J Incl Phenom Macrocycl Chem (2010) 67:325–334
DOI 10.1007/s10847-009-9714-7

ORIGINAL ARTICLE

The synthesis of some new imidazole and triazole derivatives: crystal Structure and DFT-TDDFT investigation on electronic structure

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Received: 22 July 2009 / Accepted: 19 November 2009 / Published online: 10 December 2009

Abstract A series of new N′-3-(1H-imidazol-1-yl)propylcarbamoyl-4-halogenebenzo hydrazonate **(3a–b)** were obtained by reaction Ethyl 2-((4-halogene phenyl) (ethoxy) methylene) hydrazinecarboxylate (1) and *N*-(3-aminopropyl)imidazole **(2)** at 120–140 °C. Compounds **(4a–b)** were obtained by the reaction compound **1** and *N*-(3-aminopropyl)imidazole **(2)** at 160–180 °C. The structures of compounds **3,4** have been inferred through UV–Vis, IR, $^{1}H/^{13}C$ NMR, mass spectrometry, elemental analyses, and X-ray crystallography. DFT level 6-31G (d) calculations provided structural information. The electronic structure of compound **3a** has been studied by DFT level 6-31G (d) calculations using the X-ray data. The results are accordance with X-ray data.

Keywords 1, 2, 4-triazoles · Imidazole · DFT calculations · UV–Vis · X-ray crystallography

Introduction

The development of resistance to current antibacterial therapy continues to search for more effective agents. In addition, primary and opportunistic fungal infections continue to increase rapidly because of the increased number of immuno compromised patients (AIDS, cancer and transplants). Several reviews have appeared illustrating the problems encountered by today's infectious disease clinicians [1–3]. As known, not only biochemical similarity of the humancell and fungi forms a handicap for selective activity, but also the easily gained resistance is the main problem encountered in developing safe and efficient antifungals. The azole antifungals may be regarded as a new class providing truly effectivedrugs those are reported to inhibit fungi by blocking the biosynthesis of certain fungal lipids, especially ergosterol incell membranes, and by additional mechanisms [4, 5]. The imidazole antifungals, such as clotrimazole, miconazole, and ketoconazole, showed good topical activity, but were only oflimited value for systematic administration. Triazole derivatives are the other major chemical group of antifungal azole derivatives. The most frequently used triazoles are fluconazole and itraconazole. They posses a broad spectrum of antifungal activity and reduced toxicity when compared with the imidazole antifungals [6–11].Triazoles are among the various heterocycles that have received the mostattention during the last two decades as potential antimicrobial agents [12–29]. Substitutions including thio [30–32], alkyl thio and alkenylthio [33–35] derivatives have been carried out primarily at the 3-position of the 1,2,4-triazole ring, as potential antimicrobial agents those will overcome the above mentioned resistance problems.

Recently, the interest in triazol and imidazol heterocyclic system has widened as it is a precursor to a class of compounds called 'room temperature ionic liquids' (For reviews, see [36–40]). Ionic liquids have high ion content, high ionic conductivity, low viscosity, nonvolatility, flame resistance, and other surprising properties as a polar liquid,

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and have therefore been investigated as novel ion conductive matrix [41, 42], as well as reaction solvent [39] and a 'green solvent' [43].

Ionic liquids, of which imidazolium salts are most widely used, have gained initial notice of synthetic chemists as enviromentally friendly organic solvents, and continue to hold their attention as reaction catalysts or promoters (Recent examples [44–49]). Additionally, they have the ability to dissolve an enormous range of inorganic, organic and polymeric materials at very high concentrations, are noncorrosive, and have low viscosities and no significant vapor pressures [50, 51].

In view of these facts, the aim of the present study is to synthesize the compounds containing imidazol and triazole ring which are fundamental compounds in the preparation of ionic liquids and used as a antimicrobial substance.

Experimental

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian XL-200 NMR spectrophotometer in (DMSO-d_6). IR spectra were recorded on a Perkin-Elmer Spectrum one FT-IR spectrometer in KBr pellets. The MS spectra were measured with an Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer with EtOH as solvent. The experiment was performed in the positive ion mode. Elemental analyses were performed on a Hewlett-Packard 185 CHN analyzer. UV/Vis spectra were recorded by means of a Unicam UV2-100 spectrophotometer. M.p. were measured on an electrothermal apparatus and are uncorrected. The compound **(1)** was prepared as described by Ikizler and Sancak [52].

Synthesis of compound 3a–b

Ethyl 2-((4-halogenophenyl)(ethoxy)methylene)hydrazinecarboxylate **(1)** (10 mmol) together with *N*-(3-aminopropyl)imidazole **(2)** (1.25 g, 10 mmol) were heated without solvent in a sealed tube for 2 h at 120–140 °C. Then, the mixture was cooled to r.t. and a solid formed. The crude product was recrystallized using acetone/petroleum ether (1:2) to afford the desired compound.

N′-3-(1H-imidazol-1-yl)propylcarbamoyl-4-chlorobenzohydrazonate (3a)

Yield: 250 mg (75%). Colorless crystals. M.p. 139–140 °C. IR (KBr, cm^{-1}): 3156 (NH), 1616 (C=N); 1666 (C=O). ^{1}H-NMR (200 MHz, $DMSO_{d6}$): 1.32 (t, 3H, CH_3); 1.87–1.93 (m, 2H, NH -CH_2-CH_2); 3.12 (q, 2H, OCH_2); 3.63 (t, 2H, CH_2-N); 3.92–3.98 (m, 2H, NH -CH_2); 6.89 (s, 1H, imid.H); 7.12 (t, 1H, NH); 7.21–7.78 (m, 6H, imid.H + arom.H); 9.43 (s, 1H, NH-C=O). ^{13}C NMR (200 MHz, $DMSO_{d6}$): 14.91 (CH_3); 31.33 ($NHCH_2$-CH_2); 36.38 (CH_2-N); 43.73 (NH-CH_2); 66.02 (OCH_2); arom. C [119.13 (CH), 119.78 (CH), 125.93 (C), 134.87 (C)]; imid. C [128.16 (CH), 128.98 (CH), 129.55 (CH)]; 145.24 (C=N); 155.39 (C=O). Anal. calc. for $C_{16}H_{20}ClN_5O_2$: C, 54.94; H, 5.76; N, 20.02. Found: C, 54.90; H, 5.81; N, 20.06. EI -MS: 350.21 $[M]^+$. UV–vis (Me_2CO, λmax, nm) (10^{-4} logε/dm^3 mol^{-1} cm^{-1}): 252(1704), 274 (1754), 287(9570), 299 (7690), 319 (10280), 334 (2220).

N′-3-(1H-imidazol-1-yl)propylcarbamoyl-4-fluorobenzohydrazonate (3b)

Yield: 285 mg (78%). Colorless crystals. M.p. 105–106 °C. IR (KBr, cm^{-1}): 3162 (NH), 1621 (C=N); 1664 (C=O). ^{1}H-NMR (200 MHz, $DMSO_{d6}$): 1.28 (t, 3H, CH_3); 1.89–1.93 (m, 2H, $NHCH_2$-CH_2); 3.10 (t, 2H, OCH_2); 3.88–4.01 (m, 4H, NH-CH_2+CH_2-N); 6.88 (s, 1H, imid.H); 7.15 (t, 1H, NH); 7.21 (s, 1H, imid.H); 7.23–7.32 (m, 3H, imid.H+arom.H); 7.61–7.66 (m, 3H, arom.H); 9.32 (s, 1H, NH-C=O). ^{13}C NMR (200 MHz, $DMSO_{d6}$): 14.90 (CH_3); 31.57 ($NHCH_2$-CH_2); 36.36 (CH_2-N); 43.69 (NH-CH_2); 65.91 (OCH_2); arom. C [115.21 (CH), 115.64 (CH), 119.27 (C), 137.20 (C)]; imid. C [128.20 (CH), 129.09 (CH), 129.25 (CH)]; 145.32 (C=N); 155.43 (C=O). Anal. calc. for $C_{16}H_{20}FN_5O_2$: C, 57.65; H, 6.05; N, 21.01. Found: C, 57.61; H, 6.09; N, 21.08. EI -MS: 334.01 $[M]^+$.

Synthesis of compound 4a–b

Ethyl 2-((4-chlorophenyl)(ethoxy)methylene]hydrazinecarboxylate **(1)** (10 mmol) together with *N*-(3-aminopropyl) imidazole **(2)** (1.25 g, 10 mmol) were heated without solvent in a sealed tube for 2 h at 160–180 °C. Then, the mixture was cooled to r.t. and a solid formed. The crude product was recrystallized using acetone/petroleum ether (1:2) to afford the desired compound.

4-(3-(1H-imidazol-1-yl)propyl)-5-(4-chlorophenyl)-2H-1,2,4-triazol-3(4H)-one (4a)

Yield: 221 mg (72%). Colorless crystals. M.p. 194–195°C. IR (KBr, cm^{-1}): 3116 (NH), 1606 (C=N); 1712 (C=O). ^{1}H-NMR (200 MHz, $DMSO_{d6}$): 1.91–2.09 (m, 2H, $NHCH_2$-CH_2); 3.66 (t, 2H, NCH_2); 3.98 (t, 2H, $CONCH_2$); 6.88 (s, 1H, imid.H); 7.13 (s, 1H, imid.H); 7.58 (s, 5H, imid.H + arom.H); 12.09 (s,1H, NH). ^{13}C NMR (200 MHz, $DMSO_{d6}$): 29.90 ($NHCH_2$-CH_2); 38.05 (N-CH_2); 43.13 (CON-CH_2); arom. C [115.28 (CH), 119.11 (CH), 125.93 (C), 134.86 (C)]; imid. C [128.31 (CH), 129.98 (CH), 129.55 (CH)]; 145.24 (C=N); 155.06 (C=O). Anal.

calc. for $C_{14}H_{14}ClN_5O$: C, 55.36; H, 4.65; N, 23.06. Found: C, 55.40; H, 4.61; N, 25.01. EI -MS: 304.25 $[M]^+$.

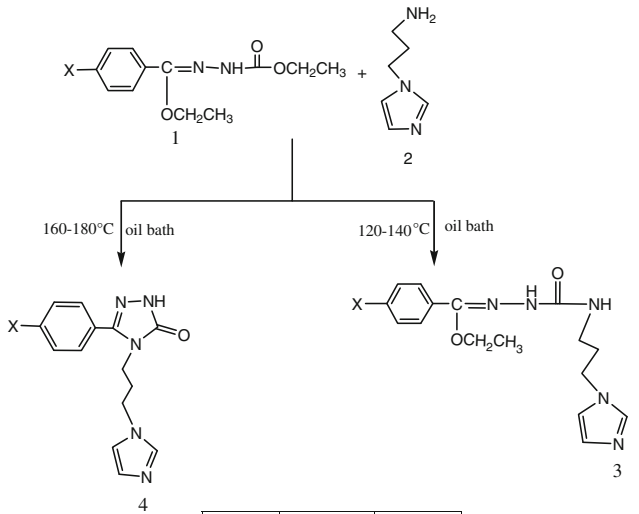
4-(3-(1H-imidazol-1-yl)propyl)-5-(4-fluorophenyl)-2H-1,2,4-triazol-3(4H)-one (4b)

Yield: 201 mg (69%). Colorless crystals. M.p. 185–186° C. IR (KBr, cm^{-1}): 3118 (NH), 1601 (C=N); 1716 (C=O). ^{1}H-NMR (200 MHz, $DMSO_{d6}$): 1.86–2.01 (m, 2H, $NHCH_2$-$C\underline{H}_2$); 3.61 (t, 2H, NCH_2); 3.82 (t, 2H, $CONCH_2$); 6.85 (s, 1H, imid.H); 7.19 (s, 1H, imid.H); 7.63 (s, 5H, imid.H + arom.H); 12.07 (s,1H, NH). ^{13}C NMR (200 MHz, $DMSO_{d6}$): 29.80 ($NHCH_2$-$C\underline{H}_2$); 38.11 N-CH_2); 44.21 (CON-CH_2); arom. C [115.30 (CH), 119.21 (CH), 125.90 (C), 134.81 (C)]; imid. C [128.22 (CH), 129.90 (CH), 129.67 (CH)]; 145.20 (C=N); 155.01 (C=O). Anal. calc. for $C_{14}H_{14}FN_5O$: C, 58.53; H, 4.91; N, 24.38. Found: C, 58.57; H, 4.87; N, 24.45. EI -MS: 285.56 $[M]^+$.

Results and discussion

The synthesis of compounds **3** was obtained by the reaction of compound **(1)** and compound **(2)** (Scheme 1). X-ray, analytical and spectroscopic data of the products **3a** and **3b** confirmed the success of the substution reaction.

In the ^{1}H-NMR spectra of the compound **3**, In the ^{1}H NMR spectra of the compounds **3**, two peaks are present for the NH protons. These two deuterium exchangeable singlets correspond to two nonequivalent NH protons, which also indicate the anti configuration of the NH groups relative to each other [53]. The D_2O exchangeable NH protons of compounds **3a–b** were measured at 7.12–7.15, 9.43–9.32 8.38 ppm. The addition of D_2O cause the disappearance of the NH peak. In the ^{1}H-NMR spectra of compounds **3a–b** signals from OCH_2CH_3 group were observed at 1.32–1.28 ppm ($OCH_2C\underline{H}_3$) and 3.12–3.10 ppm ($OC\underline{H}_2CH_3$) integrating for two protons and three protons, respectively. The structure of compounds **3a–b** was provided by the ^{13}C-NMR spectra. The signals for the triazole C=N and the C=O group are found at 145.24–145.32 and 155.39–155.43 ppm, respectively [54].



X	a	b
3	Cl	F
4	Cl	F

Scheme 1 Synthetic route to target compounds **3** and **4**

Synthesis of the compounds **4a–b** was performed from condensation of compound **1** with compound **2** in reasonably at temperature 160–180 °C (Scheme 1).

The IR data indicated the formation of compounds **4a–b** by the disappearance of $COCH_2$ (esteric) band of **1** at 1247 cm^{-1}, and the new band at 1712–1716 cm^{-1} belonging to the triazole C=O. The EI-MS of compounds **4a–b** confirmed the proposed structures with a molecular ion peak at m/z = 304.25 and 285.56 respectively.

In the ^{1}H-NMR spectra, the existence of **4a–b** was revealed by the disappearance of form of the ester CH_2O groups (4.18–4.24 ppm) in the precursor **1** after the cyclization and the appearance of a new peak at 12.09–12.07 ppm integrating for one H-atom (exchangeable with D_2O) belonging to H–N [53].

The $NHCH_2$-$C\underline{H}_2$ groups of the propyl residue attached to the triazol and imidazol rings resonate as a multiplet between 1.91–2.09 and 1.86–2.01 ppm, while NCH_2CH_2, linked to the imidazol ring, was recorded at 3.66–3.61 ppm as a triplet, and $CONHCH_2$ linked to the triazol ring was observed at 3.98–3.81 ppm as triplet respectively. In (DMSO-d6), H–C protons of the imidazol ring of compouns **4a–b** resonate at 6.88, 7.13, 7.58 and 6.85, 7.19, 7.63 ppm, respectively [55].

More detailed information about the structure of compounds **4a–b** was provided by the ^{13}C-NMR spectra. The signals for the triazole C=N and the C=O group are found at 145.24–145.20 and 155.06–155.01 ppm, respectively.

Crystal-structure determination of 3a

The crystal structure of the compound 3a, $C_{16}H_{20}ClN_5O_2$, was determined by single crystal X-ray diffraction technique, Fig. 1. The compound 3a crystallizes in the triclinic space group in the asymmetric unit, with the following unit-cell parameter: a = 7.5513(7) Å, b = 9.1809(9) Å, c = 14.6989(13) Å, α = 74.409(8)°, β = 87.525(7)°, γ = 70.346(7)° and V = 923.11(15) Å^3, with Z = 2, crystallographic data shown in Table 1.

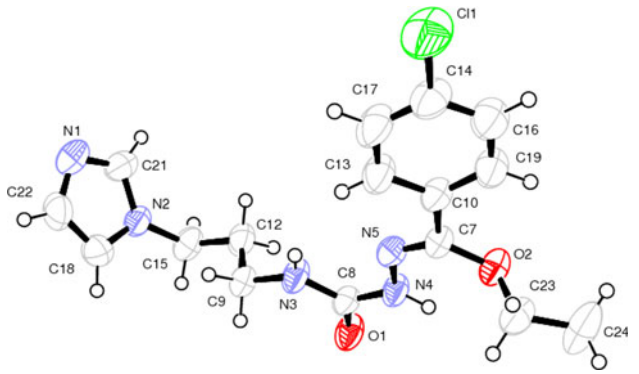


Fig. 1 Ortep III diagram of the compound **3a**. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii

Table 1 Crystal and experimental data

Formula: $C_{16}H_{20}ClN_5O_2$
Formula weight: 349.82
Crystal system: triclinic
Space group: $P\bar{1}$
Z = 2
a = 7.5513(7) Å
b = 9.1809(9) Å
c = 14.6989(13) Å
$\alpha = 74.409(8)^{\circ}$, $\beta = 87.525(7)^{\circ}$, $\gamma = 70.346(7)^{\circ}$ and V = 923.11(15) $Å^3$
No. of reflections used = 9720
$\theta_{min} = 1.44^{\circ}$ $\theta_{max} = 28.49^{\circ}$
Absorption correction type = integration with $T_{min} = 0.9001$ and $T_{max} = 0.9563$
wr2 = 0.143
$R_1 = 0.083$
$(\Delta/\sigma)_{max} = 0.000$
$(\Delta\rho)_{max} = 0.471$ e$Å^{-3}$
$(\Delta\rho)_{min} = -0.481$ e$Å^{-3}$
F(000) = 368
($\mu = 0.225$)
Measurement: STOE IPDS II
Program system: STOE X-RED
Structure determination: direct methods
Refinement: full matrix

Data collection

A block single crystal with dimensions 0.550 × 0.380 × 0.240 mm was mounted on goniometer and data collection was performed on a STOE IPDS II [56] diffractometer by the ω scan technique using graphite-monochromatic MoK_{α} radiation ($\lambda = 0.71073$ Å) at 296 K. The intensity symmetries indicate the triclinic $P\bar{1}$ space group. A total of reflections 9720 (3619 unique) were performed within 2θ range 1.44° and 28.49.

Correction for absorption ($\mu = 0.225$), by comparison of the intensities of equivalent reflections, was applied using X-RED software [56] and cell parameters were determined by using X-AREA software [56].The initial partial solution obtained by direct methods as implemented in the program SHELXS-97 [57] was expanded and refined by means of the program SHELXL-97 [57]. The program ORTEP-3 for windows [58] has been used in the preparation of the figure. All non-hydrogen atoms were refined anisotropically. The refinement carried out by full matrix least squares method on the positional and anisotropic temperature parameters of non-hydrogen atoms corresponding to 217 crystallographic parameters. All H atoms were included in calculated positions and refined using a riding model. The structure was refined to $R_{int} = 0.0460$ with 2434 observed reflections by the condition of $I > 2\sigma(I)$ threshold. The absorption correction is applied with integration type ($T_{min} = 0.9001$and $T_{max} = 0.9563$).

In the compound **3a**, $C_{16}H_{20}ClN_5O_2$, molecular structure is not planar but the ring systems are perfect planar. The maximum deviations are 0.006(3) Å for atom C21 in the imidazol ring and −0.005(3) Å for atom C16 in the phenyl ring. The dihedral angle between the imidazol ring (N1/N2/C18/C21/C22) and phenyl ring (C10/C13/C14/C16/C17/C19) is 63.7(1)°. The bond lengths and the bond angles in the molecule **3a** are in good agreement with our previous work, Experimental and DFT studies of ethyl *N*-3-(1H-imidazol-1-yl)propylcarbamoyl benzohydrazonate monohydrate [59].

The molecular conformation of the compound can be defined in terms of two torsion angles, which are defined as $\tau_1(C10/C7/N5/N4)$ and $\tau_2(N2/C15/C12/C9)$. The torsion angles $\tau_1(C10/C7/N5/N4)$ and $\tau_2(N2/C15/C12/C9)$ shows that for the title compound, the molecular conformation induced by the anti and gauche conformations in τ_1 andτ_2, respectively.

In the molecular structure, the organic compound forms N–H…N, N–H…O and C–H…O type intramolecular hydrogen bonds, namely N3-H3…N5, N4-H4…O2, which are producing S(5) motif [60], and C19-H19…O2, Fig. 2. The molecules are connected via N–H…N, N–H…O and C–H…O intermolecular interactions link the molecules infinite chains. Namely, N3-H3…N1 (symmetry code: −x, −y + 1,−z + 2), N4-H4…O1 (symmetry code: −x + 2, −y,−z + 2) producing $R_2^2(8)$ motif [5] and C15-H15A…O2 (symmetry code: −x + 1,−y, z + 2). N3-H3 and N4-H4 bonds form bifurcated contact to two acceptors, namely N5/N1 and O1/O2. The bifurcated nature of the contact explains the relatively large H…A distances and relatively small D-H…A angles, the detail of the hydrogen bonds shown in Table 2.

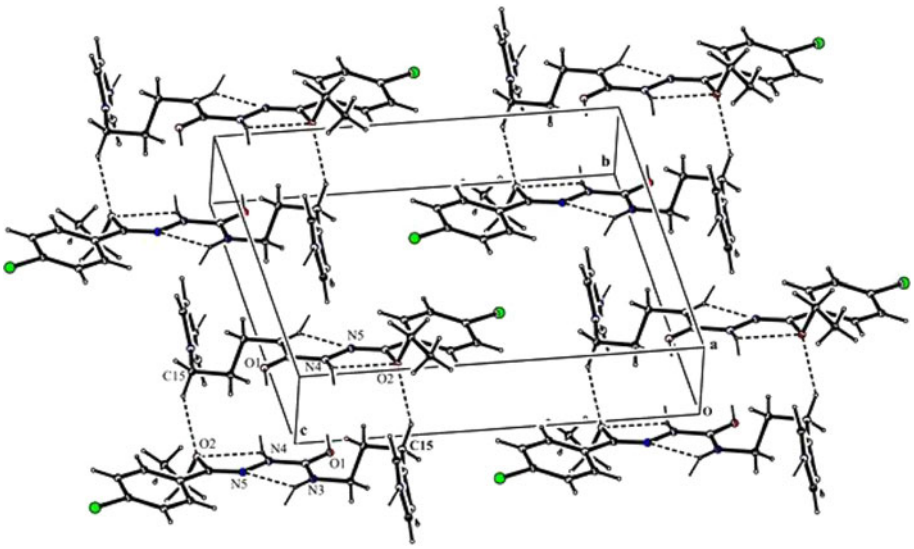


Fig. 2 Packing diagram of the title compound

Table 2 Hydrogen-bond geometry (Å, °)

D-H…A	D-H	H…A	D…A	D-H…A
N3-H3…N5	0.86	2.25	2.623(3)	105.8
N3-H3…N1^{i}	0.86	2.30	2.999(3)	138.7
N4-H4…O2	0.86	2.37	2.671(2)	100.9
N4-H4…O1^{ii}	0.86	2.03	2.871(2)	166.7
C15-H15A…O2^{iii}	0.97	2.54	3.383(3)	145.6
C19-H19…O2	0.93	2.52	2.842(3)	100.7

Symmetry codes: (i) −x,−y + 1,−z + 2 (ii) −x + 2,−y,−z + 2 (iii) −x + 1,−y, z + 2

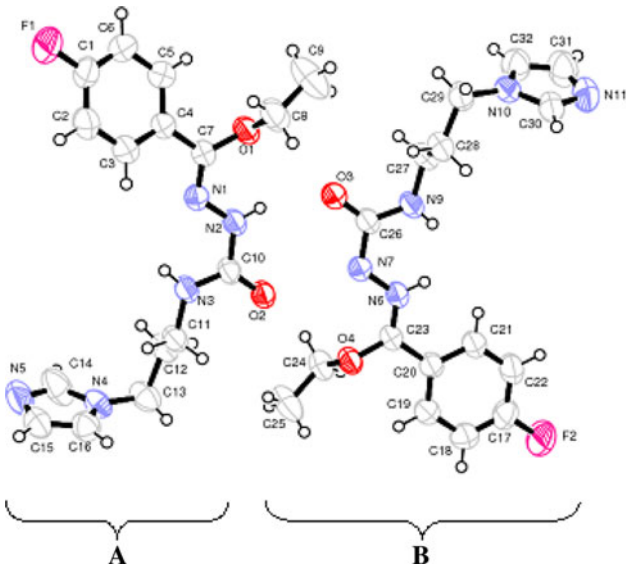


Fig. 3 Ortep III diagram of the compound **3b**. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii

Crystal-structure determination of 3b

The crystal structure of the compound **3b**, $C_{16}H_{20}FN_5O_2$, was determined by single crystal X-ray diffraction technique, Fig. 3. The compound **3b** crystallizes in the triclinic space group $P\bar{1}$with two molecules in the asymmetric unit, with the following unit-cell parameters: a = 11.1443(6) Å, b = 12.8632(7) Å, c = 14.1440(7) Å, α = 65.472(4)°, β = 72.503(4)°, γ = 75.253(4)° and V = 1739.47(16) Å^3, with $Z = 4$, crystallographic data shown in Table 3. The crystal structure has crystallographic inversion center and stabilized by N–H…N, C–H…O and N–H…O type intramolecular hydrogen bonds and N–H…N, C–H…N, C–H…F and C–H…O type intermolecular hydrogen bonds.

Data collection

A block single crystal with dimensions 0.800 × 0.593 × 0.310 mm was mounted on goniometer and data collection was performed on a STOE IPDS II [56] difractometer by the ω scan technique using graphite-monochromatic MoK_α radiation (λ = 0.71073 Å) at 296 K. The intensity symmetries indicate the triclinic $P\bar{1}$ space group. A total of reflections 20386 (6831 unique) were performed within 2θ range 1.62° and 28.42°.

Correction for absorption ($\mu = 0.095$), by comparison of the intensities of equivalent reflections, was applied using X-RED software [56] and cell parameters were determined by using X-AREA software [56].The initial partial solution obtained by direct methods as implemented in the program SHELXS-97 [57] was expanded and refined by means of the program SHELXL-97[57]. The program ORTEP-3 for windows [58] has been used in the preparation of the figure. All non-hydrogen atoms were refined

Table 3 Crystal and experimental data

Formula: $C_{16}H_{20}FN_5O_2$
Formula weight: 333.37
Crystal system: triclinic
Space group: $P\bar{1}$
Z = 4
a = 11.1443(6) Å
b = 12.8632(7) Å
c = 14.1440(7) Å
$\alpha = 65.472(4)^{\circ}$, $\beta = 72.503(4)^{\circ}$, $\gamma = 75.253(4)^{\circ}$ and V = 1739.47(16) $Å^3$
No. of reflections used = 20386
$\theta_{min} = 1.62^{\circ}$ $\theta_{max} = 28.42^{\circ}$
Absorption correction type = integration with $T_{min} = 0.9401$ and $T_{max} = 0.9770$
wr2 = 0.148
$R_1 = 0.072$
$(\Delta/\sigma)_{max} = 0.000$
$(\Delta\rho)_{max} = 0.542$ e$Å^{-3}$
$(\Delta\rho)_{min} = -0.403$ e$Å^{-3}$
F(000) = 704
($\mu = 0.095$)
Measurement: STOE IPDS II
Program system: STOE X-RED
Structure determination: Direct methods
Refinement: Full matrix

anisotropically. The refinement carried out by full matrix least squares method on the positional and anisotropic temperature parameters of non-hydrogen atoms corresponding to 434 crystallographic parameters. All H atoms were included in calculated positions and refined using a riding model. The structure was refined to $R_{int} = 0.0355$ with 4718 observed reflections by the condition of $I > 2\sigma(I)$ threshold. The absorption correction is applied with integration type ($T_{min} = 0.9401$and $T_{max} = 0.9770$).

In the compound **3b**, $C_{16}H_{20}FN_5O_2$, the imidazol and triazole ring systems are bridged by propyl moiety for both independent molecules and the crystal structure utilizes the symmetry of the crystallographic inversion center.

Both molecules in the asymmetric unit are not planar but ring systems are almost perfect planar. The dihedral angles between the triazole and imidazol ring systems are 60.16(8)° and 63.07(9)°, respectively for molecule A and B. The bond lengths and bond angles in the title molecule are in good agreement with in those related structure Ethyl N′-3-(1Himidazol-1-yl) propylcarbamoyl benzohydrazonate monohydrate [59].

In the molecular structure, the organic molecule forms N–H…O, N–H…N and C–H…O intramolecular hydrogen bonds [namely, N2-H2…O3, N2-H2…O1 producing S(5) ring motif [60], N6-H6…N9, N9-H9…N6, C19-H19…O4] and molecules are linked trough N–H…N, C–H…N, C–H…F and C–H…O type intermolecular hydrogen bonds [namely, N3-H3…N11 (symmetry code: x + 1,y − 1,z), N9-H9…N5 (symmetry code: x − 1,y + 1,z), C16-H16…N1 (symmetry code: -x+2,-y+1,-z+1), C22-H22…F1 (symmetry code: x − 1,y + 1,z − 1) and C29-H29B…O4 (symmetry code: -x+1,-y+2,-z+1)], Fig. 4. N2-H2, N3-H3 and N9-H9 bonds form bifurcated contact to two acceptors, namely O1/O3, N1/N11 and N5/N6, respectively. The bifurcated nature of the contact explains the relatively large H…A distances and relatively small D-H…A angles, the detail of the hydrogen bonds shown in Table 4.

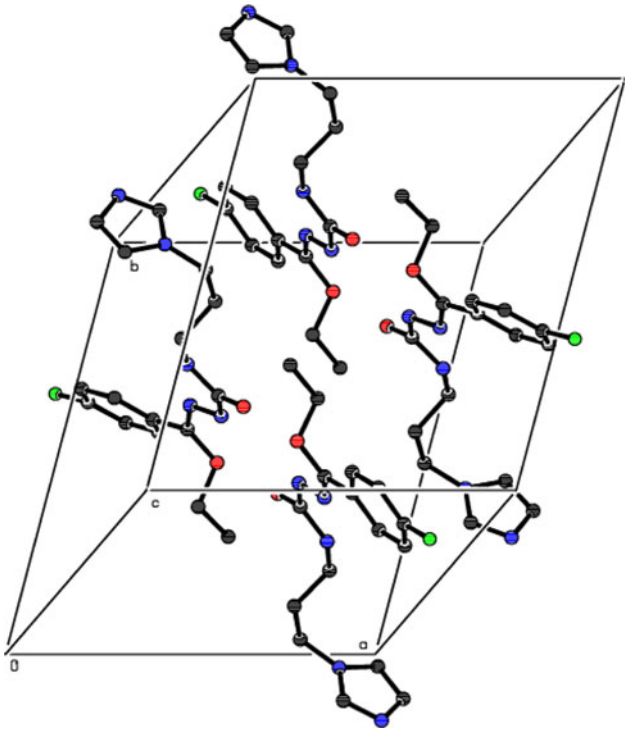


Fig. 4 Packing diagram of the compound **3b** (H atoms are omitted for clarity)

Method of calculations

Computational details

To better understanding experimental data for compound 3a, theoretical calculations in B3LYP/6-31G(d) level were performed. The molecular geometry is directly taken from the X-ray diffraction experimental result without any constrained. The molecular structure of ligand in the ground state was optimized by density functional using Becke's three-parameter hybrid method (B3) with the Lee, Yang and Parr correlation functional methods (LYP) with the Standard 6-31G(d) basis set [61, 62]. The optimized

Table 4 Hydrogen-bond geometry (Å, °)

D-H…A	D-H	H…A	D…A	D-H…A
N3-H3…N11^{i}	0.86	2.30	3.031(2)	142.7
N9-H9…N5^{ii}	0.86	2.31	3.002(3)	138.2
C16-H16.. N1^{iii}	0.93	2.55	3.437(2)	159.5
C29-H29B…O4^{iv}	0.97	2.59	3.378(2)	138.1
C22-H22…F1^{v}	0.93	2.45	3.335(3)	158.5
N2-H2…O1	0.86	2.36	2.6470(18)	100.2
N2-H2…O3	0.86	2.11	2.9044(19)	153.7
N3-H3…N1	0.86	2.22	2.605(2)	106.9
N6-H6…N9	0.86	2.29	2.623(2)	103.1
C19-H19…O4	0.93	2.51	2.830(2)	100.7

Symmetry code: (i) x + 1, y − 1,z (ii) −x + 2,−y + 1,−z + 1 (iii) −x + 2,−y + 1,−z + 1 (iv) −x + 1,−y + 2,−z + 1
(v) x − 1, y + 1, z − 1

structural parameters were used in the vibrational frequency calculations at DFT level to characterize all stationary points as minima. 6-31G(d) basis set was used for all elements. All calculations were performed with the Gaussian 03 W program package [63]. In calculations, tight converge criteria was used. By allowing that all the parameters could relax, all the calculations converged to optimized geometries, which corresponded to true energy minima. On the basis of the optimized ground state structure, the spectroscopic properties and UV–vis absorption calculations in vacuum have been carried out by using the time-dependent density functional theory (TD-DFT) at B3LYP level, providing an accurate description of UV–vis transitions of ligand system. This method was used to compute the 20 singlet → singlet transitions in vacuum.

Interpretation of UV–vis absorption spectrum of ligand molecule via DFT and TD-DFT calculations

UV absorption spectrum of compound **3a** was calculated using time-dependent density functional theory (TD-DFT) method based on B3LYP/6-31G(d) basis set in order to compare with experimental results. This strategy leads to an average discrepancy of 1–25 nm between theoretical and experimental λ_{max} due to several influencing factors, such as solvent effect and intermolecular interaction, etc. DFT calculations were carried out in order to know the geometry of the frontier orbitals of the related compound. The highest four energy occupied orbitals are mainly localized on the chlorine and carbonyl oxygen atoms, benzene carbons, imidazole ring and C=N/N–C groups with small contribution of related $–CH_2$ groups. Similarly, the lowest four energy unoccupied orbitals are mainly located on the chlorine and carbonyl oxygen atoms, imidazole ring with some contribution of C=N/N–C, −NH and related $–CH_2$ groups.

TD-DFT studies have been very useful in order to assign the electronic absorption transitions of the compounds. The low-energy excitations obtained by this method are in good/moderate agreement with the experimental results. Specifically, the HOMO is composed of the π-bonding-$2p_z$-orbitals of the chelating benzene ring, $3p_x$ orbitals with antibonding interaction of the chlorine, $2p_z$ orbitals with antibonding interaction of the oxygen, orbitals with π-symmetry of C=N/N–C chromophores and $\pi - p_y$ orbitals of –NH group. The HOMO − 1 is also a chlorine/benzene/C=N/N–C based orbital teams and partially non-bonding orbitals of imidazole moiety. The HOMO − 2 is related p orbitals of chlorine and oxygen atoms and orbitals with π-symmetry of imidazole ring (mixed $\pi - p_y/p_z$ orbitals of nitrogen and benzene carbons). The HOMO − 3 is also antibonding $\pi - p_x$ orbitals of chlorine and non-bonding orbitals of arene carbons and HOMO − 4 is a set of degenerated orbitals as those of other HOMOs [64].

The LUMO and LUMO + 3 are also a set of quasi degenerated orbitals. These orbitals show a predominant character of the chlorine/oxygen/benzene/C=N/N–C based orbital combinations and mixed with less character of $–CH_2$ group. On the other hand, the LUMO + 2 is composed of orbital sets with π-symmetry of imidazole annular and related $–CH_2$ group. The LUMO + 1 has an important contribution of the arene carbons and chlorine and the LUMO + 4 has also a noticeable contribution of the imidazole and presents a decrease of the electronic density of the –NH group. The intensity of these transitions has been assessed from the oscillator strength (f). All these transitions are of intra-ligand $\pi \rightarrow \pi^*$ charge transfer origin (LLCT) mainly arene with some contributions of carbonyl oxygen/chlorine/imidazole → arene/chlorine, imidazole and arene/chlorine/oxygen in nature mixed with LLCT (arene/chlorine → arene/chlorine) transitions [65]. The involved orbitals in these transitions are presented in Fig. 5 and the most relevant electronic transitions are present in Table 5.

Conclusions

In this study, It has been synthesized and characterized new triazol and imidazol derivatives.In addition, these key compounds were characterized UV–Vis, IR, ^{1}H and ^{13}C NMR, mass spectrometry, elemental analyses, and X-ray crystallography. The investigations of ionic liquid derivatives and pharmacology properties of these synthesized key compounds are thought to be next studies.

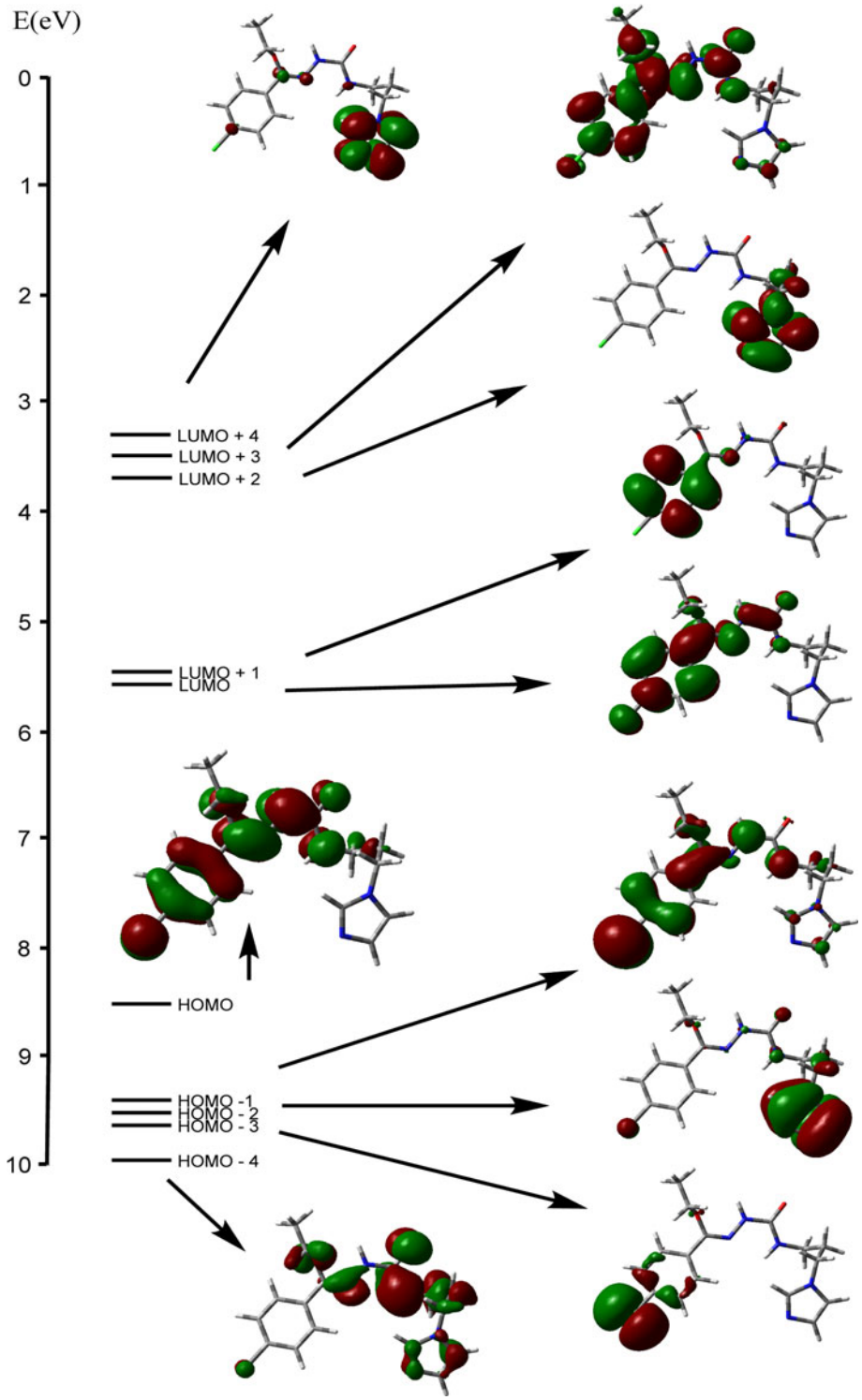


Fig. 5 The energy (eV) and some contours of the occupied and unoccupied molecular orbitals of compound **3a**

Table 5 Calculated TD-DFT wavelengths, oscillator strengths (f), allowed transitions and experimental data for ligand

Orbital (transitions)	Oscillator (f)	Assignment	λ_{exp} (nm)	λ_{calc} (nm)
[a]HOMO − 3 → LUMO	0.523	$\pi \rightarrow \pi^*$	334	339.9
HOMO − 2 → LUMO + 4	0.0017	$\pi \rightarrow \pi^*$	319	316.6
HOMO − 1 → LUMO + 1				
HOMO − 4 → LUMO	0.5292	$\pi \rightarrow \pi^*$	299	274.3
HOMO − 1 → LUMO				
HOMO − 1 → LUMO + 4				
HOMO → LUMO + 2	0.1861	$\pi \rightarrow \pi^*$	287	262.3
HOMO − 1 → LUMO + 2	0.0009	$\pi \rightarrow \pi^*$	274	258.5
HOMO − 1 → LUMO + 3				
HOMO − 2 → LUMO + 1	0.1982	$\pi \rightarrow \pi^*$	252	253.9

[a] HOMO is No. 92 orbital

Acknowledgements This study was supported by grants from Karadeniz Technical University (proje no: 2007.111.002.11) and the scientific and technological research council (TUBITAK proje no: 107T065) of Turkey.

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