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Gaussian calculations of novel 3-(methyl/ethyl/*n*-propyl)-4-[3-ethoxy-4-(4-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-*1H*-1,2,4-triazol-5-ones

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In this study, three new 3-alkyl-4-[3-ethoxy-4-(4-methoxybenzoxy)-benzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-ones (**3a-c**) were synthesized by the reaction of 3-alkyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-ones (**1a-c**) with 3-ethoxy-4-(4-methoxybenzoxy)-benzaldehyde (**2**), which was synthesized by the reaction of 3-ethoxy-4-hydroxybenzaldehyde with 4-methoxybenzoyl chloride by using triethylamine. The compounds synthesized were characterized by IR, ^{1}H-NMR,^{13}C-NMR and UV spectral data. These compounds were optimized by using the B3LYP/6-31G(d,p) and HF/6-31G(d,p) basis sets. ^{1}H and ^{13}C-NMR isotropic shift values were calculated by the method of GIAO using the program package Gaussian G09W. Experimental and theoretical values were inserted into the grafic according to equation of δ exp=a+b. δ calc. IR absorption frequencies of analysed molecules were calculated by two methods. The experimental and theoretical values were compared and found by regression analysis that are accurate. Furthermore, geometric properties (bond angles, bond lengths and dihedral angles), thermodynamic parameters, electronic properties (total energy, dipole moment), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), Mulliken atomic charges of compounds **3a-c** have been investigated by using Gaussian G09W program. The structural data of these compounds have been calculated by using 6-31G(d,p) basis set with density functional method (DFT/B3LYP) and Hartree-Fock method (HF).

Key words: 1,2,4-Triazol-5-one, 6-31G(d,p) basis set, DFT(B3LYP), HF

INTRODUCTION

Triazole is an unsymmetrical heterocyclic organic compound having three nitrogen atoms in the five-membered ring. 4,5-Dihydro-1*H*-1,2,4-triazol-5-one and 1,2,4-triazole derivatives are published to possess a broad spectrum of extensively biological activities such as antimicrobial, antitumor, anticancer, antifungal, anti-HIV, antiviral, anti-inflammatory, analgesic and antioxidant properties [1-10]. As well as, articles on the synthesis of some *N*-arylidenamino-4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives have been published [11-22].

Indeed, the thermodynamic properties, theoretical and experimental spectroscopic properties of some 4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives have been reported [20, 23-25].

In this paper, 3-alkyl-4-[3-ethoxy-4-(4-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-ones (**3a-c**) were obtained from the reaction of compound **(2)** with 3-ethoxy-4-(4-methoxybenzoxy)-benzaldehyde **(1)**, which was synthesized by the reaction of 3-ethoxy-4-hydroxybenzaldehyde with 4-methoxybenzoyl chloride by using triethylamine (Scheme **1**). The starting compounds 2a-i were prepared as described in the literature [26, 27]. The purpose of this study is to synthesize new compounds **3a-c** and to identify the structures of these compounds with spectroscopic methods (^{1}H-NMR, ^{13}C-NMR and FT- IR). Also, these compounds were optimized by using the B3LYP/6-31G(d,p) and HF/6-31G(d,p) basis sets. ^{1}H and ^{13}C-NMR isotropic shift values were calculated by the method of GIAO using the program package Gaussian G09W. Experimental and theoretical values were inserted into the grafic according to equation of δ exp=a+b. δ calc. IR absorption frequencies of analysed molecules were calculated by two methods. The experimental and theoretical values were compared and found by regression analysis that are accurate.

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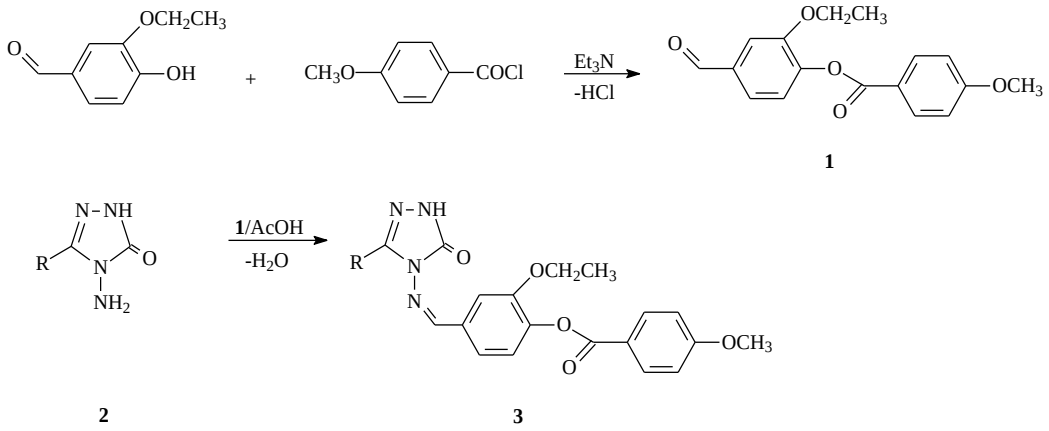

a) R=CH_3, b) R=CH_2CH_3, c) R=$CH_2CH_2CH_3$

Scheme 1. Synthetic pathway of compounds **3a-c.**

EXPERIMENTAL

General method for the preparation of 3-alkyl-4-[3-ethoxy-4-(4-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1H-1,2,4-triazol-5-ones (**3**)

The corresponding compound 2 (0.01 mol) was dissolved in acetic acid (15 mL) and treated with 3-ethoxy-4-(4-methoxybenzoxy)-benzaldehyde (1) (0.01 mol). The mixture was refluxed for 1.5 h and then evaporated at 50-55 °C in vacuo. Several recrystallizations of the residue from appropriate solvent gave pure compounds **3a-c** as colorless crystals.

3-Methyl-4-[3-ethoxy-4-(4-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one (3a). Yield 3.73 g (94.23%). mp. 94 ºC. IR (KBr) ν 3173 (NH), 1730, 1697 (C=O), 1602 (C=N), 1256 (COO), 844 cm^{-1} (1,4 disubstituted benzenoid ring); ^{1}H NMR (200MHz, DMSO-d_6) δ 1.21 (t, 3H, OCH_2CH_3, *J*=7.52 Hz), 2.30 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 4.11 (q, 2H, $O\underline{CH_2}CH_3$, *J*=7.20 Hz), 7.13 (d, 2H, Ar-H, *J*=8.80 Hz), 7.35 (d, 1H, Ar-H, *J*=8.00 Hz), 7.49 (d, 1H, Ar-H, *J*=8.40 Hz), 7.61 (s, 1H, Ar-H), 8.09 (d, 2H, Ar-H, *J*=8.80 Hz), 9.73 (s, 1H, N=CH), 11.85 (s, 1H, NH); ^{13}C NMR (50MHz, DMSO-d_6) δ 11.60 (CH_3), 14.93 ($OCH_2\underline{CH_3}$), 56.13 (OCH_3), 64.68 ($O\underline{CH_2}CH_3$), 112.96, 114.82 (2C), 121.00, 121.06, 124.16, 132.51 (2C), 132.87, 142.76, 151.68, 163.97 (arom-C), 144.80 (triazole C_3), 151.16 (triazole C_5), 153.48 (N=CH), 164.24 (COO).

3-Ethyl-4-[3-ethoxy-4-(4-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one (3b). Yield 3.99 g (97.50%). mp. 205 ºC. IR (KBr) ν 3174 (NH), 1733, 1696 (C=O), 1605 (C=N), 1256 (COO), 847 cm^{-1} (1,4 disubstituted benzenoid ring); ^{1}H NMR (200MHz, DMSO-d_6) δ 1.22 (t, 3H, $OCH_2\underline{CH_3}$, *J*=6.80 Hz), 1.22 (t, 3H, $CH_2\underline{CH_3}$, *J*=7.20 Hz), 2.71 (q, 2H, $\underline{CH_2}CH_3$, *J*=7.42 Hz), 3.89 (s, 3H, OCH_3), 4.11 (s, 2H, $O\underline{CH_2}CH_3$, *J*=6.80 Hz), 7.13 (d, 2H, Ar-H, *J*=8.80 Hz), 7.35 (d, 1H, Ar-H, *J*=8.80 Hz), 7.48 (d, 1H, Ar-H, *J*=8.40 Hz), 7.60 (s, 1H, Ar-H), 8.10 (d, 2H, Ar-H, *J*=8.80 Hz), 9.75 (s, 1H, N=CH), 11.90 (s, 1H, NH); ^{13}C NMR (50MHz, DMSO-d_6) δ 9.91 ($CH_2\underline{CH_3}$), 14.39 ($OCH_2\underline{CH_3}$), 18.49 ($\underline{CH_2}CH_3$), 55.57 (OCH_3), 64.16 ($O\underline{CH_2}CH_3$), 112.91, 114.25(2C), 120.33, 120.63, 123.62, 131.98 (2C), 132.43, 142.28, 151.17, 163.49 (arom-C), 148.02 (triazole C_3), 150.68 (triazole C_5), 152.78 (N=CH), 163.74 (COO).

3-*n*-Propyl-4-[3-ethoxy-4-(4-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one (3c). Yield 4.07 g (96.00%). mp. 172 ºC. IR (KBr) ν 3165 (NH); 1724, 1697 (C=O), 1601 (C=N), 1254 (COO), 847 cm^{-1} (1,4 disubstituted benzenoid ring); ^{1}H NMR (200MHz, DMSO-d_6) δ 0.97 (t, 3H, $CH_2CH_2\underline{CH_3}$, *J*=7.20 Hz), 1.22 (t, 3H, $OCH_2\underline{CH_3}$, *J*=7.20 Hz), 1.71 (sext, 2H, $CH_2\underline{CH_2}CH_3$, *J*=7.20 Hz), 2.67 (t, 2H, $\underline{CH_2}CH_2CH_3$, *J*=7.20 Hz), 3.89 (s, 3H, OCH_3), 4.12 (s, 2H, $O\underline{CH_2}CH_3$, *J*=7.20 Hz), 7.13 (d, 2H, Ar-H, *J*=8.40 Hz), 7.36 (d, 1H, Ar-H, *J*=8.00 Hz), 7.49 (d, 1H, Ar-H, *J*=8.40 Hz), 7.60 (s, 1H, Ar-H), 8.09 (d, 2H, Ar-H, *J*=8.80 Hz), 9.74 (s, 1H, N=CH), 11.89 (s, 1H, NH); ^{13}C NMR (50MHz, DMSO-d_6) δ 13.45 ($CH_2CH_2\underline{CH_3}$), 14.36 ($OCH_2\underline{CH_3}$), 18.91 ($CH_2\underline{CH_2}CH_3$), 26.67 ($\underline{CH_2}CH_2CH_3$), 55.56 (OCH_3), 64.11 ($O\underline{CH_2}CH_3$), 112.91, 114.36 (2C), 120.25, 120.57, 123.64, 131.96 (2C), 132.40, 142.24, 151.56, 163.45 (arom-C), 146.88 (triazole C_3), 150.62 (triazole C_5), 152.82 (N=CH), 163.71 (COO).

THEORETICAL

The optimized molecular structures, Mulliken atomic charges, UV–Vis spectroscopic parameters, molecular electrostatic potential (MEP), vibrational frequencies, thermodynamic parameters and HOMO, LUMO energies of the compounds **3a-c** have been calculated by using DFT(B3LYP)/HF methods with 6-31G(d,p) basis set. All theoretical calculations were performed by using Gaussian 09W program and

GaussView program [28, 29]. IR absorption frequencies of analysed molecules were calculated by two methods. The veda4f program was used in defining IR data which were calculated theoretically [30].

RESULTS AND DISCUSSION

In this study, the structures of three new 3-alkyl-4-[3-ethoxy-4-(4-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-ones (**3a-c**) were carried out by using ^{1}H NMR, ^{13}C NMR and IR spectral data.

Molecular geometry

The optimized chemical structures and molecular of these compounds **3a-c** are shown in (Fig. 1). The calculated double N21=C1, N23=C3 bond lengths according to DFT/HF methods with 6-31G(d,p) basis sets of compounds **3a-c** were found as 1.30/1.27, 1.29/1.26 A^0 while the single N22-C1, N22-C2 and N20-C2 bond lengths in 1,2,4-triazol ring are calculated as 1.39/1.38, 1.42/1.38 and 1.37/1.35 A^0 respectively. The calculated double C2=O24 and C10=O27 bond lenghts were found as 1.22/1.20 and 1.21/1.18 A^0, respectively. Also the single bond lenghts of C6-O25, C10-O27, C14-O28, C7-O26, O25-O18 and O28-C17, were found as 1.37/1.35, 1.21/1.18, 1.36/1.36, 1.39/1.37, 1.44/1.42 and 1.42/1.41 A^0, respectively (Table 1). The largest C2-N22-N23 bond angles were found as 130.53/130.79, 130.44/130.73 and 130.42/130.70 ^{0} while the smallest N20-C2-N22 bond angles in 1,2,4-triazol ring were found as 101.17/102.00, 101.18/101.95 and 101.18/101.95 ^{0} for compounds **3a, 3b** and **3c**, respectively (Table 2).

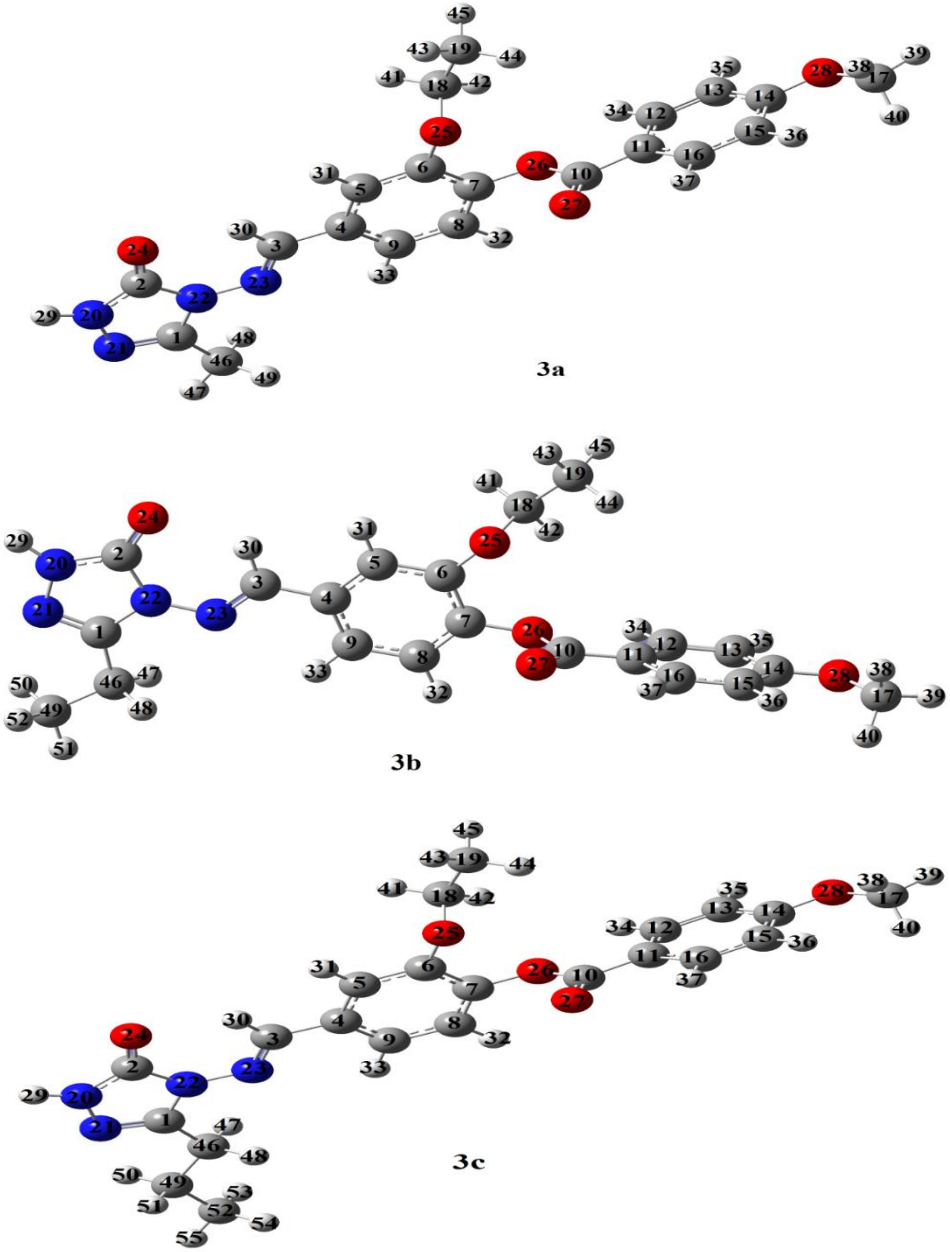

Fig. 1. Optimized molecular structure of compounds **3a-c** with DFT(B3LYP)/HF 6–31G(d,p) level

Table 1. The calculated bond lenghts of compounds **3a-c**

Bond Lenghts (A^0)	**B3LYP/HF (3a)**	**B3LYP/HF (3b)**	**B3LYP/HF (3c)**
C(1)-N(21)	1.30/1.27	1.30/1.27	1.30/1.27
C(1)-N(22)	1.39/1.38	1.39/1.38	1.39/1.38
C(1)-C(46)	1.49/1.49	1.49/1.49	1.49/1.49
N(20)-C(2)	1.37/1.35	1.37/1.35	1.37/1.35
C(2)-O(24)	1.22/1.20	1.22/1.20	1.22/1.20
C(2)-N(22)	1.42/1.38	1.42/1.38	1.42/1.38
N(20)-H(29)	1.00/0.99	1.00/0.99	1.00/0.99
N(20)-N(21)	1.38/1.37	1.38/1.37	1.38/1.37
N(22)-N(23)	1.37/1.37	1.37/1.37	1.37/1.37
N(23)-C(3)	1.29/1.26	1.29/1.26	1.29/1.26
C(3)-H(30)	1.09/1.08	1.09/1.08	1.09/1.08
C(3)-C(4)	1.47/1.48	1.47/1.48	1.47/1.48
C(4)-C(5)	1.40/1.39	1.40/1.39	1.40/1.39
C(4)-C(9)	1.41/1.39	1.41/1.39	1.41/1.39
C(5)-H(31)	1.09/1.08	1.09/1.08	1.09/1.08
C(5)-C(6)	1.39/1.38	1.39/1.38	1.39/1.38
C(6)-O(25)	1.37/1.35	1.37/1.35	1.37/1.35
O(25)-C(18)	1.44/1.42	1.44/1.42	1.44/1.42
C(18)-H(41)	1.09/1.08	1.09/1.08	1.09/1.08
C(18)-H(42)	1.09/1.08	1.09/1.08	1.09/1.08
C(18)-C(19)	1.52/1.51	1.52/1.51	1.52/1.51
C(19)-H(42)	1.09/1.08	1.09/1.08	1.09/1.08
C(19)-H(43)	1.09/1.08	1.09/1.08	1.09/1.08
C(19)-H(44)	1.09/1.08	1.09/1.08	1.09/1.08
C(6)-C(7)	1.40/1.38	1.40/1.38	1.40/1.38
C(7)-O(26)	1.39/1.37	1.39/1.37	1.39/1.37
C(7)-C(8)	1.39/1.38	1.39/1.38	1.39/1.38
C(8)-H(32)	1.08/1.07	1.08/1.07	1.08/1.07
C(8)-C(9)	1.39/1.38	1.39/1.38	1.39/1.38
C(9)-H(33)	1.08/1.07	1.08/1.07	1.08/1.07
O(26)-C(10)	1.39/1.34	1.39/1.34	1.39/1.34
C(10)-O(27)	1.21/1.18	1.21/1.18	1.21/1.18
C(10)-C(11)	1.48/1.48	1.48/1.48	1.48/1.48
C(11)-C(12)	1.40/1.39	1.40/1.39	1.40/1.39
C(11)-C(16)	1.40/1.39	1.40/1.39	1.40/1.39
C(12)-H(34)	1.08/1.07	1.08/1.07	1.08/1.07
C(12)-C(13)	1.39/1.38	1.39/1.38	1.39/1.38
C(13)-C(14)	1.41/1.38	1.41/1.38	1.41/1.38
C(13)-H(35)	1.09/1.07	1.09/1.07	1.09/1.07
C(14)-O(28)	1.36/1.36	1.36/1.36	1.36/1.36
C(14)-C(15)	1.40/1.39	1.40/1.39	1.40/1.39
O(28)-C(17)	1.42/1.41	1.42/1.41	1.42/1.41
C(17)-H(38)	1.09/1.09	1.09/1.08	1.09/1.08
C(17)-H(39)	1.09/1.09	1.09/1.08	1.09/1.08
C(17)-H(40)	1.09/1.09	1.09/1.08	1.09/1.08
C(15)-H(36)	1.08/1.07	1.08/1.07	1.08/1.07
C(15)-C(16)	1.39/1.38	1.39/1.38	1.39/1.38
C(16)-H(37)	1.08/1.07	1.08/1.07	1.08/1.07
C(46)-H(47)	1.09/1.08	1.09/1.08	1.09/1.08
C(46)-H(48)	1.09/1.08	1.09/1.08	1.09/1.08
C(46)-H(49)	1.09/1.08	-	-
C(46)-C(49)		1.53/1.53	1.53/1.53
C(49)-H(50)		1.09/1.08	1.09/1.08
C(49)-H(51)		1.09/1.08	1.09/1.08
C(49)-H(52)		1.09/1.08	-
C(49)-C(52)			1.53/1.53
C(52)-H(53)			1.09/1.09
C(52)-H(54)			1.09/1.09
C(52)-H(55)			1.09/1.09

Table 2. The calculated bond angles of compounds **3a-c**

Bond Angles (^{0})	**B3LYP/HF (3a)**	**B3LYP/HF (3b)**	**B3LYP/HF (3c)**
C(1)-N(21)-N(20)	104.48/104.96	104.59/105.12	104.60/105.03
C(1)-N(22)-N(23)	121.10/121.05	121.14/121.08	121.16/121.10
C(1)-N(22)-C(2)	108.37/108.12	108.42/108.18	108.43/108.19
N(21)-C(1)-N(22)	111.46/111.32	111.33/111.16	111.30/111.13
N(21)-N(20)-H(29)	120.43/120.62	120.46/121.02	120.47/121.01
N(21)-N(20)-C(2)	114.52/113.56	114.49/113.70	114.49/113.68
N(21)-C(1)-C(46)	125.16/125.45	125.66/126.06	125.72/126.18
H(29)-N(20)-C(2)	125.05/124.81	125.05/125.29	125.04/125.30
N(20)-C(2)-N(22)	101.17/102.00	101.18/101.95	101.18/101.95
N(20)-C(2)-O(24)	129.93/129.37	129.89/129.36	129.87/129.36
O(24)-C(2)-N(22)	128.90/128.63	128.93/128.69	128.94/128.69
C(2)-N(22)-N(23)	130.53/130.79	130.44/130.73	130.42/130.70
N(22)-N(23)-C(3)	118.73/119.69	118.77/119.81	118.75/119.82
N(23)-C(3)-H(30)	122.05/122.32	122.03/122.34	122.03/122.34
N(23)-C(3)-C(4)	120.04/120.30	120.05/120.28	120.08/120.27
H(30)-C(3)-C(4)	117.92/117.39	117.92/117.39	117.90/117.39
C(3)-C(4)-C(5)	118.32/118.15	118.31/118.16	118.29/118.17
C(3)-C(4)-C(9)	122.55/122.47	122.57/122.49	122.59/122.48
C(4)-C(5)-H(31)	120.71/120.71	120.70/120.84	120.71/120.84
C(4)-C(5)-C(6)	121.01/120.81	121.01/120.86	121.00/120.86
H(31)-C(5)-C(6)	118.28/118.70	118.29/118.30	118.29/118.30
C(5)-C(6)-O(25)	120.22/121.78	120.25/120.71	120.28/120.71
C(5)-C(6)-C(7)	118.88/118.96	118.89/118.95	118.90/118.95
O(25)-C(6)-C(7)	120.86/119.75	120.82/120.32	120.78/120.32
C(6)-O(25)-C(18)	115.16/116.21	115.11/116.05	115.10/116.05
O(25)-C(18)-H(41)	109.68/109.56	109.68/109.58	109.68/109.58
O(25)-C(18)-H(42)	109.20/109.45	109.20/109.37	109.20/109.37
O(25)-C(18)-C(19)	107.69/107.89	107.69/107.83	107.69/107.83
H(41)-C(18)-H(42)	108.00/107.93	107.98/108.01	107.96/108.01
H(41)-C(18)-C(19)	111.12/111.06	111.11/110.10	111.11/111.09
H(42)-C(18)-C(19)	111.16/110.94	111.17/111.05	111.19/111.05
C(18)-C(19)-H(43)	110.62/110.45	110.63/110.51	110.63/110.51
C(18)-C(19)-C(44)	110.11/110.18	110.12/110.15	110.54/110.15
C(18)-C(19)-C(45)	110.56/110.42	110.55/110.41	110.13/110.41
H(43)-C(19)-H(44)	108.56/108.60	108.55/108.64	108.37/108.64
H(43)-C(19)-H(45)	108.37/108.41	108.37/108.43	108.55/108.43
H(44)-C(19)-H(45)	108.56/108.74	108.56/108.65	108.57/108.65
C(6)-C(7)-O(26)	119.72/119.27	119.72/119.34	119.68/119.34
C(6)-C(7)-C(8)	120.75/120.90	120.75/120.86	120.75/120.86
C(7)-C(8)-H(32)	118.72/118.97	118.72/118.94	118.72/118.94
C(7)-C(8)-C(9)	120.05/119.93	120.04/119.97	120.04/119.97
H(32)-C(8)-C(9)	121.24/121.10	121.24/121.09	121.24/121.09
C(8)-C(9)-H(33)	120.62/120.32	120.62/120.31	120.62/120.32
C(8)-C(9)-C(4)	120.18/120.02	120.18/120.01	120.19/120.01
H(33)-C(9)-C(4)	119.20/119.67	119.20/119.68	119.19/119.67
C(9)-C(4)-C(5)	119.13/119.38	119.12/119.35	119.12/119.35
C(7)-O(26)-C(10)	117.45/118.66	117.37/118.65	117.30/118.65
O(26)-C(10)-O(27)	122.81/122.96	122.80/122.86	122.78/122.86
O(26)-C(10)-C(11)	111.47/112.29	111.50/112.16	111.54/112.16
O(27)-C(10)-C(11)	125.72/124.75	125.69/124.98	125.67/125.98
C(10)-C(11)-C(16)	117.82/117.86	117.79/118.10	117.76/118.09
C(10)-C(11)-C(12)	123.17/122.57	123.20/122.96	123.23/122.96
C(11)-C(12)-H(34)	119.63/119.89	119.62/119.85	118.47/119.85
C(11)-C(12)-C(13)	120.42/120.21	120.42/120.49	121.09/120.49
H(34)-C(12)-C(13)	119.95/119.90	119.96/119.66	120.44/119.66
C(12)-C(13)-C(14)	120.18/119.74	120.18/120.12	119.43/120.12
C(13)-C(14)-O(28)	115.55/119.54	115.56/115.67	115.56/115.67

C(14)-O(28)-C(17)	118.61/120.81	118.60/120.17	118.59/120.17
O(28)-C(17)-H(38)	111.55/111.19	111.54/111.37	111.54/111.37
O(28)-C(17)-H(39)	105.88/106.77	105.88/106.13	105.88/106.13
O(28)-C(17)-H(40)	111.52/110.98	111.51/111.37	111.51/111.37
H(38)-C(17)-H(39)	109.27/109.01	109.28/109.22	109.30/109.22
H(38)-C(17)-H(40)	109.26/109.40	109.26/109.46	109.28/109.46
H(39)-C(18)-H(40)	109.29/109.44	109.29/109.22	109.30/109.21
C(13)-C(14)-C(15)	119.87/119.58	119.43/119.92	119.87/119.34
C(14)-C(15)-H(36)	121.04/119.38	121.03/121.30	121.03/121.30
C(14)-C(15)-C(16)	119.43/119.58	119.43/119.34	119.43/119.34
H(36)-C(15)-C(16)	119.53/121.04	119.53/119.36	119.54/119.36
C(15)-C(16)-H(37)	120.43/120.63	120.44/119.95	120.44/119.95
H(37)-C(16)-C(11)	118.49/118.96	118.48/118.87	118.47/118.87
C(15)-C(16)-C(11)	121.08/120.41	121.09/121.18	121.09/121.18
C(16)-C(11)-C(12)	119.02/119.58	119.01/118.94	119.01/118.94
C(1)-C(46)-H(47)	110.98/110.54	108.34/108.08	108.48/108.08
C(1)-C(46)-H(48)	110.96/110.51	108.33/108.07	108.44/108.08
C(1)-C(46)-H(49)	108.66/108.56	-	-
H(47)-C(46)-H(49)	109.45/109.79	-	-
H(48)-C(46)-H(49)	109.43/109.66	-	-
H(47)-C(46)-H(48)	107.34/107.68	105.22/105.94	105.16/105.87
C(1)-C(46)-C(49)	-	112.98/112.88	113.36/113.24
C(46)-C(49)-H(50)	-	111.15/111.21	109.22/109.39
C(46)-C(49)-H(51)	-	111.19/111.22	109.19/109.39
C(46)-C(49)-H(52)	-	109.10/109.66	-
H(50)-C(49)-H(52)	-	108.48/108.42	-
H(51)-C(49)-H(52)	-	108.45/108.43	-
H(50)-C(49)-H(51)	-	107.51/107.81	105.91/106.31
C(46)-C(49)-C(52)	-	-	112.06/111.74
H(50)-C(49)-C(52)	-	-	110.14/110.81
H(51)-C(49)-C(52)	-	-	110.14/110.81
C(49)-C(52)-H(53)	-	-	111.04/111.37
C(49)-C(52)-H(54)	-	-	111.39/111.32
C(49)-C(52)-H(55)	-	-	111.40/111.52
H(53)-C(52)-H(54)	-	-	107.54/107.74
H(53)-C(52)-H(55)	-	-	107.64/107.69
H(54)-C(52)-H(55)	-	-	107.54/107.74

Atomic charges and dipole moments

The electronegative N20, N21, N22, N23, O24, O25, O26, O27, O28 atoms have negative atomic charge values. The C1, C2, C3, C6, C7, C10, C14, C18 atoms surrounded with electronegative atoms have positive atomic charge values for compounds **3a, 3b** and **3c**. The Mulliken atomic charges of these atoms given in Table **3**. The C1 atom which is surrounded with two electronegative atoms (N, N), C2 atom surrrounded with three electronegative atoms (N, N, O), C10 atom surrrounded with two electronegative atoms (O, O), C3 atom surrrounded with one electronegative atom (N) and C6, C7, C14 and C18 atoms surrrounded with one electronegative atom (O) have positive atomic charge values. The C1 atom which is surrounded with two electronegative atoms (N, N), C2 atom surrrounded with three electronegative atoms (N, N, O) have the highest positive atomic charge values. All hydrogen atoms of these compounds **3a, 3b** and **3c** have positive atomic charge values. Total energy values and dipole moments of above mentioned compounds (**3a-c**) were calculateted by using B3LYP/HF 6-31G(d,p) methods. The calculated dipole moment and energy values are given in Table **4** and **5.**

Table 3. Mulliken atomic charges of compounds **3a-c**

Comp. 3a Atoms	DFT/HF	Comp. 3b Atoms	DFT/HF	Comp. 3c Atoms	DFT/HF
C1	0.53/0.50	**C1**	0.54/0.61	**C1**	0.54/0.61
C2	0.82/0.88	**C2**	0.82/1.05	**C2**	0.82/1.05
C3	0.12/0.18	**C3**	0.12/0.18	**C3**	0.12/0.18
C4	0.09/-0.08	**C4**	0.08/-0.08	**C4**	0.09/-0.08
C5	-0.17/-0.17	**C5**	-0.17/-0.17	**C5**	-0.17/-0.17
C6	0.33/0.36	**C6**	0.33/0.38	**C6**	0.33/0.38
C7	0.32/0.36	**C7**	0.32/0.36	**C7**	0.32/0.36
C8	-0.11/-0.12	**C8**	-0.11/-0.15	**C8**	-0.11/-0.15
C9	-0.11/-0.14	**C9**	-0.11/-0.13	**C9**	-0.11/-0.13
C10	0.60/0.86	**C10**	0.60/0.86	**C10**	0.60/0.86
C11	0.01/-0.18	**C11**	0.01/-0.23	**C11**	0.01/-0.23
C12	-0.10/-0.11	**C12**	-0.10/-0.09	**C12**	-0.10/-0.09
C13	-0.12/-0.18	**C13**	-0.12/-0.20	**C13**	-0.12/-0.20
C14	0.36/0.37	**C14**	0.36/0.44	**C14**	0.36/0.44
C15	-0.14/-0.18	**C15**	-0.14/-0.24	**C15**	-0.14/-0.24
C16	-0.11/-0.10	**C16**	-0.11/-0.09	**C16**	-0.11/-0.09
C17	-0.08/-0.02	**C17**	-0.08/-0.04	**C17**	-0.08/-0.04
C18	0.06/0.06	**C18**	0.06/0.11	**C18**	0.06/0.11
C19	-0.34/-0.34	**C19**	-0.33/-0.35	**C19**	-0.34/-0.35
N20	-0.44/-0.46	**N20**	-0.43/-0.56	**N20**	-0.43/-0.56
N21	-0.36/-0.37	**N21**	-0.35/-0.36	**N21**	-0.35/-0.36
N22	-0.41/-0.48	**N22**	-0.42/-0.63	**N22**	-0.43/-0.64
N23	-0.33/-0.38	**N23**	-0.33/-0.33	**N23**	-0.32/-0.33
O24	-0.54/-0.61	**O24**	-0.54/-0.66	**O24**	-0.54/-0.66
O25	-0.54/-0.69	**O25**	-0.54/-0.69	**O25**	-0.54/-0.69
O26	-0.57/-0.77	**O26**	-0.57/-0.72	**O26**	-0.57/-0.72
O27	-0.47/-0.58	**O27**	-0.47/-0.56	**O27**	-0.47/-0.56
O28	-0.51/-0.68	**O28**	-0.51/-0.66	**O28**	-0.51/-0.66
H29	0.29/0.33	**H29**	0.29/034	**H29**	0.29/0.34
H30	0.16/0.25	**H30**	0.16/0.23	**H30**	0.16/0.23
H31	0.11/0.19	**H31**	0.11/0.18	**H31**	0.11/0.18
H32	0.10/0.19	**H32**	0.10/0.18	**H32**	0.10/0.18
H33	0.11/0.18	**H33**	0.11/0.18	**H33**	0.11/0.18
H34	0.11/0.19	**H34**	0.11/0.18	**H34**	0.11/0.18
H35	0.10/0.18	**H35**	0.11/0.17	**H35**	0.10/0.19
H36	0.10/0.18	**H36**	0.10/0.16	**H36**	0.10/0.17
H37	0.12/0.21	**H37**	0.12/0.20	**H37**	0.12/0.20
H38	0.12/0.11	**H38**	0.12/0.12	**H38**	0.12/0.20
H39	0.13/0.14	**H39**	0.13/0.15	**H39**	0.13/0.15
H40	0.12/0.11	**H40**	0.12/0.12	**H40**	0.12/0.12
H41	0.09/0.10	**H41**	0.09/0.11	**H41**	0.09/0.10
H42	0.10/0.10	**H42**	0.10/0.11	**H42**	0.10/0.11
H43	0.13/0.13	**H43**	0.13/0.14	**H43**	0.13/0.14
H44	0.11/0.12	**H44**	0.11/0.13	**H44**	0.11/0.11
H45	0.12/0.10	**H45**	0.12/0.11	**H45**	0.12/0.13
C46	-0.36/-0.35	**C46**	-0.23/-0.25	**C46**	-0.22/-0.24
H47	014/0.17	**H47**	0.13/0.16	**H47**	0.13/0.15
H48	0.14/0.16	**H48**	0.13/0.16	**H48**	0.13/0.15
H49	0.14/0.16	**C49**	-0.32/-0.34	**C49**	-0.18/-0.22
		H50	0.12/0.14	**H50**	0.11/0.13
		H51	0.10/0.12	**H51**	0.10/0.13
		H52	0.13/0.14	**C52**	-0.32/-0.34
				H43	0.10/0.11
				H44	0.10/0.11
				H45	0.11/0.12

Table 4. The calculated dipole moment values of compounds **3a-c**

	Dipole Moment	μ_x	μ_y	μ_z	μ_{Toplam}
3a	**B3LYP**	4.2668	-1.0725	-1.9183	4.4779
	HF	2.8429	0.5341	-2.4618	3.7984
3b	**B3LYP**	4.0357	-1.4042	-1.8976	4.6754
	HF	3.7971	-1.5293	-2.1154	4.6078
3c	**B3LYP**	3.8611	-1.7072	-1.8355	4.6035
	HF	3.6058	-1.8493	-2.0616	4.5466

Table 5. The total energy of the compounds **3a-c**

	Energy	**B3LYP**	**HF**
3a	**(a.u.)**	-1369.30	-1361.12
3b	**(a.u.)**	-1408.61	-1400.17
3c	**(a.u.)**	-1447.93	-1439.20

Vibrational frequencies

3-(methyl/ethyl/*n*-propyl)-4-[3-ethoxy-4-(4-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-ones (**3a-c**) have 49, 52 and 55 atoms. The vibrational numbers of these molecules **3a-c** are 141, 150 and 159. The observed and calculated vibrational frequencies for compund **3a, 3b** and **3c** are summarized (Table 6) (Fig. 2).

Table 6. The experimental and calculated frequencies values of compounds **3a-c**

Assignment	**Experimental**			**Scaled B3LYP**			**Scaled HF**		
	3a	**3b**	**3c**	**3a**	**3b**	**3c**	**3a**	**3b**	**3c**
ν NH	3173	3174	3166	3557	3557	3557	3552	3557	3557
ν =CH	3065	3067	3072	3044	3053	3053	3024	3024	3024
ν C=O	1730	1733	1724	1755	1755	1755	1878	1808	1808
ν C=O	1697	1696	1697	1753	1753	1752	1855	1773	1773
ν C=C	1602	1605	1602	1601	1601	1601	1714	1682	1681
ν C=N	1578	1594	1578	1613	1611	1611	1774	1714	1714
δ COO	1256	1256	1254	1252	1251	1251	1271	1270	1262

ν, stretching; δ, bending; δ_s, scissoring; ρ, rocking; γ, out-of-plane bending; τ, torsion

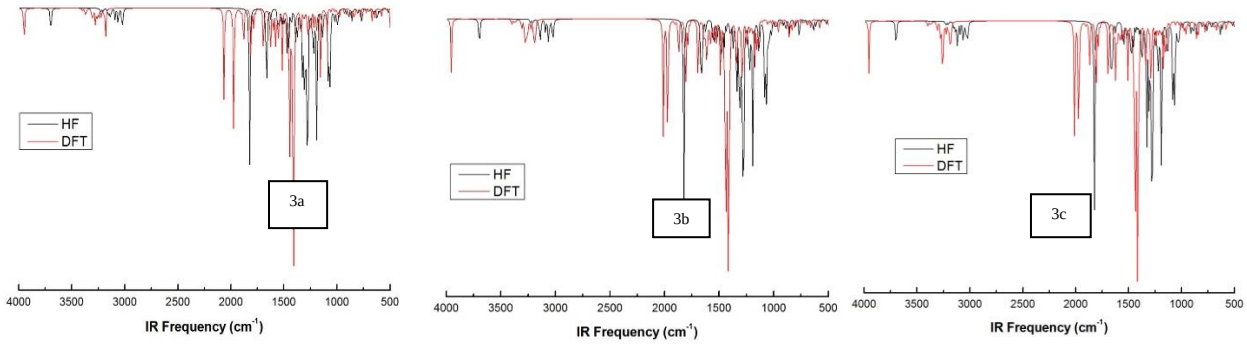

Fig. 2. IR spectrum simulated DFT/HF 6-31G(d,p) level of compounds **3a-c**

^{1}H-^{13}C-NMR chemical shifts and regression analyses

The ^{1}H-^{13}C NMR chemical shifts in gase phase and in DMSO solvent of the title compounds **3a-c** have been calculated by using the DFT(B3LYP/HF methods with 6-31G(d,p) basis set. The R^2 values of compounds **3a-c** were evaluated and ^{1}H and ^{13}C NMR chemical shift values of the compounds **3a-c** were plotted graphs. Experimental and theoretical between ^{1}H-,^{13}C-NMR chemical shifts ratios of compounds **3a-c** were observed a linear correlation except for NH proton by R^2 because N-H proton of triazole ring (namely 4,5-dihydro-1*H*-1,2,4-triazol-5-one) was displayed the acidic character. The calculated ^{1}H-,^{13}C- NMR chemical shifts values for the mentioned compounds **3a-c** are best agreement with the experimental values (Fig. 3).

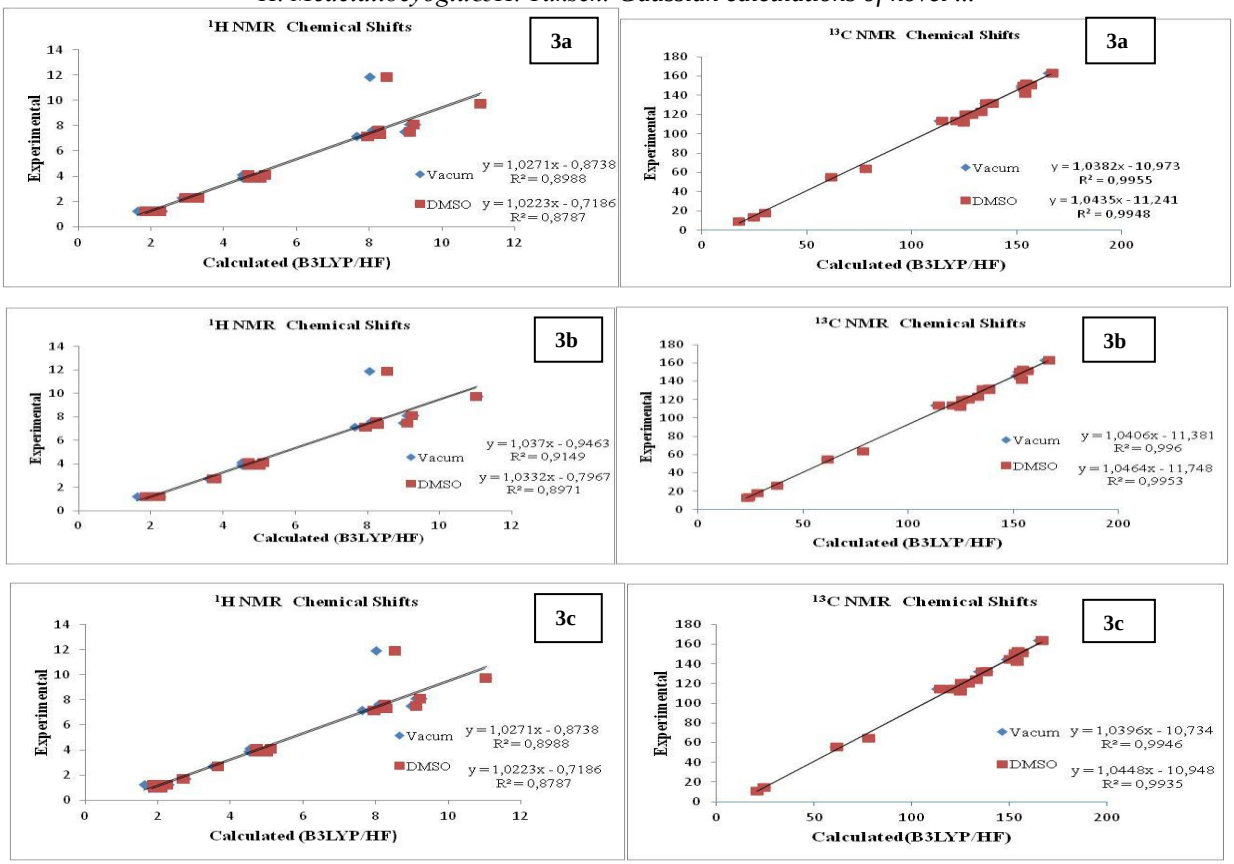

Fig. 3. The correlation graphics for ^{13}C-NMR/^{13}C-NMR (DMSO), ^{1}H-NMR/^{1}H-NMR (DMSO), chemical shifts of compounds **3a-c**

UV-vis. spectroscopy, molecular electrostatic potential (MEP) and HOMO-LUMO analyses

The oscillator strengths (*f*), absorption wavelengths (λ) and excitation energies of UV–Vis electron absorption spectroscopy of the title molecules **3a-c** have been calculated in ethanol by using DFT(B3LYP)/HF methods with 6-31G(d,p) basis set that presented in Fig. 4 and Table 6. Futhermore, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been simulated for compounds **3a-c** have been determined. In our study, HOMO and LUMO energies and their 3D plots of the compounds **3a-c** are shown in Fig. 5. The molecular electrostatic potential (MEP) of these compounds **3a-c** have been performed (Fig. 6).

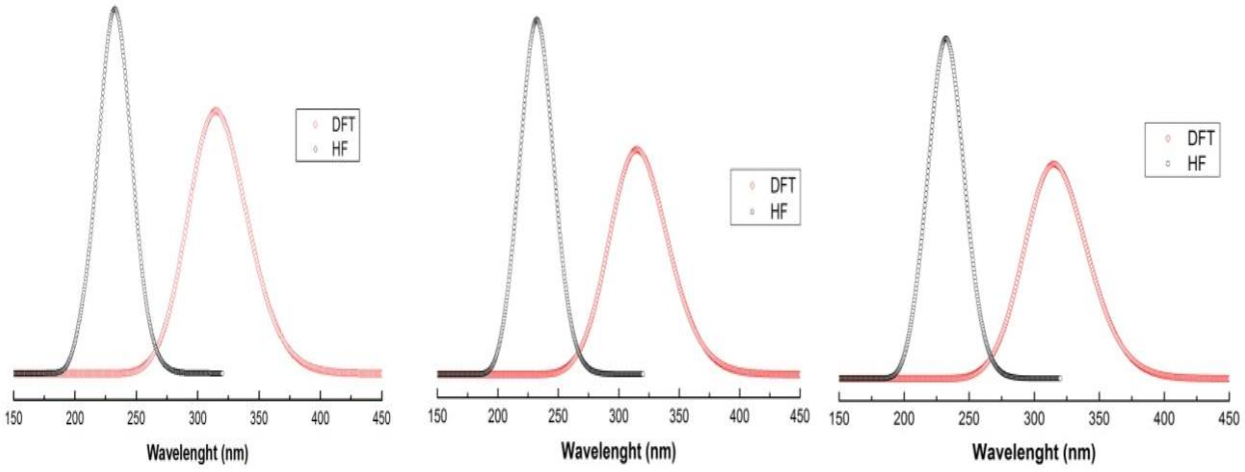

Fig. 4. UV-Visible spectra simulated with DFT/B3LYP/6-31G(d,p) and HF /6-31G(d,p) levels of compounds **3a-c.**

Table 6. The calculated absorption wavelength (λ), excitation energies and oscillator strengths (*f*) of compounds **3a-c**

Comp.	λ (nm)	Excitation energy (eV)	*f* (oscillator strength)
3a	315.17/233.52	3.9240/5.3095	0.5804/0.8013
	287.23/213.28	4.3165/5.8131	0.0353/0.0718
	282.90/213.03	4.3826/5.8201	0.0309/0.0936
3b	316.25/233.93	3.9205/5.3001	0.5772/0.8695
	286.97/216.59	4.3204/5.7243	0.0389/0.2054
	283.15/213.05	4.3788/5.7373	0.086/0.0184
3c	316.37/233.94	3.9190/5.2999	0.5738/0.8679
	286.93/216.58	4.3211/5.7245	0.0391/0.2059
	283.13/213.04	4.3791/5.8197	0.0279/0.0185

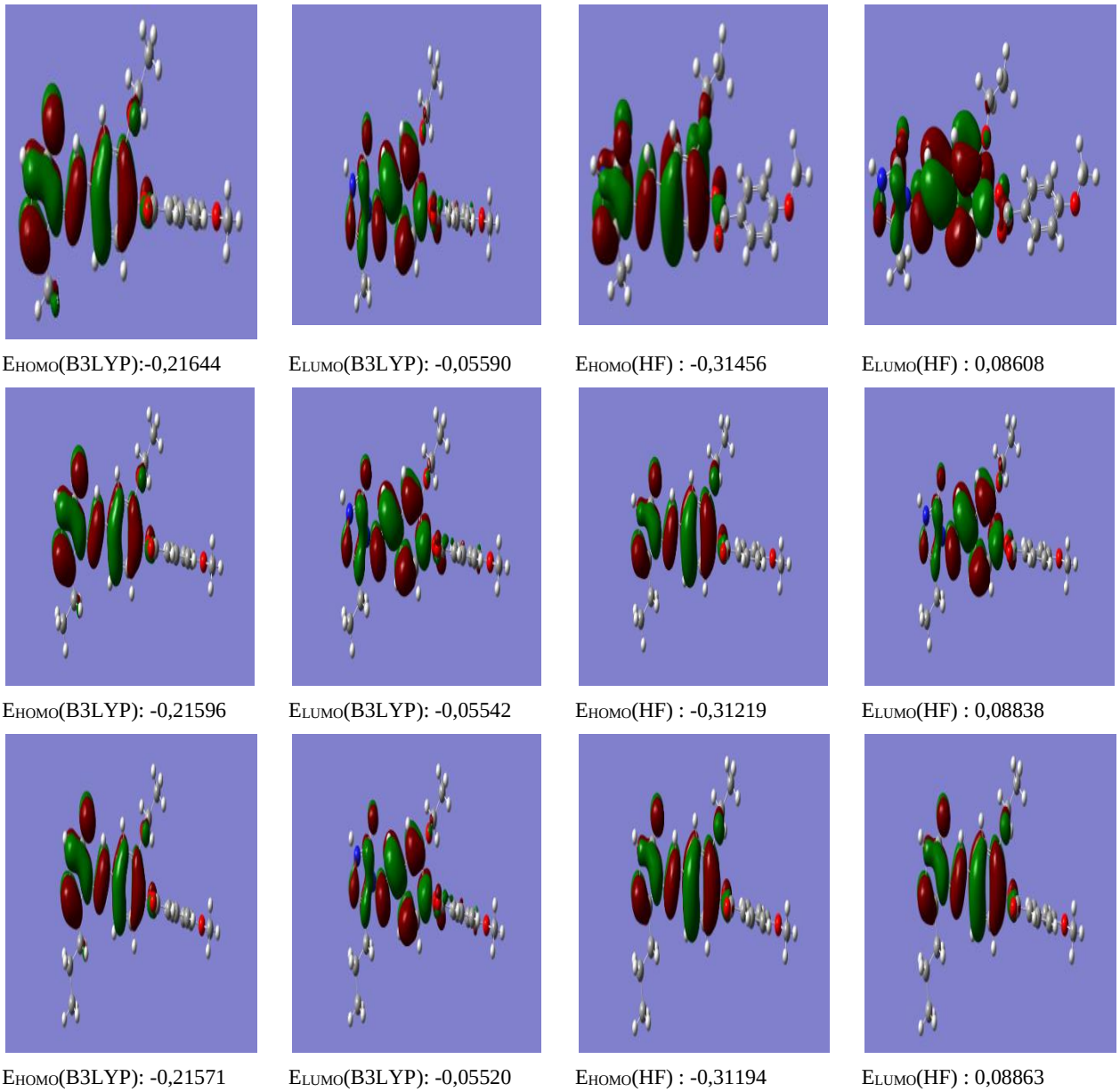

Fig. 5. 3D plots of HOMO and LUMO energies (Hatree) of compounds **3a-c** at the B3LYP/HF 6-31G(d,p) level

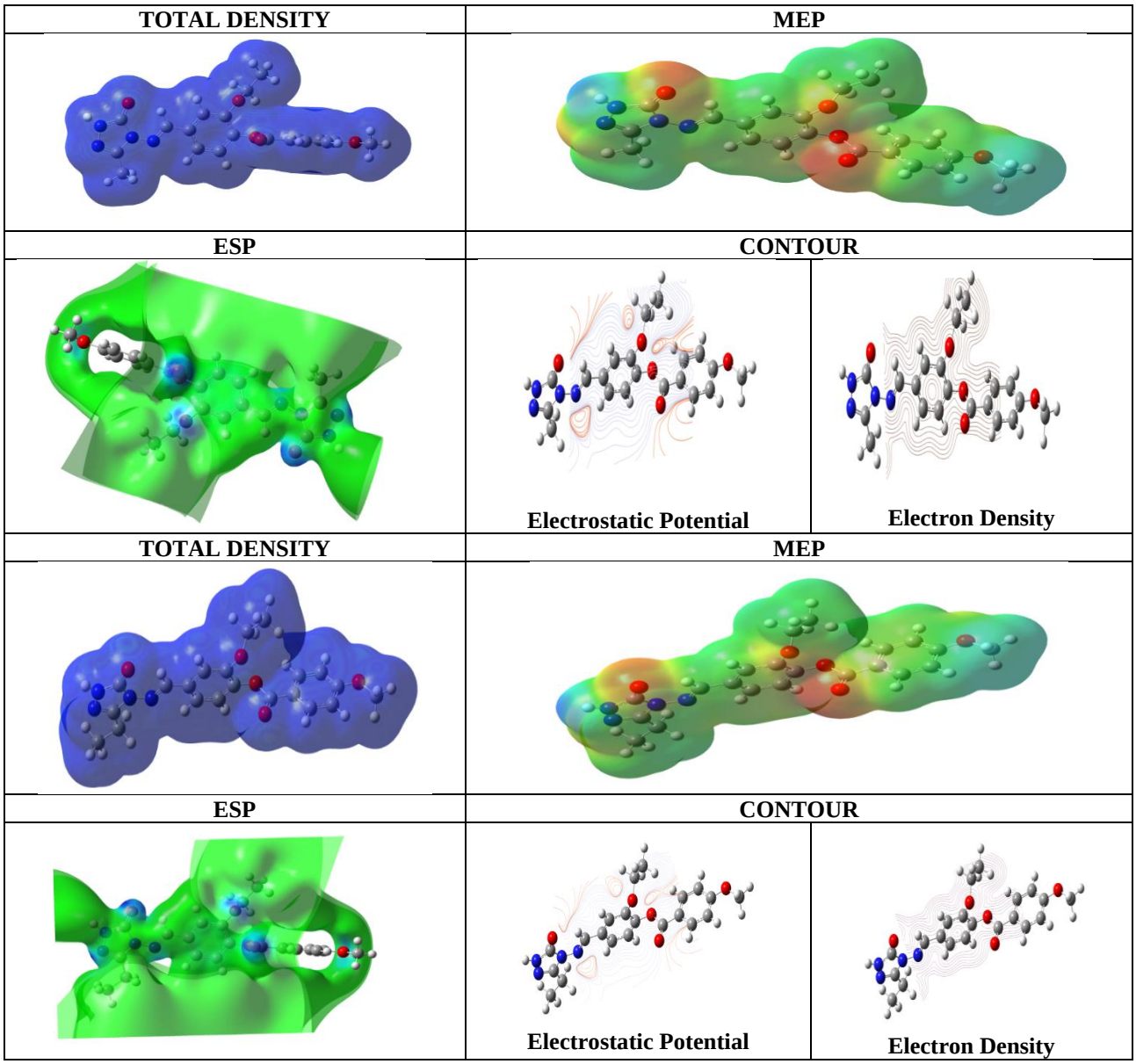

Fig. 6. The calculated molecular surfaces for compounds **3a-c**

CONCLUSION

The molecular structure, molecular electrostatic potential (MEP), vibrational wavenumbers, HOMO-LUMO, Mulliken atomic charges, electronic absorption maximum wavelenghts, and thermodynamic parameters of the synthesized new 3-(methyl/ethyl/*n*-propyl)-4-[3-ethoxy-4-(4-methoxy-benzoxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-ones (**3a-c**) have been calculated by using DFT(B3LYP)/HF 6-31G(d,p) levels. The theoretical spectral values were seen as compatible with experimental values.

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