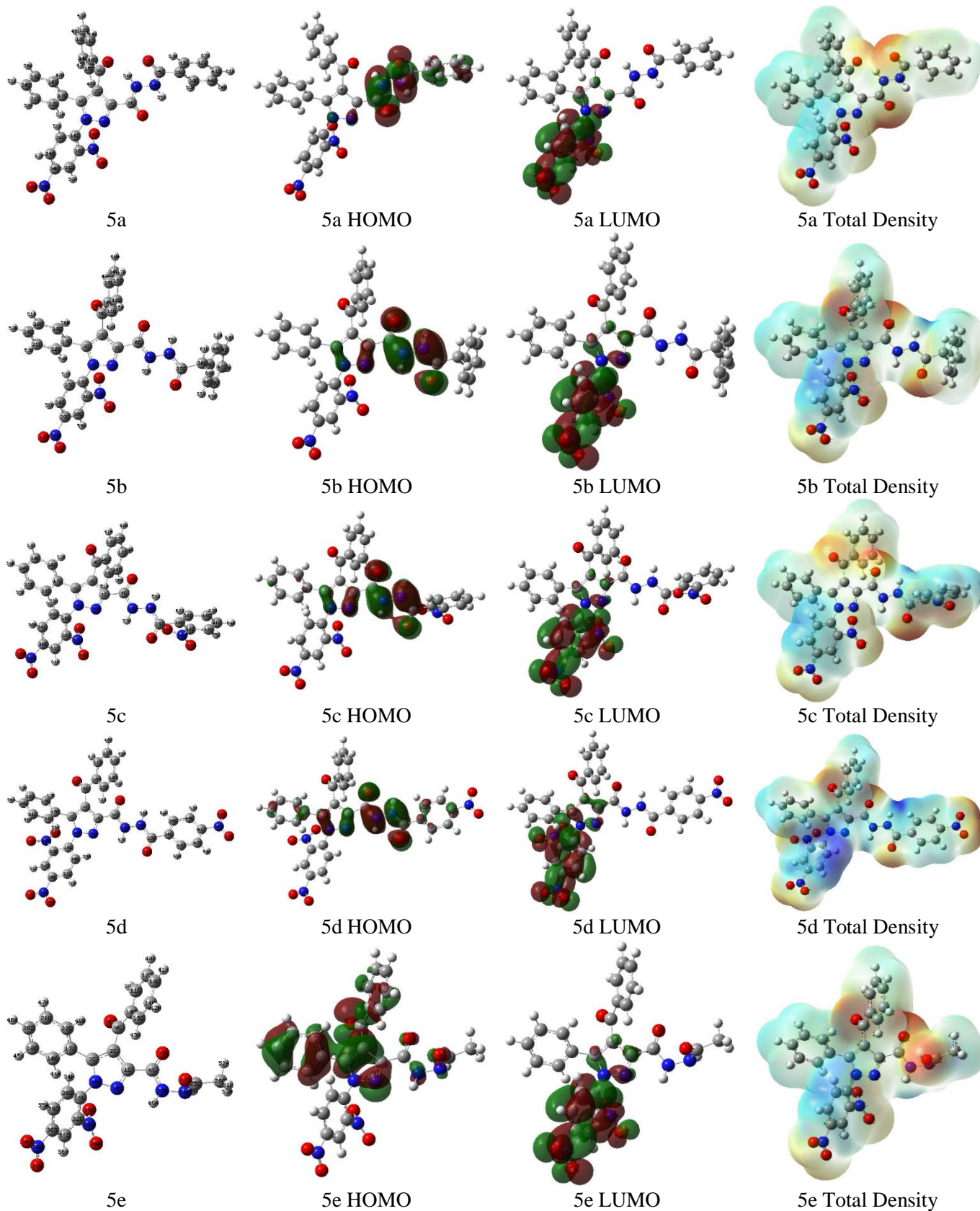
The average value of the HOMO and LUMO energies is related to the electronegativity (χ) and addition. The HOMO-LUMO gap is related to the hardness (η) and softness (σ). These are used extensively to make predictions about chemical behavior [38-44]. There are two nitro groups at the ortho and meta positions of the phenyl group in molecules **5a-5e** and one nitro group at the para position in molecules **5f-5k**. There is no significant change in the E_{HOMO} values of these molecules according to position and number of nitro groups. However, the E_{LUMO} values of molecules **5a-5e** are lower than those of **5g-5k**; this means that substitution of the NO₂ group at the ortho position decreases the E_{LUMO} values of the molecules. We can say the following for the **5a-e** and **5f-k** series of compounds: phenyl > benzyl > o-nitrophenyl > p-nitrophenyl > methyl. **5f-5k** molecules are harder than **5a-5e** molecules. The electronegativity values of **5a-5k** are less than those of **5f-5k**.

The fragment contributions (in the MPA framework) to the HOMO and the LUMO for **5a-5k** which were calculated by the AOMIX program after the B3LYP/6-31G(d,p) method are given in Table 3. These are calculated with the following formula:

$$f_k^+ = \sum_{a \in k} c_{ai}^2 + c_{ai} \sum_{b \in k} c_{bi} S_{ab}, \text{ where } i = \text{LUMO}$$

$$f_k^- = \sum_{a \in k} c_{ai}^2 + c_{ai} \sum_{b \in k} c_{bi} S_{ab}, \text{ where } i = \text{HOMO}$$

The Fukui functions are calculated automatically from the compositions of the molecular orbitals. The compositions of the HOMO and the LUMO of the **5a-5k** molecules are given in **Table 4**. For the HOMO, the contributions at the O7 atom for **5a-5j** are 14.66, 12.06, 11.85, 11.03, 14.27, 11.11, 10.39 and 10.13 %. At the N23 atom they are 30.90, 31.03, 31.90, 30.82, 30.86, 30.98, 31.56 and 20.74 %; at the N24 atom they are 31.38, 31.06, 29.21, 27.80, 31.20, 29.99, 27.94 and 27.37 %. The other contributions for molecules **5a-5k** are from the O/C27 atom or O/C26 atoms.



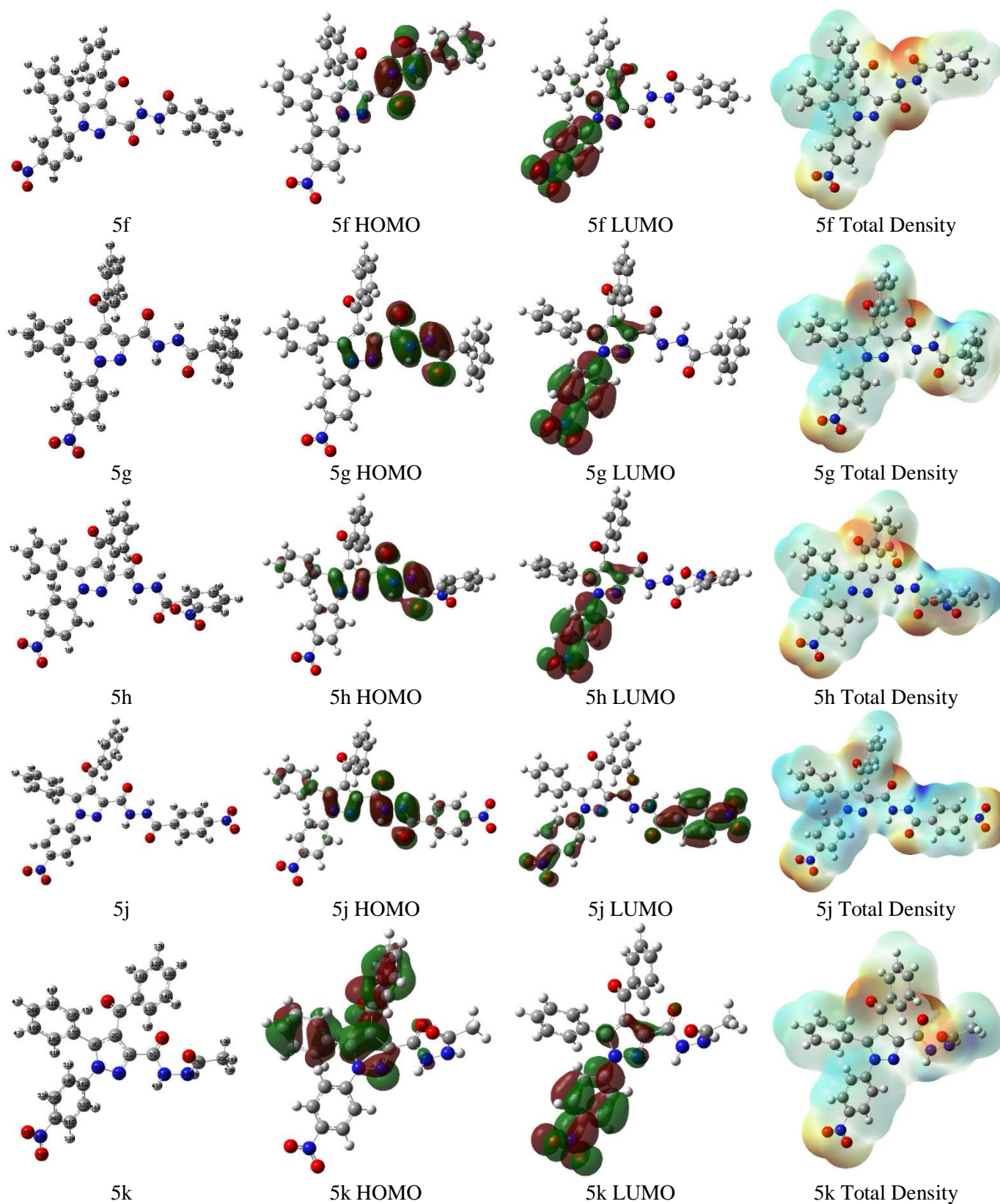


Figure 1 The optimized molecular structures, HOMO, LUMO and total density of the **5a-5k** molecules using B3LYP/6-31G(d,p)

Table 2 The fragment contributions (in the MPA framework) to the HOMO and the LUMO calculated by the AOMix method after the B3LYP/6-31G method

Mol.	
HOMO	
5a	+ 11.8% 2pz (N23) - 11.2% 2pz(N24) + 7.4% 3pz(N23) - 7.3% 2py(N24) + 7.0% 2py(N23) - 6.8% 3pz(N24)
5b	+ 17.3% 2pz(N23) - 16.6% 2pz(N24) - 10.2% 3pz(N24) + 10.1% 3pz(N23) + 8.3% 2pz(O26) - 5.5% 2pz(O7)
5c	+ 17.8% 2pz(N23) - 17.0% 2pz(N24) + 10.4% 3pz(N23) - 10.3% 3pz(N24) - 6.8% 2pz(O7) + 6.3% 2pz(O27)
5d	+ 18.2% 2pz(N23) - 16.2% 2pz(N24) + 10.7% 3pz(N23) - 9.7% 3pz(N24) - 6.5% 2pz(O7) + 5.4% 2pz(O27)
5e	+ 12.5% 2px(O8) - 7.9% 2pz(C2) + 6.8% 3px(O8) + 6.7% 2py(O8) - 6.0% 2pz(C3) + 5.7% 2pz(N5)
5f	+ 10.5% 2pz(N23) - 10.1% 2pz(N24) + 8.4% 2py(N24) - 8.3% 2py(N23) + 6.6% 3pz(N23) - 6.1% 3pz(N24)
5g	+ 17.5% 2pz(N23) - 16.6% 2pz(N24) + 10.2% 3pz(N23) - 10.2% 3pz(N24) + 8.4% 2pz(O26) + 5.2% 3pz(O26)
5h	+ 18.1% 2pz(N23) - 16.4% 2pz(N24) + 10.5% 3pz(N23) - 9.8% 3pz(N24) - 6.0% 2pz(O7) + 5.8% 2pz(O27)
5j	+ 17.9% 2pz(N23) - 15.8% 2pz(N24) + 10.6% 3pz(N23) - 9.4% 3pz(N24) - 5.9% 2pz(O7) + 5.0% 2pz(O27)
5k	+ 11.6% 2px(O8) + 8.0% 2py(O8) + 6.5% 3px(O8) - 6.2% 2pz(C2) - 5.2% 2pz(C3) + 4.9% 2pz(N5)
LUMO	
5a	+ 7.5% 2py(C16) + 6.2% 2py(N36) - 5.4% 2py(O37) - 4.9% 2py(O38) - 4.4% 2py(C29) + 4.1% 3py(C16)
5b	+ 6.8% 2pz(N35) + 6.5% 2pz(C16) - 5.9% 2pz(O36) - 5.4% 2pz(O37) - 4.8% 2pz(C28) - 3.8% 3pz(C28)
5c	+ 3.8% 2px(C16) + 3.7% 2py(C16) + 3.5% 2px(N36) + 3.3% 2pz(N36) - 3.2% 2px(O37) - 3.0% 2px(C29)
5d	+ 4.7% 2px(C16) + 3.3% 2py(N33) - 3.0% 2pz(C16) - 2.9% 2py(C16) + 2.9% 2px(N36) - 2.8% 2py(O35)
5e	+ 6.7% 2py(C16) + 5.7% 2py(N36) - 5.0% 2py(O37) - 4.5% 2py(O38) - 4.0% 2py(C29) + 3.6% 3py(C16)
5f	+ 6.3% 2py(N33) - 5.2% 2pz(N33) - 4.8% 2py(O34) - 4.8% 2py(O35) + 4.0% 2pz(O35) + 4.0% 2pz(O34)
5g	+ 13.0% 2pz(N32) - 10.0% 2pz(O33) - 10.0% 2pz(O34) + 6.5% 2pz(C16) - 5.3% 3pz(O33) - 5.3% 3pz(O34)
5h	+ 9.2% 2pz(N33) - 7.1% 2pz(O34) - 7.1% 2pz(O35) + 4.7% 2pz(C16) - 3.8% 3pz(O34) - 3.8% 3pz(O35)
5j	+ 5.8% 2pz(N41) + 5.1% 2py(N41) - 4.7% 2pz(O43) - 4.7% 2pz(O42) - 4.2% 2py(O42) - 4.2% 2py(O43)
5k	+ 7.5% 2pz(N33) - 6.1% 2py(N33) - 5.7% 2pz(O34) - 5.7% 2pz(O35) + 4.7% 2py(O34) + 4.6% 2py(O35)

For the LUMO, the contributions at the C16, C29, C30, N/O/C36, O/C37 and O/C38 atoms are 15.95, 13.62, 7.03, 13.74, 13.21 and 12.16%, respectively for **5a**; 15.67, 13.01, 7.03, 14.10, 13.46, 12.51% for **5e**. In general the most contribution comes from the aryl group.

Table 3 The calculated quantum chemical parameters by using the B3LYP/6-31G(d,p) method

Mol.	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	DM (D)	TNC (e)	η (eV)	σ (eV ⁻¹)	μ (eV)	χ (eV)	SEZPE ^a (eV)
5a	-5.90	-3.32	2.58	6.650	-2.866	1.290	0.775	-4.610	4.610	-54685.793
5b	-6.26	-3.29	2.97	5.866	-2.929	1.485	0.673	-4.775	4.775	-55754.835
5c	-6.38	-3.31	3.07	5.246	-2.943	1.535	0.651	-4.845	4.845	-60250.218
5d	-6.59	-3.40	3.19	6.085	-2.909	1.595	0.627	-4.995	4.995	-60250.433
5e	-6.75	-3.30	3.45	3.625	-2.896	1.725	0.580	-5.025	5.025	-49469.669
5f	-5.92	-2.70	3.22	6.338	-2.846	1.610	0.621	-4.310	4.310	-49121.616
5g	-6.28	-2.71	3.57	4.394	-2.918	1.785	0.560	-4.495	4.495	-50190.685
5h	-6.40	-2.70	3.70	5.405	-2.923	1.850	0.541	-4.550	4.550	-54686.035
5j	-6.55	-2.86	3.69	6.028	-2.924	1.845	0.542	-4.705	4.705	-54686.312
5k	-6.70	-2.70	4.00	2.662	-2.856	2.000	0.500	-4.700	4.700	-43905.496

^aSum of electronic and zero point energy

Conclusions

In this study, we developed convenient preparative procedures for the efficient synthesis of previously unknown pyrazole-3-carboxamides and pyrazole-3-carboxylate derivatives. The above approach proved very useful for the construction of novel heterocycles of potential pharmacological interest. The newly synthesized compounds may be of interest as a potential biologically active substance, as well as for precursors and reagents for the design of complex polyfunctional structures. Although the number and position of nitro groups in the phenyl ring did not affect the E_{HOMO} values, they affected the E_{LUMO} values.

Table 4 The compositions of the HOMO and the LUMO of the **5a-5k** molecules (atoms are taken its contribution more than 5.00)

Compound/HOMO											
Atom	5a	5b	5c	5d	5f	5g	5h	5j	Atom	5k	5e
O7	14.66	12.06	11.85	11.03	14.27	11.11	10.39	10.13	C2	13.16	14.22
N23	30.90	31.03	31.90	30.82	30.86	30.98	31.56	30.74	C3	-	9.56
N24	31.38	31.06	29.21	27.80	31.20	29.99	27.94	27.37	N5	9.22	10.67
O/C26	-	13.92	-	-	-	13.85	-	-	O8	34.45	30.86
O/C27	10.56	-	13.07	11.13	10.50	-	12.45	10.90	C17	5.05	6.44
	-	-	-	-	-	-	-	-	C20	5.76	7.53
Compound/LUMO											
Atom	5a	5b	5c	5d	5e	5f	5g	5h	5k	Atom	5j
C16	15.95	15.76	15.94	16.22	15.67	11.26	11.50	11.34	11.49	-	-
O/C26	-	-	-	-	-	-	-	-	-	-	10.02
C28	-	13.08	-	-	-	-	7.90	-	-	C/N41	15.12
C29	13.62	7.11	13.58	13.82	13.01	7.58	6.40	7.72	7.96	O42	13.60
C30	7.03	-	6.88	6.64	7.03	6.28	7.69	6.38	6.30	O43	13.60
C31	-	-	-	-	-	7.67	-	7.57	7.75	C39	6.39
C/N32	-	-	-	-	-	-	20.15	-	-	-	-
N/O33	-	-	5.28	6.09	-	19.73	17.55	19.69	20.44	-	-
O34	-	-	5.28	6.22	-	17.18	17.47	17.17	17.71	-	-
O/N35	-	14.07	4.58	5.37	-	17.11	-	17.12	17.68	-	-
N/O/C36	13.74	13.48	12.98	11.58	14.10	-	-	-	-	-	-
O/C37	13.21	12.48	12.58	11.43	13.46	-	-	-	-	-	5.88
O/C38	12.16	-	11.52	10.32	12.51	-	-	-	-	-	6.58

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