Struct Chem
DOI 10.1007/s11224-014-0422-6

ORIGINAL RESEARCH

One-pot microwave-assisted solvent-free synthesis, theoretical and experimental studies on barrier rotation of C–N bond of *N*-alkenyl-1,2,3-triazoles

Maryam Malekdar · Avat Arman Taherpour · Issa Yavari · Kambiz Larijani

Received: 7 August 2013 / Accepted: 5 March 2014

Abstract The reactions on benzotriazoles continue to happen to reach interesting varieties of their derivatives. This study reports a fast one-pot microwave-assisted solvent-free synthesis of *N*-alkenyl-1,2,3-benzotriazole (**3**, **5**, and **7**) and 1-(2-Alkyloxycarbonyl-vinyl)-1*H*-[1–3] triazole-4-carboxylic acid methyl ester (**8** and **9**) derivatives by nucleophilic addition reactions of 1,2,3-benzotriazole ($C_6H_5N_3$) (**1**) and 1*H*-[1–3] triazole-4-carboxylic acid methyl ester ($C_4H_4N_3O_2$) (**1′**) with R-propiolates (R = Me, Et; **2** & **4**) and phenylacetylene **6** in good yields. The values of activation energy for rotation around C–N bond in the synthesized *N*-alkenyl-1,2,3-triazole compounds were studied by DFT-B3LYP/6-31G* method.

Keywords Microwave-assisted synthesis · 1,2,3-Triazoles · *N*-alkenyl-1,2,3-benzotriazole · Solvent free · Alkylpropiolates · Solvent-free synthesis · DFT-B3LYP method · Molecular modeling

M. Malekdar
Chemistry Department, Science Faculty, Islamic Azad University, Arak Branch, P.O. Box 38135-567, Arak, Iran

A. A. Taherpour (✉)
Department of Organic Chemistry, Faculty of Chemistry, Razi University, P.O. Box 67149-67346, Kermanshah, Iran
e-mail: avatarman.taherpour@gmail.com

I. Yavari
Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

K. Larijani
Research Council of Science and Research Campus, Islamic Azad University, P.O. Box 14155-4933, Tehran, Iran

Introduction

Triazoles are known to be relatively resilient to metabolic degradation and have known utility in several medicinal chemistry campaigns as isosteres for phenyl rings and carboxyl functionalities [1]. In general, 1,2,3-triazole formation requires harsh conditions, that is, high temperature and longer reaction times. In the original description, the explored examples showed that although these were relatively clean processes, they could take from 12 to 48 h at high temperatures (~110 °C) [1]. The triazoles may display a wide range of biological activities as anti-HIV and anti-microbial agents as well as selective β_3-adrenergic receptor agonist and anti-allergic agents [2–6]. Additionally, 1,2,3-triazoles are found in herbicides, fungicides, and dyes [7, 8]. As an aromatic heterocycle, Benzotriazole is a commonly used corrosion inhibitor. Benzotriazoles are also a class of compounds containing the benzotriazole skeleton. The [3 + 2] cycloaddition reactions under microwave irradiation and theoretical conditions were previously investigated and reported to produce 1,2,3-triazoles [9–14]. The 1,2,3-triazole derivatives are produced by reaction of o-phenylenediamine, sodium nitrite, and acetic acid. The conversion proceeds via diazotization of one of the amine groups [15, 16]. Benzotriazole is a complexing agent and as such is a useful corrosion inhibitor, e.g., for silver protection in dishwashing detergents and an anti-fog agent in photographic development. Aircraft deicer and anti-icer fluid contain benzotriazole. Benzotriazole derivatives are found in pharmaceuticals such as antifungal, antibacterial, and anthelmintic drugs. Benzotriazole is fairly water soluble, not readily degradable, and has a limited sorption tendency. Hence, it is only partly removed in wastewater treatment plants and a substantial fraction reaches surface waters such as rivers and lakes [15, 16]. In 2008, Shi et al.

Published online: 29 March 2014

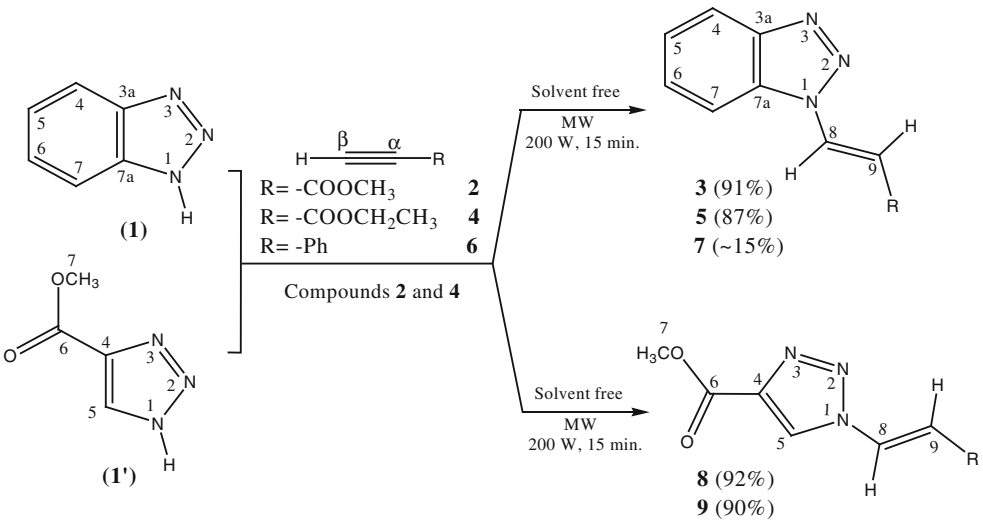


Fig. 1 The one-pot microwave-assisted solvent-free with high-oriented synthesis of simple *N*-substituted-1,2,3-triazoles (**3**, **5**, **7**, **8**, and **9**)

[17] reported a rapid and easy entry to a variety of substituted, functionalized benzotriazoles under mild conditions by a [3 + 2] cycloaddition of azides to benzynes. Benzotriazole-containing polymers have recently emerged in organic electronic applications and are increasingly attracting a great deal of attention. These polymers are reviewed from a general perspective in terms of their potential use in three main fields, electrochromics, organic solar cells, and organic light-emitting diodes [18]. It is well demonstrated that substitution reactions on triazoles (**1** and **1′**) and its *N*-substituent derivatives have not been widely utilized. This is due to the triazole action as a deactivating group on the benzene ring while the orientation is largely influenced by the nature and the position of the substituent groups [19]. The microwave solvent-free synthesis of 1*H*-[1–3] triazole-4-carboxylic acid methyl ester (**1′**) was reported before [10]. The ^{13}C-NMR analysis of the chemical shifts of carbon atoms in the benzotriazoles was already investigated by Carta et al. [20]. The results of ^{13}C-NMR analysis in benzotriazole derivatives demonstrated bearing a substituent on the ring, and an alkyl substituent on the nitrogen position of the triazole moiety proved to be a tool for identification of the *N*-alkyl isomers [20]. By the use of the reported ^{13}C-NMR data [20], it is possible to observe that the chemical shifts assigned to the quaternary carbon atoms C-3a and C-7a fall in different regions no matter if they are close to the ring substituent or not. The results have prompted investigations to see if these recurring differences were maintained in both ring and $N_{1(2)(3)}$ structure benzotriazoles [20]. Using the analysis of results obtained from ^{13}C-NMR method, it is obviously possible to distinguish different isomers. [20] Microwave-assisted synthesis has been utilized as a powerful and effective technique to promote a group of chemical reactions [21–37]. Since the first publications on the use of microwave irradiation in organic chemistry, the accelerated process described has been a lure for chemists to further apply new reactions to this technology [30]. Some of the different methods to syntheses of compounds **3**–**7** were reported before [38–40].

This study reports a fast one-pot microwave-assisted (200 W/100 °C and 15 min.) solvent-free with high-oriented synthesis of *N*-alkenyl-1,2,3-triazoles (**3**, **5**, **7**, new derivatives **8** & **9**) by the nucleophilic addition reactions of 1,2,3-benzotriazole (**1**) and 1*H*- [1–3] triazole-4-carboxylic acid methyl ester (**1′**) with alkyl-propiolates (**2** and **4**) in good yields. The GC yield of **7** was about 15 %. There was not any successful reaction between **1** and **1′** with DMAD and DEAD in the conditions and by changing the MW-irradiation conditions. Another (Fig. 1) aspect of this study was the molecular modeling of the values of activation energy for rotation around C–N Bond in the synthesized *N*-alkenyl-1,2,3-triazole compounds. This study was carried out by DFT-B3LYP/6-31G* method.

Experiments

The N_1-alkenyl-1,2,3-triazole derivatives that were synthesized (**3**, **5**, **7**, **8**, and **9**) were known by their physical data, FT-IR, ^{1}H-NMR, ^{13}C-NMR, mass (MS) spectra, and CHN analysis. The FT-IR spectra were recorded as KBr pellets on a Shimadzu FT-IR 8000 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were determined on a 300 MHz Brüker spectrometer. The solvent for NMR recording was $CDCl_3$. GC and GC–MS analysis were performed on a Shimadzu QP5050A GC–MS instrument, injector 200 °C; temperature program: 100 °C (2 min), then 16 °C per min till 250 °C on a Zebron capillary column ZB-5 (0.25 µm thickness, 0.32 mm diameter, and 30 m length). It should

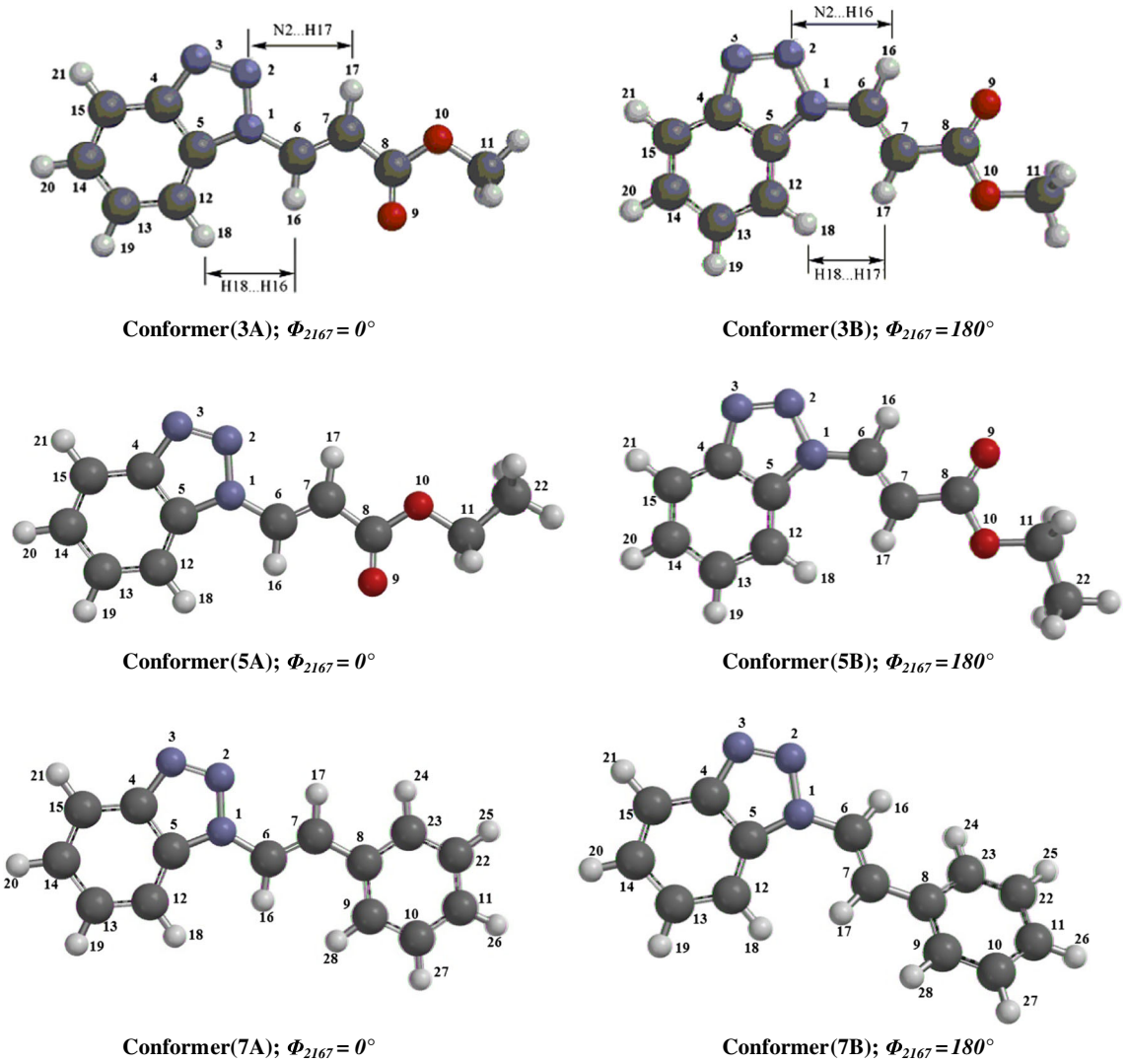
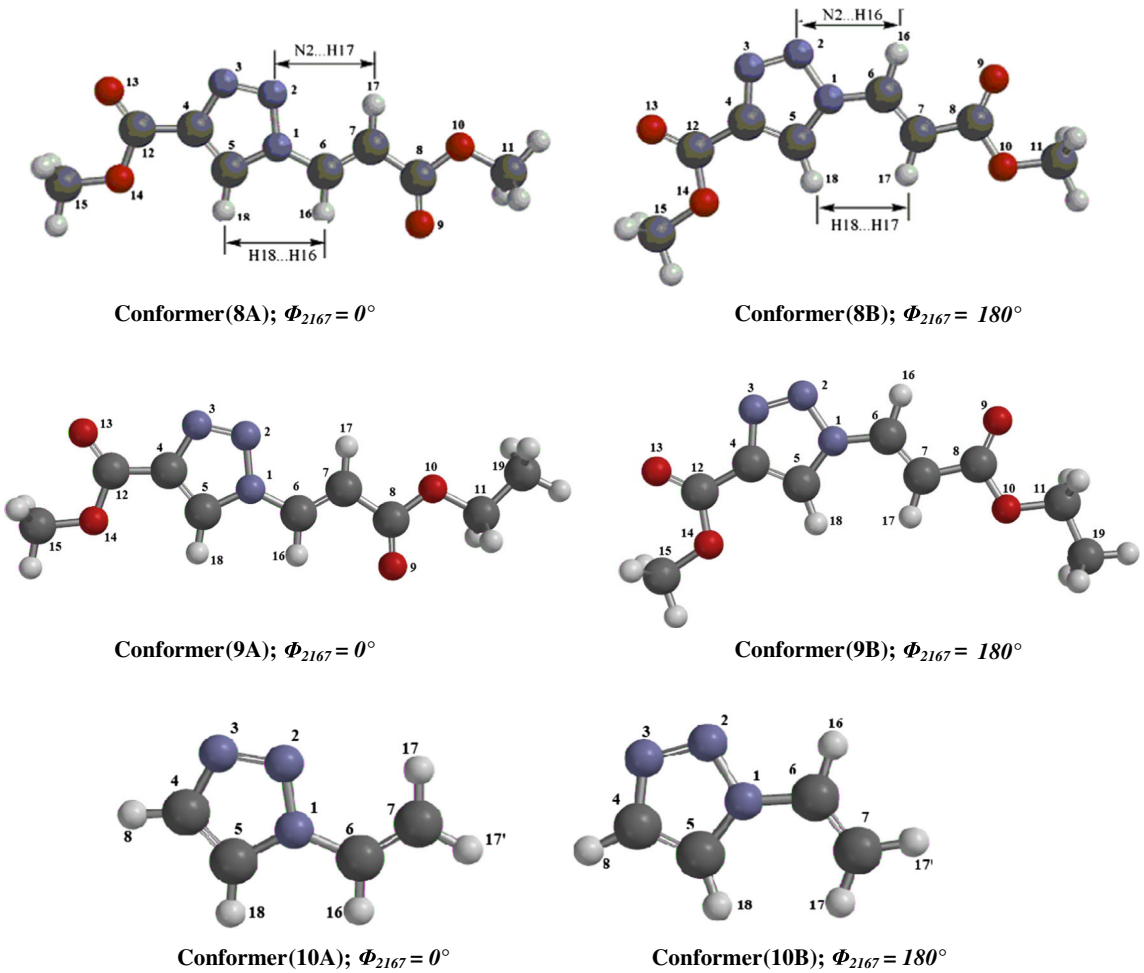


Fig. 2 The structure and the conformers (**A** and **B** with $\Phi_{2167} = 0°$ and 180°, respectively) of the 1,2,3-triazoles **3**, **5**, and **7**

be noted that a limited amount of compounds is required for the experiment. Therefore, some small quantity of vapor is evolved during irradiation. A Labmate microwave reactor (Milstone-Ethos 1.; 2,540 Hz, Max 1,200 W) was used for the MW-assisted syntheses; temperatures were measured externally by infrared fiber optics.

Molecular modeling

The calculations on the structures of the synthesized *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, and **9**) have been performed by the density functional theory (DFT) method. The structure of the *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, and **9**) was optimized by DFT-B3LYP/6-31G* method. All calculations have been performed by *Spartan* '10 package [41]. To calculate the values of activation energy for rotation around the C–N bond in the synthesized triazoles, appropriate dihedral angle change around the C–N bond (reaction coordinate method) and optimization in each step were utilized. The *Hartree*'s energy was converted to kcal mol^{-1}, and the relative energies were calculated. The graphs and the related tables demonstrated the appropriate data. All of the graphing operations for the synthesized *N*-alkenyl-1,2,3-triazoles were performed using the *Microsoft Office Excel*-2013 program. The optimized structures of the synthesized *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, and **9**) were carried out to calculate the ^{1}H-NMR by DFT-B3LYP/6-31G* method. The experimental and calculated ^{1}H-NMR by the DFT method were compared and discussed.



Conformer(8A); $\Phi_{2167} = 0°$ **Conformer(8B); $\Phi_{2167} = 180°$**

Conformer(9A); $\Phi_{2167} = 0°$ **Conformer(9B); $\Phi_{2167} = 180°$**

Conformer(10A); $\Phi_{2167} = 0°$ **Conformer(10B); $\Phi_{2167} = 180°$**

Fig. 3 The structure and the conformers (**A** and **B** with $\Phi_{2167} = 0°$ and 180°, respectively) of the 1,2,3-triazoles **8**, **9**, and **10**

Results and discussion

Synthesis the *N*-substituted-1,2,3-triazoles

In accordance with the method explained in the experimental section, the mixture of 1,2,3-triazole **1** and **1′** with the propyolate derivatives (**2**, **4**, and **6**) in different experiments was exposed to 200 W/100 °C microwave irradiation for 15 min. The FT-IR, ^{1}H-NMR, ^{13}C-NMR, MS spectrums, and CHN analysis of the MW-irradiation process are demonstrated in the experimental section. No details are given about the by-products, and only the final products are considered. The results demonstrate high-oriented synthesis of simple N_1-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, and **9**) products. Even after changing the conditions of the reactions, the reaction between the triazoles **1** and **1′** with DMAD and DEAD did not show any result. Considering this and the low yield (about 15 % by GC method) of the nucleophilic addition reactions of **1** and **6** (H–C≡C–Ph), it seems that the C_β of the reactants **2** and **4** should have enough δ+ charge for the nucleophilic addition reactions of **1** and **1′** on **2**, **4**, and **6**. The symmetry reactants of DMAD and DEAD do not have this suitable condition for this regio- and chemo-selectivity. The results of the GC, Mass, FT-IR, ^{1}H-NMR, and ^{13}C-NMR of the products have been investigated. The GC spectrum of 3-benzotriazol-1-yl-acrylic acid methyl ester (**3**) shows a signal at retention time R.T. = 9.608 min that is related to the product **3**. The mass (MS) spectrum of 3-benzotriazol-1-yl-acrylic acid methyl ester (**3**) was investigated. The results have shown the omission of $-N_2$, $-CO_2CH_3$, $-N-CH=CH-CO_2CH_3$, and $-N_3-CH=CH-CO_2CH_3$ from $[M]^+ = 203$ in the MS spectrum of **3**. The data of the FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectrums of 3-Benzotriazol-1-yl-acrylic acid methyl ester (**3**) were demonstrated in the experimental section. The GC spectrum of 3-Benzotriazol-1-yl-acrylic acid ethyl ester (**5**) showed a signal at retention time R.T. = 10.150 that is related to the product **5**. The mass spectrum of 3-benzotriazol-1-yl-acrylic acid ethyl ester (**5**) has shown the omission of $-N_2$, $-CO_2C_2H_5$, $-N-CH=CH-CO_2C_2H_5$,

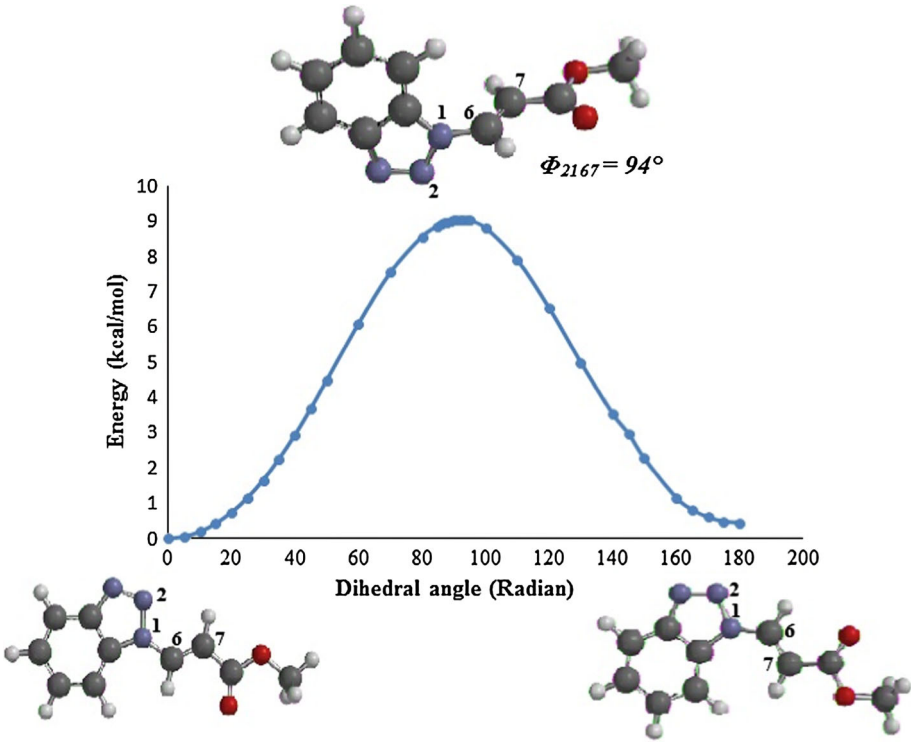


Fig. 4 The rotation process to interconversion of the conformers (**3A**, [**T.S.**]$_3$, and **3B** with $\Phi_{2167} = 0°$, 94°, and 180°, respectively) of the 1,2,3-triazole **3**

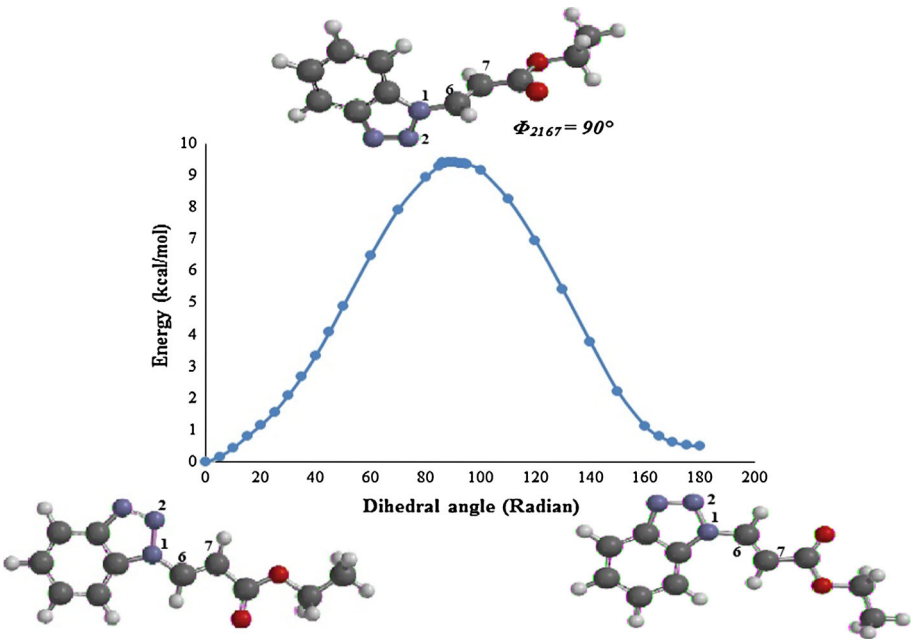


Fig. 5 The rotation process to interconversion of the conformers (**5A**, [**T.S.**]$_5$, and **5B** with $\Phi_{2167} = 0°$, 90°, and 180°, respectively) of the 1,2,3-triazole **5**

–N_3–CH=CH–$CO_2C_2H_5$, and –CO_2H group by the *Mclafferty rearrangement* from $[M]^+ = 217$ in the MS spectrum of **5**. The FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectrums of 3-benzotriazol-1-yl-acrylic acid ethyl ester (**5**) have been demonstrated in the experimental section. The results of the GC, Mass, FT-IR, ^{1}H-NMR, and ^{13}C-NMR of the products **8** and **9** have been demonstrated in the experimental section.

The FT-IR spectrums show the C=O of ester functional group at 1,712 and 1,704 cm^{-1} for **3** and **5**, respectively. The –N_3– function vibration frequencies of 1,2,3-benzotriazole (**1**) rings appeared at 1,437 & 1,279 & 1,456 and

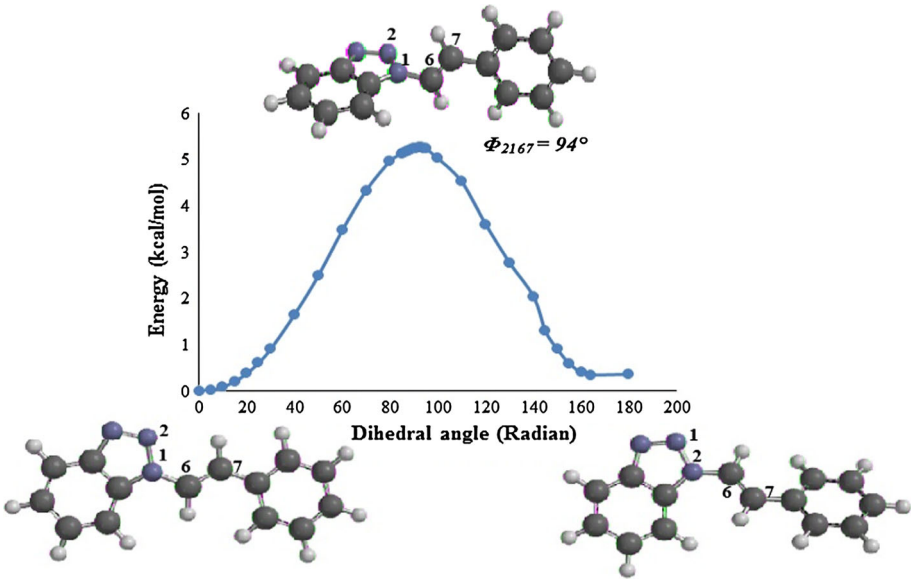


Fig. 6 The rotation process to interconversion of the conformers (**7A**, $[\mathbf{T.S.}]_7$, and **7B** with $\Phi_{2167} = 0°$, 94°, and 180°, respectively) of the 1,2,3-triazole **7**

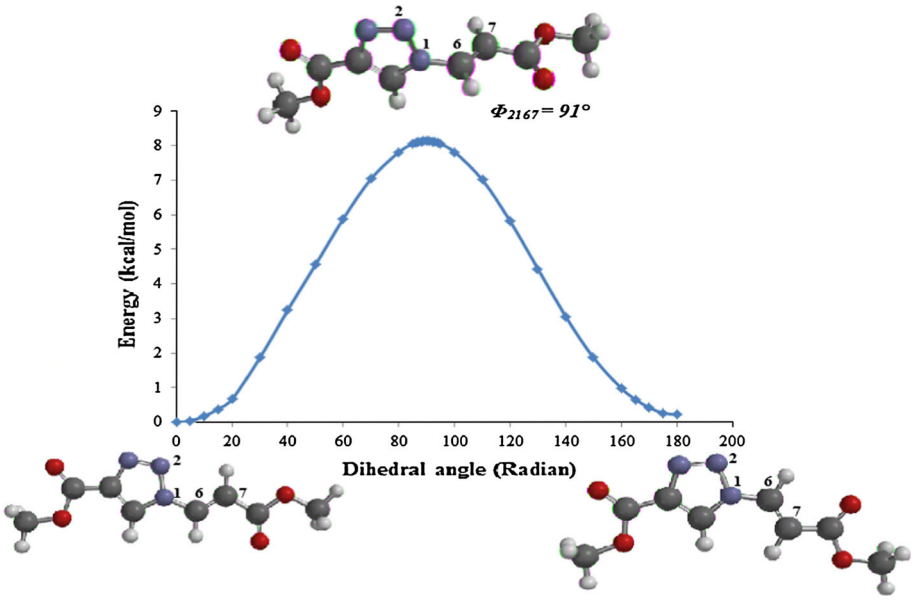


Fig. 7 The rotation process to interconversion of the conformers (**8A**, $[\mathbf{T.S.}]_8$, and **8B** with $\Phi_{2167} = 0°$, 91°, and 180°, respectively) of the 1,2,3-triazole **8**

1,276 cm^{-1} for the products **3** and **5**, respectively. The C=C stretching of N_1-alkene branch of the products **3** and **5** appeared at 1,656 and 1,650 cm^{-1}, respectively. The C^2_{sp}–H stretching of the products appeared at 3,000–3,150 and 3,000–3,100 cm^{-1} for **3** and **5**, respectively. The C^3_{sp}-H stretching of the products **3** and **5** appeared at 2,958 and 2,986 cm^{-1}, respectively. The N_1-H stretching frequency of benzotriazole **1** as a single absorption has been removed from the FT-IR spectrum of the products **3** and **5**, respectively. The ^{1}H-NMR spectrum of **3** shows a singlet signal for CH_3 group at 3.84 ppm. The quartet and triplet for $–CH_2CH_3$ appeared at 1.33–1.38 ppm (q, 2H, 7.0 Hz) and 4.28–4.35 ppm (t, 3H, 7.0 Hz) for **5**. In ^{1}H-NMR spectrums, the trans pattern of $H–C^2_{sp}=C^2_{sp}–H$ of the products **3** and **5** appeared as an AX doublet of doublet in 6.72–6.77 & 8.48–8.53 ppm (d.d-AX, 2H, 15 Hz) and 6.71–6.76 & 8.47–8.52 ppm (d.d-AX, 2H, 15 Hz), respectively. The ^{13}C-NMR results show 10 and 11 C-atom types for **3** and **5**, respectively. See the results at the experimental section. The $[M^+]$ for **3**, **5**, and **7** were 203, 217, and 221, respectively. The mass spectrums of **3**, **5**, and **7** show *m/z* 175, 189, and 193, respectively, meaning that each of the products under mass conditions has lost 28 weight unit. This is due to the omission of $–N_2=N_3–$ from the structure of the products. These evidences and the reported results of ^{13}C-NMR analysis

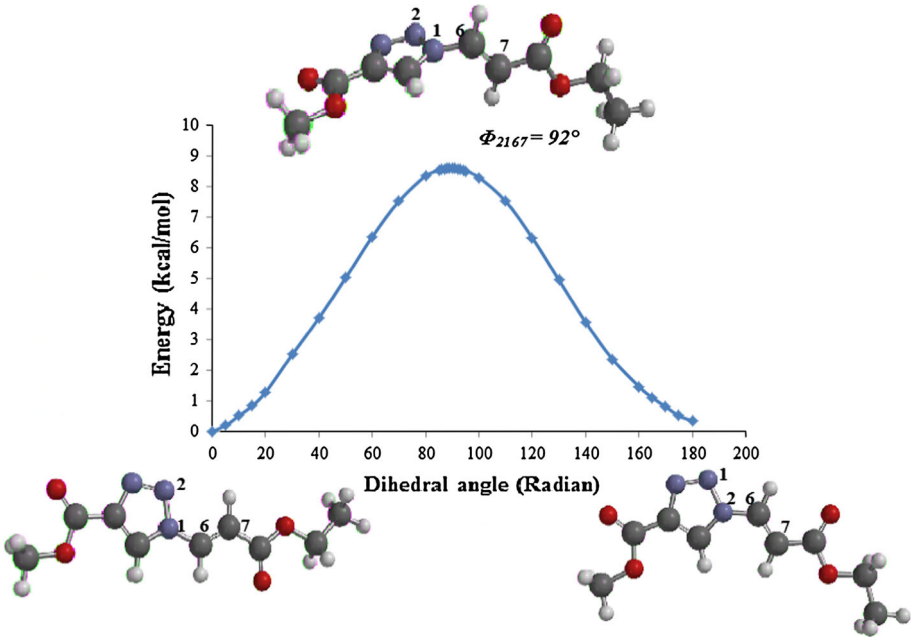


Fig. 8 The rotation process to interconversion of the conformers (**9A**, [**T.S.**]$_9$, and **9B** with $\Phi_{2167} = 0°$, 92°, and 180°, respectively) of the 1,2,3-triazole **9**

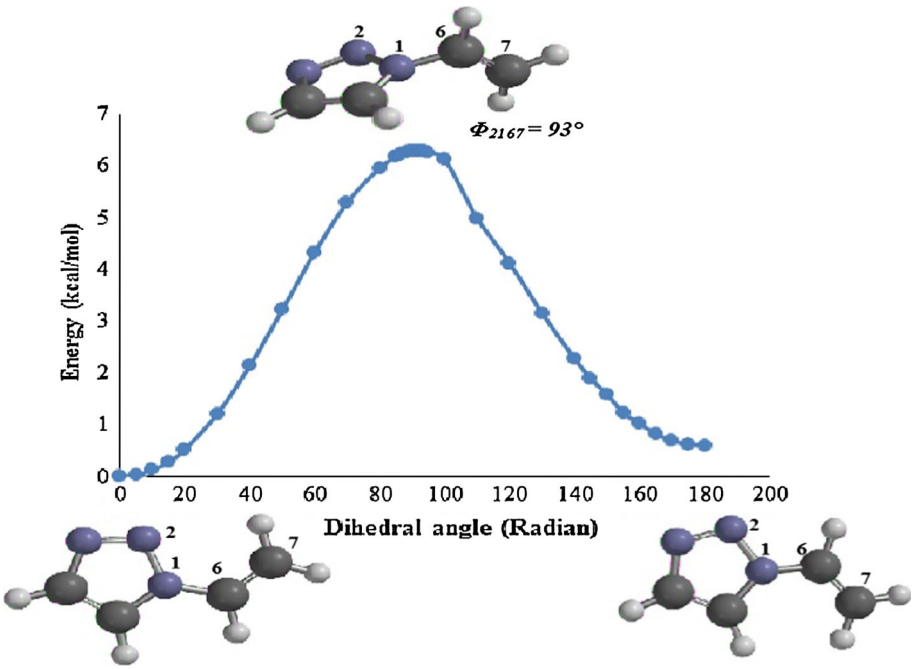


Fig. 9 The rotation process to interconversion of the conformers (**10A**, [**T.S.**]$_{10}$, and **10B** with $\Phi_{2167} = 0°$, 93°, and 180°, respectively) of the 1,2,3-triazole **10**

method by Carta et al. [20] confirm that the substituted alkene group was located on N_1 in the structures of **3**, **5**, and **7** products. There were almost the same interpretations for the structures of products **8** and **9** from compound **1′**. The percentages of C, H, and N were explained in the experimental section. Based on the results shown in the experimental section, the MS spectrums and CHN analysis demonstrated the formation of products during the synthesis process.

Activation energy for rotation around C–N bond in the synthesized N-alkenyl-1,2,3-triazoles

The principles of rotation about the C=C bond through the dipolar transition state (the thermal mechanism of the *Z*, *E*-isomerization) have been discussed in previous studies [42–44]. The main factors concerning C=C rotation are: increasing the electron-donating power and the acceptor capacity promotes polarization of the C=C bond in the

Table 1 The selected structural data of the 1,2,3-triazoles (**3**, **5**, and **7**) and the saddle form of interconversions of the conformers **A** and **B**

Selected data	**3A** ↔ **3B**			**5A** ↔ **5B**			**7A** ↔ **7B**		
	3A $\Delta G = 0.45$	$[\mathbf{T.S.}]_{\mathbf{3}}$ $\Delta G^* = 9.05$	**3B**	**5A** $\Delta G = 0.50$	$[\mathbf{T.S.}]_{\mathbf{5}}$ $\Delta G^* = 9.41$	**5B**	**7A** $\Delta G = 0.36$	$[\mathbf{T.S.}]_{\mathbf{7}}$ $\Delta G^* = 5.26$	**7B**
Bond length (Å)									
N1–N2	1.386	1.386	1.396	1.386	1.386	1.395	1.377	1.377	1.385
N2–N3	1.283	1.283	1.278	1.284	1.283	1.278	1.289	1.289	1.284
N3–C4	1.386	1.385	1.386	1.385	1.385	1.386	1.381	1.381	1.382
C4–C5	1.405	1.406	1.409	1.406	1.406	1.409	1.408	1.408	1.410
C5–N1	1.378	1.379	1.381	1.378	1.379	1.381	1.375	1.375	1.377
N1–C6	1.388	1.388	1.385	1.389	1.388	1.385	1.402	1.402	1.399
C6–C7	1.341	1.341	1.343	1.341	1.341	1.343	1.343	1.343	1.344
C7–C8	1.474	1.474	1.475	1.475	1.474	1.476	1.464	1.464	1.466
C6–H16	1.085	1.085	1.085	1.085	1.085	1.085	1.084	1.084	1.084
C7–H17	1.083	1.083	1.081	1.083	1.083	1.081	1.086	1.086	1.086
H16···H18	2.461	3.511	–	2.466	3.453	–	2.442	3.496	–
H17···N2	2.669	3.512	–	2.664	3.463	–	2.535	3.403	–
H17···H18	–	3.771	2.071	–	3.883	2.074	–	3.711	2.107
H16···N2	–	2.965	2.439	–	2.992	2.438	–	2.950	2.443
Bond angle (°)									
N1N2N3	109.02	109.05	109.31	109.04	109.05	109.32	109.27	109.27	109.49
N2N3C4	109.15	109.13	109.06	109.13	109.13	109.04	108.80	108.80	108.72
N3C4C5	108.60	108.63	108.92	108.61	108.63	108.92	108.59	108.59	108.91
C4C5N1	103.73	103.69	103.53	103.72	103.69	103.53	103.76	103.76	103.53
C5N1C6	128.42	128.64	133.99	128.49	128.64	134.02	128.33	128.33	133.53
N1C6C7	125.69	125.47	127.33	125.63	125.47	127.50	124.10	124.10	125.94
C6C7C8	118.11	118.27	118.48	118.20	118.27	118.25	126.28	126.28	125.28
N1C6H16	114.28	114.41	112.33	114.37	114.41	112.30	112.52	112.52	110.93
C6C7H17	122.52	122.42	124.11	122.48	122.42	124.20	117.47	117.47	119.30
Torsional angle (°)									
N2N1C6C7	0.00	94.14	180	0.00	90.14	180	0.63	94.00	164.18
N2N1C6H16	180	−85.81	0.00	180	−89.81	0.00	179.37	−86.00	−14.13
N1C6C7C8	180	180	180	180	180	180	179.87	180	178.57
C8C7C6H16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−3.30

The values of ΔG and ΔG^* were reported in kcal mol^{-1}. $[T.S.]_n$ means transition state form. See the graphs

molecular ground state and stabilizes the charges in the transition state, thereby decreasing the values of activation energy to rotation. An increase in the size of the substituents at the double bond increases steric strain in the molecular ground state, which also decreases the rotation values of activation energy. Increasing the dielectric constant of the medium favors polarization of the C=C bond in the ground state and separation of charges in the transition saddle, which decreases the barrier to rotation about the C=C bond. The values of activation energy for rotation around the C–N bond are a very useful quantitative characteristic of the structure of enamines [42–44].

The transition state forms of the compounds **3**–**10** were confirmed by the applied DFT method. For this procedure, in this study, the transition state forms ($[\mathbf{T.S.}]_n$; n = **3**, **5**, **7**, **8**, **9**, and **10**) were optimized for the first-order saddle point, which was characterized with only one imaginary frequency.

Due to the delocalization of the electron pair of the nitrogen atom in the aromatic ring of 1,2,3-triazole, the rotation around C–N bond in the structures of *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, **9**, and **10**) calculated by DFT-B3LYP/6-31G* was rather low. The delocalization of the electron pair of the nitrogen atom (inside the aromatic rings and out of the structures N–C=C–C=O) has been restricted due to this reason; so, the energy rotation around C–N bond is low. It is assumed, in this study, that the barrier rotation around C–N is of a greater importance compared to C=C bond. The stable conformers of the *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, **9**, and **10**) were calculated and optimized by

Table 2 The selected structural data of the 1,2,3-triazoles (**8**, **9**, and **10**) and the saddle form of interconversions of the conformers **A** and **B**

Selected data	**8A** ↔ **8B**			**9A** ↔ **9B**			**10A** ↔ **10B**		
	8A $\Delta G = 0.22$	$[\mathbf{T.S.}]_8$ $\Delta G^* = 8.14$	**8B**	**9A** $\Delta G = 0.35$	$[\mathbf{T.S.}]_9$ $\Delta G^* = 8.56$	**9B**	**10A** $\Delta G = 0.60$	$[\mathbf{T.S.}]_{10}$ $\Delta G^* = 6.29$	**10B**
Bond length (Å)									
N1–N2	1.378	1.384	1.384	1.378	1.384	1.383	1.362	1.367	1.367
N2–N3	1.289	1.286	1.286	1.289	1.286	1.286	1.301	1.298	1.298
N3–C4	1.374	1.375	1.375	1.374	1.375	1.376	1.367	1.368	1.368
C4–C5	1.376	1.376	1.376	1.377	1.376	1.376	1.373	1.372	1.372
C5–N1	1.358	1.358	1.358	1.358	1.358	1.359	1.363	1.363	1.363
N1–C6	1.398	1.395	1.395	1.399	1.395	1.395	1.411	1.406	1.406
C6–C7	1.338	1.339	1.339	1.338	1.339	1.339	1.332	1.332	1.332
C7–C8	1.479	1.479	1.479	1.480	1.479	1.480	–	–	–
C6–H16	1.085	1.084	1.085	1.085	1.084	1.084	1.085	1.084	1.084
C7–H17	1.083	1.084	1.081	1.083	1.084	1.085	1.084	1.085	1.084
H16…H18	2.582	3.342	–	2.581	3.332	–	2.543	3.294	–
H17…N2	2.632	3.427	–	2.632	3.414	–	2.622	3.396	–
H17…H18	–	3.826	2.418	–	3.846	2.411	–	3.856	2.404
H16…N2	–	2.938	2.481	–	2.945	2.485	–	2.929	2.453
Bond angle (°)									
N1N2N3	107.49	107.65	107.65	107.49	107.65	107.65	107.45	107.61	107.61
N2N3C4	109.52	109.36	109.36	109.52	109.36	109.35	109.30	109.12	109.12
N3C4C5	108.44	108.68	108.68	108.43	108.68	108.66	108.62	108.87	108.87
C4C5N1	104.52	104.45	104.45	104.52	104.45	104.46	104.35	104.27	104.27
C5N1C6	127.92	131.82	131.82	127.92	131.82	131.68	127.66	131.47	131.47
N1C6C7	124.54	125.47	125.47	124.55	125.47	125.45	124.40	125.58	125.58
C6C7C8	118.36	118.96	118.96	118.42	118.96	118.96	–	–	–
N1C6H16	114.51	112.78	112.78	114.52	112.78	112.90	112.68	111.02	111.02
C6C7H17	122.30	123.32	123.32	122.28	123.32	123.32	121.78	123.28	123.28
Torsional angle (°)									
N2N1C6C7	0.00	91	180	0.00	92	180	0.00	93	180
N2N1C6H16	180	−89	0.00	180	−88	0.00	180	−87	0.00
N1C6C7C8	180	180	180	180	180	180	–	–	–
C8C7C6H16	0.00	0.00	0.00	0.00	0.00	0.00	–	–	–

The values of ΔG and ΔG^* were reported in kcal mol^{-1}. $[\mathbf{T.S.}]_n$ means transition state form. See the graphs

DFT-B3LYP/6-31G* method. The results of the selected structural data i.e., bond lengths in Å, bond angle, (θ) and dihedral angles (Φ) (in °) are demonstrated in the Figs. 2, 3, 4, 5, 6, 7, 8 and 9 for the *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, **9**, and **10**) and Tables 1 and 2. In *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, **9**, and **10**), the conformers "**A**" ($\Phi_{2167} = 0°$) are more stable compared to "**B**" forms ($\Phi_{2167} = 180°$). The **3A**, **5A**, **7A**, **8A**, **9A**, and **10A** are ($\Delta G = 0.45$, 0.50, 0.36, 0.22, 0.35, and 0.60 kcal mol^{-1}) more stable than **3B**, **5B**, **7B**, **8B**, **9B**, and **10B**, respectively. See Tables 1 and 2. To calculate the values of activation energy for rotation around the C–N bond and investigate the interconversion process of the two stable conformers (**A** and **B**) of the *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, **9**, and **10**), the change of the Φ_{2167} dihedral angle around the C–N bond and optimization in each step by DFT-B3LYP/6-31G* method were employed. The reaction coordinate method for **A** and **B** conformers of the *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, **9**, and **10**) was carried out to gain the transition state forms by changing Φ_{2167} from 0° to about 90° and 180° to about 90°. The values of the activation energies around the C–N bond in the process of the interconversion of the two stable conformers (**A** and **B** in **3**, **5**, **7**, **8**, **9**, and **10**) are (ΔG^*) 9.05, 9.41, 5.26, 8.14, 8.56, and 6.29 kcal mol^{-1}, respectively. See Figs. 4, 5, 6, 7, 8, 9 and Tables 1 and 2.

The dihedral angles (Φ_{2167}) in the process of the interconversion of the two stable conformers (**A** and **B** in **3**, **5**, **7**, **8**, **9,** and **10**) are: 94°, 90°, 94°, 91°, 92°, and 93°, respectively. Tables 1 and 2 have shown the calculated

Table 3 The calculated chemical shifts (in vacuum) of H-16 and H-17 of the compounds **3–10**

Compounds and data	Chemical Shifts of H-16 and H-17 of the compounds **3–10**											
	3		**5**		**7**		**8**		**9**		**10**	
	Φ_{2167}		Φ_{2167}		Φ_{2167}		Φ_{2167}		Φ_{2167}		Φ_{2167}	
	0°	180°	0°	180°	0°	180°	0°	180°	0°	180°	0°	180°
H-16	8.16	8.72 (8.50)	8.14 (8.38)	8.79 (8.51)	7.58	8.24	7.72 (6.80)	8.34	7.71	8.33	6.77	7.45
H-17	6.69	5.86 (6.72)	6.73 (6.98)	5.88 (6.71)	7.52	6.57	6.78 (6.65)	5.67	6.81	5.71	6.36	5.12

The values in parentheses are the experimental values of H-16 and H-17 chemical shifts (in $CDCl_3$)

results for the distances between H6···H18 and H7···H18 in the two stable conformers (**A** and **B** in **3**, **5**, **7**, **8**, **9**, and **10**). The distances between H16···H18 and N2···H17 of the stable conformers (**A** in **3**, **5**, **7**, **8**, **9**, and **10**) are: (2.461, 2.669), (2.466, 2.664), (2.442, 2.535), (2.582, 2.632), (2.581, 2.632), and (2.543, 2.622) Å, respectively. The distances between H17···H18 and N2···H16 of the **B** rotamers (in **3**, **5**, **7**, **8**, **9**, and **10**) are: (2.071, 2.439), (2.074, 2.438), (2.107, 2.443), (2.418, 2.481), (2.411, 2.485), and (2.404, 2.453) Å, respectively. In the transition state of **A** ↔ **B**, the interatomic distances of H16···H18, N2···H17, H16···H18 and N2···H17 (**3**, **5**, **7**, **8**, **9**, and **10**) are: (3.511, 3.512, 3.771 & 2.965), (3.453, 3.463, 3.883 & 2.992), (3.496, 3.403, 3.711 & 2.950), (3.342, 3.427, 3.826 & 2.938), (3.332, 3.414, 3.846 & 2.945), and (3.294, 3.396, 3.856 & 2.929) Å, respectively. Derivative **10** was not synthesized here. This molecule was calculated to compare its data with other molecules (structures **8** and **9**). See Figs. 4, 5, 6, 7, 8, 9 and Tables 1 and 2.

In the stable conformers **7A** and **7B,** the dihedral angles Φ_{2167} are not 0 and 180°, respectively. The dihedral angles Φ_{2167} for **7A** and **7B** were calculated as 0.63° and about 164°, respectively. The conformer **7B** in $\Phi_{2167} = 164°$ is 0.018 kcal mol^{-1} more stable than this conformer in $\Phi_{2167} = 180°$. Because of aromatization in the 1,2,3-triazole rings, the values of activation energy rotation around C–N bond are lower than the ordinary enamines. See Tables 1 and 2. Due to delocalization of the electron pair of the nitrogen atom inside the 1,2,3-triazole aromatic rings, the calculated magnitude of ΔG^* for rotation around C–N bond in such structures (N–C=C–C=O) is rather low (from about 5–10 kcal mol^{-1}). An increase in electron-donating power and acceptor capacity decreases the energy barrier to the rotation.

The two rotamers **A** and **B** for each of the structures were obtained due to the low values of activation energy of C–N bond rotation in the structures of *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, **9**, and **10**). The interconversion of the isomers **A** and **B** is very simple because of the delocalization of the electron pair of the nitrogen atom in the aromatic rings of the 1,2,3-triazoles. So, there is no resonance between this nitrogen atom and C=C (like the ordinary eneamines). The interactions between these compounds with the receptors, considering their medicinal effects, are closely related to the structures of their isomers **A** and **B**. The physicochemical properties as well as the structural properties are related to this phenomenon. One of the important investigations related to this property is the chemical shifts of the H-vinyl atoms in the structures.

The chemical shifts (in vacuum state) for H-16 and H-17 of the compounds **3–10** were calculated by DFT-B3LYP/6-31G* method. The rotation around C–N bond (Φ_{2167}) in the structures of *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, **9**, and **10**) has made different chemical shifts for the H-atoms. The calculated chemical shifts in non-solvent conditions by DFT-B3LYP/6-31G* method are demonstrated in Table 3. The values in parentheses are the experimental values of H-16 and H-17 chemical shifts (in $CDCl_3$). The different chemical shifts are related to the different local shielding of the H-atoms that occurs because of the interconversion between the rotamers **A** and **B** of compounds **3–10**. There is good agreement between the theoretical and experimental results. As it can be seen in Table 3, the calculated chemical shifts of H-16 and H-17 for **3** and **5** were 8.72 and 5.86 ppm, respectively, when Φ_{2167} was 180°. The ^{1}H-NMR experimental data for the introduced hydrogen atoms in the structures and in $CDCl_3$ were obtained: 8.50 and 6.72 ppm, respectively. The experimental and calculated data for the chemical shifts of H-16 and H-17 in **5** and **8** (when $\Phi_{2167} = 0°$) were: {8.14 (8.38), 6.73 (6.98)} and {7.72 (6.80), 6.78 (6.65)}, respectively. See Table 3.

Typical procedure for synthesis

3-Benzotriazol-1-yl-acrylic acid methyl ester (**3**)

A mixture of benzotriazole **1** (0.06 g, 5 mmol) and methyl propiolate **2** (0.8 g, 1.0 ml, 0.01 mol) was made in a dried heavy wall Pyrex tube. The tube was sealed and then exposed to microwave oven. After 15 min irradiation at 200 W (100 °C) power, the mixture was cooled to room temperature. The residue of compounds was evaporated under air and reduced pressure. An off-white solid was afforded. The product **3** can be recrystallized from dried diethyl ether.

Conclusion

Here a fast one-pot microwave-assisted solvent-free with high-oriented synthesis of simple *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, and **9**) derivatives by nucleophilic addition reactions of 1,2,3-benzotriazole **1** and **1′** with alkyl-propiolates (**2** and **4**) and phenylacetylene **6** is reported. The C_β of the reactants **2** and **4** should have enough $\delta+$ charge for the reactions of **1** and **1′** on **2** and **4**. The symmetry reactants of **6**, DMAD, and DEAD do not have this suitable condition for this regio- and chemo-selectivity. The results of the procedure confirmed the facility and rapidity of this solvent-free with high-oriented synthesis of **3**, **5**, **7**, **8**, and **9** derivatives by the nucleophilic additional reaction. The calculations on the structures of the synthesized *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, and **9**) were performed by the DFT method. In this study, the computational method employed cover density functional theory (DFT) approaches. The structure of the *N*-alkenyl-1,2,3-triazole (**3**, **5**, **7**, **8**, and **9**) was optimized by DFT-B3LYP/6-31G* method. The values of activation energy for rotation around C–N bond in the synthesized *N*-alkenyl-1,2,3-triazole compounds were studied by DFT-B3LYP/6-31G* method.

Acknowledgments The corresponding author gratefully acknowledges Professor Curt Wentrup and the colleagues in Chemistry Department of The University of Queensland, Australia, for their useful suggestions and for permitting to use CEM Labmate microwave reactor for some of the MW tests during the sabbatical opportunity. We have also acknowledged Theoretical and Computational Research Center of Chemistry Faculty of Razi University, Kermanshah, Iran and the Research Council of Science and Research Campus, Islamic Azad University, Tehran, Iran for permitting to use the Labmate microwave reactor (Milstone-Ethos 1.; 2,540 Hz, Max 1,200 W).

References

1. Savin KA, Robertson M, Gernet D, Green S, Hembre EJ, Bishop J (2003) Mol Diver 7:171
2. Garanti L, Molteni G (2003) Tetrahedron Lett 44:1133
3. Molteni G, Buttero PD (2005) Tetrahedron 61:4983
4. Alvarez R, Velazquez S, San F, Aquaro S, De C, Perno C, Karlsson A, Balzarini J, Camarasa JM (1994) J Med Chem 37:4285
5. Velazquez S, Alvarez R, Perez C, Gago F, De C, Balzarini J, Camarasa MJ (1998) Antivir Chem Chemother 9:481
6. Genin MJ, Allwine DA, Andersn DJ, Barbachyn MR, Grega KC, Hester JB et al (2000) J Med Chem 43:953
7. Appukkuttan P, Dehaen W, Fokin VV, Van der Eyken E (2004) Org Lett 6(23):4223
8. Wamhoff H (1984) In: Katrizky AR, Rees CW (eds) Comprehensive heterocyclic chemistry, vol 5. Pergamon Press, New York, p 669
9. Taherpour AA, Kvaskoff D, Bernhardt PV, Wentrup C (2010) J Phys Org Chem 23:382
10. Taherpour AA, Kheradmand K (2009) J Heterocycl Chem 246:131
11. Taherpour AA, Faraji M (2008) Molbank M577:1
12. Taherpour AA, Rajaian E (2008) J Mol Struct (THEOCHEM) 849:23
13. Taherpour AA, Adams N, Wentrup C (2007) Fourth Heron island conference on reactive intermediates and unusual molecules, Queensland, Australia, 7–14 July 2007
14. Taherpour AA, Rajaeian E, Shafiei H, Malekdar M (2013) Struct Chem 24:523
15. Smiley RA (2002) Phenylene- and toluene diamines in Ullmann's encyclopedia of industrial chemistry. Wiley, Weinheim
16. Giger W, Schaffner C, Kohler HP (2006) Environ Sci Technol 40:7186
17. Shi F, Waldo JP, Chen Y, Larock RC (2008) Org Lett 10:2409
18. Balan A, Baran D, Toppare L (2011) Polym Chem 2:1029
19. Carta A, Piras S, Boatto G, Paglietti G (2005) Heterocycles 65(10):2471
20. Carta A, Sanna P, Paglietti G, Sparatore F (2001) Heterocycles 65(6):1133
21. Stadier A, Kappe CO (2005) Microw Assist Org Synth 2:177
22. Kappe CO (2004) Angew Chem Int Ed 43:6250
23. Kappe CO, Stadler A (2005) Microwaves in organic and medicinal chemistry. Wiley, Weinheim
24. Zbancioc NG, Caprosu DM, Moldoveanu CC, Ionel II (2005) ARKIVOC 10:189
25. Katrisky AR, Singh SK (2003) ARKIVOC 13:68
26. Ling MJ, Sun CM (2004) Synlett 4:663
27. Dai W-M, Guo D-S, Sun L-P, Huang X-H (2003) Org Lett 5(16):2919
28. Finaru A, Berthault A, Besson T, Guillaument G, Berteina-Raboin S (2002) Org Lett 4(16):2613
29. Hoel MLA, Nielsen J (1999) Tetrahedron Lett 40(20):3941
30. Gedye R, Smith F, Westaway K, Ali H, Baldisera L, Laberge L, Rousell J (1986) Tetrahedron Lett 27:279
31. Katrisky AR, Singh SK (2002) J Org Chem 67:9077
32. Sha C-K, Mohanakrishnan AK (2002) In: Padwa A, Pearson WH (eds) Chemistry of heterocyclic compounds, vol 59. Wiely, New York
33. Gilchrist TL, Gymer GE (1974) In: Katrizky AR, Boulton AJ (eds) Advances in heterocyclic chemistry, vol 16. Academic Press, New York
34. Padwa A (1984) In: Taylor EC, Weissberger A (eds) 1,3-Dipolar cycloaddition chemistry, vol 1. Wiely, New York
35. Sheradsky T (1971) In: Patai S (ed) The chemistry of the Azido group. Wiley, New York
36. Guezguez R, Bougrin K, El Akriand K, Benhida R (2006) Tetrahedron Lett 47:4807
37. Molteni G, Del Buttero P (2005) Tetrahedron 61(21):4983
38. Kabir MS, Namjoshi OA, Verma R, Lorenz M, Phani Babu Tiruveedhula VVN, Monte VVN, Bertz SH, Schwabacher AW, Cook JM (2012) J Org Chem 77(1):300
39. Kabir MS, Namjoshi OA, Verma R, Verma R, Polanowski R, Krueger SM, Sherman D, Rott MA, Schwan WR, Monte A, Cook JM (2010) Bioorg Med Chem 18(12):4178
40. Katritzky AR, Rachwal S, Caster KC, Mahni F, Law KW, Rubio O (1987) J Chem Soc Perkin Trans 1(4):781
41. (2011) All of the calculations were performed by: Spatran'10-Quantum Mechanics Program: (PC/x86) 1.1.0v4. Wavefunction, USA
42. Bakhmutov VI, Fedin EI (1982) Bull Mag Reson 6(3):142
43. Kalinowski HO, Kessler H (1972) In: Allinger NL, Eliel EL (eds) Topics in stereochemistry, vol 7. Wiley, New York, p 296
44. Azzaro M, Geribaldi S, Videau B (1985) Magn Reson Chem 23(1):28