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DFT studies of the structure and vibrational and NMR spectra of 1-(2-methylpropenyl)-2-methylbenzimidazole

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ABSTRACT

Synthesis of two new 1-(2-methylpropenyl)-2-methylbenzimidazoles by reaction of 2-methylbenzimidazole with 3-chloro-2-methylpropene using a strong base as a catalyst is described. Gas chromatography–mass spectrometry (GC–MS) allowed the characterization of the structural isomers: the slightly more stable 1-(2-methyl-1-propenyl)-2-methylbenzimidazole (51%) and a less stable 1-(2-methyl-2-propenyl)-2-methylbenzimidazole (49%). The results of theoretical calculations indicate that the difference in the energy between the two structural isomers is 3.21 kcal mol^{-1} at the B3LYP/6-311+G** level. The structures were confirmed by ^{1}H and ^{13}C Nuclear Magnetic Resonance, elemental analysis and spectroscopic methods such as FT-Raman, FT-IR and UV–VIS. The experimental results were supported by performing DFT calculations for energies, geometries, vibrational frequencies and shieldings constants using 6-311+G** basis sets and B3LYP functional. The theoretical data have satisfactorily reproduced the experimental results. The consistency and efficiency of the GIAO method used to calculate absolute shielding of the studied compounds were checked by the analysis of statistical parameters and were found to be in excellent agreement with experimental values. This correlation has been used for unambiguous NMR signal assignments for studied compounds.

1. Introduction

Substituted benzimidazoles have drawn considerable attention in medicinal chemistry due to a wide range of biological activities exerted by this class of compounds [1–7]. Benzimidazole is also of interest as a corrosion inhibitor for metal and alloys and other industrial applications [8–9]. In previous recent works, the structural properties of two 1-alkyl-2-methylbenzimidazoles compounds [10] and the isomers of 1-alkenyl-2-propenyl-2-methylbenzimidazoles [11] were studied. In the present work, as part of our investigations in the field of *N*-substituted benzimidazoles, we extend the studies to the synthesis and the experimental and theoretical structural characterization of the isomers of new 1-(2-methylpropenyl)-2-methylbenzimidazole derivatives. In the synthesis of these derivatives a method that has been applied successfully for *N*-alkylation of indoles and pyrroles using KOH as base in DMSO [12] was employed. Scheme 1 shows the structures of the investigated compounds. GC–MS analyses of the purified product allowed identification and characterization of two structural isomers: the 1-(2-methyl-1-propenyl)-2-methylbenzimidazole and the 1-(2-methyl-2-propenyl)-2-methylbenzimidazole with 51% and 49% abundance, respectively. The structures of the compounds were confirmed by Nuclear Magnetic Resonance (^{1}H and ^{13}C) analysis and their purity was checked by elemental analysis. The experimental FT-IR and FT-Raman spectra were obtained for the mixture of structural isomers of 1-(2-methylpropenyl)-2-methylbenzimidazole. For the interpretation of the experimental results, the energies, geometries, harmonic vibrations and shieldings constants of the structural isomers were calculated by density functional theory (DFT) [13] using 6-311+G** basis set and B3LYP functional [14,15]. The theoretical Raman and IR DFT spectra were obtained incorporating the contribution of each isomer in accordance the respective percentage in the isomeric mixture that was determined by gas chromatography analysis. The wavenumber-linear scale (WLS) method [16] was used to reproduce the experimental vibrational data in order to reduce the overestimation associated with DFT calculations. Vibrational frequency assignments were made with the aid of the GaussView 03 program [17]. Calculations on proton and carbon magnetic shielding values were carried out in solution and using the gauge independent atomic orbital (GIAO) [18] approach. The solvent effects on NMR data were introduced by the IEF-PCM method [19] implemented in the GAUSSIAN 03 program [20]. Basic experimental and theoretical information about a 1-(2-methylpropenyl)-2-methylbenzimidazole and its structural isomer is presented and discussed. To the best of our knowledge to date, no evidence of similar studies for the 2-methylbenzimidazole and this alkenyl derivative has been reported in the open chemical literature.

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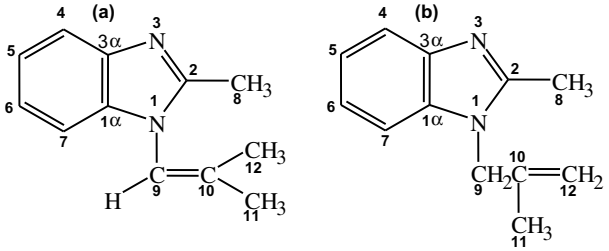

Scheme 1. Atom numberings and studied compounds. (a) 1-(2-Methyl-1-propenyl)-2-methylbenzimidazole and (b) 1-(2-methyl-2-propenyl)-2-methylbenzimidazole.

2. Materials and methods

2.1. General procedure for the synthesis

The compound 2-methylbenzimidazole was obtained in solid form from Sigma–Aldrich Chemical Co., and was used without further purification. In the synthesis of 1-(2-methylpropenyl)-2-methylbenzimidazole derivatives, 2-methylbenzimidazole and alkenyl halide were added to powder KOH stirred in DMSO at room temperature under nitrogen. The crude product was purified by recrystallization with methylene chloride. The compounds included in this study are shown in Scheme 1.

2.2. Physical methods

GC–MS analyses were performed using a Hewlett–Packard 5890 series II Gas Chromatograph coupled with a Hewlett–Packard model 5970 mass selective detector. A Supelco SPB-5 capillary column (length: 30 m × 0.25 mm i.d.) was used for the chromatographic separation. The helium carrier gas was set to a flow rate of 0.9 mL/min. The oven temperature was initially at 70 °C (held for 10 min) and then increased to 250 °C at 10 °C/min. The percentage composition of the compounds was computed from GC peak areas using the area normalization method. The mass spectrometer was operated in positive ion detection after electron impact ionization mode with ionization energy of 70 eV. The ion source temperature was maintained at 280 °C.

The room temperature Fourier transform infrared spectra of the title compound were measured on a Perkin-Elmer System 2000 FT-IR spectrometer in the 4000–400 cm^{-1} region with 4 cm^{-1} resolution. Raman spectra were recorded with a Bruker Optics RFS-100 Fourier transform Raman spectrometer (excitation source: Nd:YAG, 1064 nm). The measurement of the spectra was performed in the range of 100–3600 cm^{-1}, Stokes region, with 1 cm^{-1} spectral resolution.

The ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 FT-NMR spectrometer. Internal lock was provided by a deuterated DMSO solvent (δ = 39.51 ppm) and both proton and carbon signals were referenced to TMS. All NMR spectra were measured at room temperature.

2.3. Computational methods

GAUSSIAN 03 [20] software package was used for all theoretical calculations. Absolute, relative, and zero-point energies of 1-(2-methyl-1-propenyl)-2-methylbenzimidazole 1-(2-methyl-2-propenyl)-2-methylbenzimidazole are given in Table 1. The bond lengths and bond angles determined at the DFT level of theory for the structural isomers of the 1-(2-methylpropenyl)-2-methylbenzimidazole are listed in Table 2. The vibrational frequencies and corresponding normal modes were then evaluated at the optimized geometry using the same basis set. The vibrational modes were analyzed using the GaussView 03 software [17]. Also, the same basis set and computational method was used for the ^1H and ^{13}C NMR shielding constants calculations by applying the GIAO method. The effect of solvent on the theoretical NMR parameters was included using the default model IEF-PCM provided by Gaussian 03. Dimethylsulfoxide (DMSO), which has a dielectric constant (ε) of 46.7, was used as solvent.

3. Results and discussion

3.1. Synthesis of 1-(2-methylpropenyl)-2-methylbenzimidazole

Potassium hydroxide KOH (2.13 g, 47.9 mmol) was dissolved in 20.0 mL of dimethylsulfoxide with stirring in a 250 mL round-bottomed flask under a N_2 atmosphere. 2-Methylbenzimidazole (4.07 g, 30.8 mmol) was added and the mixture was stirred for 2 h, upon which 3-chloro-2-methylpropene (3.0 mL, 30.7 mmol) was transferred. The mixture was stirred at room temperature for 20 h under a N_2 atmosphere. The reaction mixture was diluted with dichloromethane and washed several times with water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed. Purified product was isolated and GC–MS method analysis evidenced the presence of two isomers. 1-(2-Methylpropenyl)-2-methylbenzimidazole was obtained as a brown solid: 93% yield (2-propenyl isomer 49% and 1-propenyl isomer 51%); mp 49–50 °C. The mass spectrum produced by electron impact (EI) ionization showed signals at *m/e*: 186(M^+.), 171, 156, 145, 130, 118, 102, 91, 77, 63, 50 and 39. Elemental analysis confirmed the calculated percent compositions of $C_{12}H_{14}N_2$: C, 77.41%; H, 7.52%; N, 15.05%. The values obtained were C, 77.45%; H, 7.58; N, 15.03%.

3.2. Theoretical and experimental spectroscopic data

UV–VIS spectrum of 1-(2-methylpropenyl)-2-methylbenzimidazole is characterized by four bands in the deep UV (DUV) region: 283, 276, 253 and 228 nm. The absorption bands of parent compound (280, 274 and 245 nm) were displaced to longer wavelength and intensified by conjugation with the double bond of the 2-methylpropenyl group. The absorptions that result from transitions within 2-methylbenzimidazole and derivatives chromophore are basically of the $\pi \rightarrow \pi^*$ type. To explore the effect of 2-methylpropenyl substituent in relation to its attachment on the π-system, we compared the experimental UV–Vis absorptions with those obtained by DFT configuration interaction approach (CIS). The excitation energies were systematically underestimated in gas phase. Theoretically, we observed major energetic shifts for the $\pi \rightarrow \pi^*$ excitations. Table 3 summarizes the observed and calculated absorption energies for benzimidazole and its *N*-substituted derivatives. Concerning the 1-propenyl-2-methylbenzimidazole spectrum, the deviations between theoretical and experimental results is of the same order of magnitude as those obtained for 1-(2-methylpropenyl)-2-methylbenzimidazole.

Table 1
Absolute and relative energies for the studied compounds

Isomer	Absolute energy (Hartrees)	Zero point energy (kcal/mol)	Relative[a] energy (kcal/mol)
1-(2-Methyl-1-propenyl)-2-methylBZM	−575.367380	146.36	0.00
1-(2-Methyl-2-propenyl)-2-methylBZM	−575.361325	146.94	3.21

[a] Zero-point-corrected energies relative to 1-(2-methyl-1-propenyl)-2-methylbenzimidazole isomer BZM, benzimidazole.

Table 2
Optimized parameters of 1-(2-methylpropenyl)-2-methylbenzimidazole and isomers obtained by B3LYP/6-311+G** calculations

Parameters	2-MethylBZM		1-(2-Methyl-1-propenyl) 2MBZM	1-(2-Methyl-2-propenyl) 2MBZM
Bond lengths (Å)	*X-ray*[a]	*Calculated*	*Calculated*	*Calculated*
N_1—C_2	1.335	1.3827	1.3914	1.3884
C_2—N_3	1.339	1.3083	1.3088	1.3103
N_3—$C_{3\alpha}$	1.389	1.3891	1.3868	1.3853
$C_{3\alpha}$—$C_{1\alpha}$	1.395	1.4130	1.4120	1.4128
$C_{1\alpha}$—N_1	1.383	1.3852	1.3930	1.3892
$C_{3\alpha}$—C_4	1.379	1.3975	1.3976	1.3977
C_4—C_5	1.382	1.3901	1.3903	1.3899
C_5—C_6	1.395	1.4068	1.4068	1.4067
C_6—C_7	1.360	1.3918	1.3922	1.3920
C_7—$C_{1\alpha}$	1.389	1.3933	1.3935	1.3951
C_2—C_8		1.4918	1.4912	1.4920
C_9—C_{10}			1.3377	1.5188
C_{10}—C_{11}			1.5035	1.5051
C_{10}—C_{12}			1.5055	1.3340
C_4—H_4		1.0834	1.0836	1.0836
C_5—H_5		1.0839	1.0841	1.0840
C_6—H_6		1.0839	1.0841	1.0840
C_7—H_7		1.0841	1.0834	1.0839
C_8—H_8		1.0917	1.0925	1.0924
C_9—H_9			1.0865	1.0931
C_{11}—H_{11}			1.0942	1.0936
C_{12}—H_{12}			1.0934	1.0845/1.0852
N_1—C_9			1.4243	1.4617
Bond angles (°)				
N_1—C_2—N_3	112.7	112.4	123.0	112.9
C_2—N_3—$C_{3\alpha}$	106.3	105.6	105.6	105.6
N_3—$C_{3\alpha}$—$C_{1\alpha}$	107.6	110.1	110.2	110.1
$C_{3\alpha}$—$C_{1\alpha}$—N_1	107.2	110.1	105.1	105.0
$C_{1\alpha}$—N_1—C_2	106.1	107.3	106.2	106.4
$C_{3\alpha}$—C_4—C_5	118.2	118.1	118.1	118.1
C_4—C_5—C_6	121.9	121.3	121.3	121.3
C_5—C_6—C_7	120.7	121.4	121.5	121.5
C_6—C_7—$C_{1\alpha}$	117.6	116.7	116.9	117.0
C_7—$C_{1\alpha}$—$C_{3\alpha}$	122.1	122.5	122.4	122.1
C_7—$C_{1\alpha}$—N_1			132.6	132.8
$C_{1\alpha}$—N_1—C_9			127.1	126.6
N_1—C_9—C_{10}			124.3	114.3
C_9—C_{10}—C_{11}			120.0	116.9
C_9—C_{10}—C_{12}			123.8	120.2
$C_{3\alpha}$—C_4—H_4			120.3	120.2
C_4—C_5—H_5			119.6	119.6
C_5—C_6—H_6			119.3	119.3
C_6—C_7—H_7			121.4	120.7
C_2—C_8—H_8			110.5	110.5
C_9—C_{10}—H_{12}			123.8	120.2
C_{10}—C_9—H_9			120.6	109.8
C_{10}—C_{11}—H_{11}			111.1	111.1
C_{10}—C_{12}—H_{12}			111.1	121.6/121.7
N_1—C_9—H_9			115.1	107.9

[a] Ref. [21]; BZM, benzimidazole; for numbering of atoms refer to Scheme 1.

Table 3
Observed and calculated absorption spectra of benzimidazole and its 1-propenyl derivatives

Compound	Experimental λ's max (nm)	Calculated[a] λ's max (nm)
Benzimidazole	278, 272, 267, 248	250, 224, 204, 198
2-Methylbenzimidazole	280, 274, 245	251, 238, 202
1-Propenyl-2-methylbenzimidazole	283, 276, 252, 230	
E-1-Propenyl-2-methylbenzimidazole		269, 256, 240, 231
Z-1-Propenyl-2-methylbenzimidazole		261, 254,242, 230
2-Propenyl-2-methylbenzimidazole		256, 254, 244, 231
1-(2-Methylpropenyl)-2-methylbenzimidazole	283, 276, 253, 228	
1-(2-Methyl-1-propenyl)-2-methylbenzimidazole		256, 250, 244, 233
1-(2-Methyl-2-propenyl)-2-methylbenzimidazole		256, 244, 242, 230

[a] Calculated with CIS/DFT 6-311+G**.

The molecular structures with atom numbering taken from geometries optimizations are shown in Scheme 1. Absolute, relative and zero-point energies obtained by the DFT structure optimization for both isomers are presented in Table 1. The calculations yielded a difference of 3.21 kcal mol^{-1} between the two structural isomers. As expected, the model shows that the lowest-energy for 1-propenyl isomer is in accordance with the stabilizing effect generated by the higher degree of substitution on a double bond system.

Table 2 presents the optimized structure parameters of 1-(2-methylpropenyl)-2-methylbenzimidazole molecules calculated by B3LYP level with the 6-311+G** basis. These structures were compared with that of 2-methylbenzimidazole, for which the crystal structure has been solved [21]. The bicycle system of 2-methylbenzimidazole is planar and the methyl group at atom C_8 deviates from the plane by 0.054°. As a result of partial protonation of both nitrogen atoms the C—N bond lengths area approximately equal in imidazole ring. The optimized geometry of 2-methylbenzimidazole in the ground state corresponds to *Cs* symmetry and the calculated bond lengths and bond angles with the computational method yielded a 0.04 Å and 2.9° discrepancy relative to the X-ray values.

Substitution of hydrogen atom by a 2-methylpropenyl group in N_1 causes small changes in imidazole ring interatomic distances. The benzimidazole nitrogen bonds have a shorter distance than amine, which is due to the lone pair electron of nitrogen involved in benzimidazole rings. The optimized bond lengths of C—N in imidazole ring fall in the range from 1.3083 to 1.389 Å for 2-mehylbenzimidazole and 1.3088 to 1.395 Å for 1-(2-methylpropenyl)-2-methylbenzimidazole. By comparing these values with experimental values it is observed that the B3LYP overestimates them. The C—N bond distance is found overestimated by 0.04 ± 0.01 Å. The results show essentially non-planar benzimidazole and 2-methylpropenyl groups (heavy atoms) and an angle between the two planes (torsion angle C_2—N_1—C_9—C_{10}) of 117°. The 6-31G basis set with d and p polarization functions predict a planar geometry for the benzimidazole skeleton and no-planar methyl groups in the 2-methylpropenyl fragment. It is the inclusion of polarization functions which determines the non planarity of the methyl groups.

For the structural isomers of 1-(2-methylpropenyl)-2-methylbenzimidazole, it can be seen that the corresponding bond lengths and bond angles of the benzimidazole ring are almost equal except that some corresponding imidazole ring parameters have small differences with respect to benzimidazole. From compound 1-propenyl-2-methylbenzimidazole to 1-(2-methylpropenyl)-2-methylbenzimidazole, the C=C double bond lengths exhibit an increasing tendency. The influence of propenyl and 2-methylpropenyl substitution on the imidazole ring angles is also notable, particularly in the N_1—C_2—N_3 bond angle. In the present study, the calculated C=C double bond length (C_9—C_{10} and C_{10}—C_{12}) for 1-propenyl to 2-propenyl isomer is shorter by 0.004 Å. The largest bond length difference (0.04 Å) can be attributed to a N_1—C_9 bond distance that corresponds to the bond between the 2-methylpropenyl group and the 2-methylbenzimidazole ring. There are slight differences in a few of the bond angles. The largest difference involves N_1—C_9—H_9 and the bond angles in double-bond isomers. The isomer with most highly substituted double bond has a larger angular separation between the methyl groups.

The two isomers of 1-(2-methylpropenyl)-2-methylbenzimidazole have C_1 symmetry with 28 atoms and 78 fundamental normal modes of vibration. The assignments of vibrational frequencies of the mixture of isomers of 1-(2-methylpropenyl)-2-methylbenzimidazole (1-propenyl and 2-propenyl) based on normal mode analysis are presented in Table 4, which lists the experimental and the calculated scaled frequencies. The experimental and calculated FT-IR and FT-Raman spectra for the isomeric mixture of 1-(2-methylpropenyl)-2-methylbenzimidazole are presented in a common frequency scale in Figs. 1 and 2, respectively. The mode number assignments are made from comparisons of experimental spectra and the theoretical calculations. Very weak signals were not labeled. The reported experimental FT-IR intensities for the isomer mix are comparable with the ones obtained theoretically. The problem of the overestimation common in DFT vibrational frequencies, due to neglecting of anharmonicity effects, was solved

Table 4
Observed and calculated selected frequencies (cm-1) and assignments of the fundamental modes for isomers mix of 1-(2-methylpropenyl)-2-methylbenzimidazole

Mode no.	1-(2-Methylpropenyl)-2-methylbenzimidazole			
	FT-IR (cm^{-1})	FT-Raman (cm^{-1})	Calc.[a] (cm^{-1})	Assignment[b,c] (cm^{-1})
1	3046	3061	3051	$\nu^{as}CH_{(Bz)}$
2		3004	3006	$\nu^{s}H$—C=
3	2974	2926	2897	$\nu^{s}H$—$C_{Met)}$
4	1681	1657	1677	νC=C
5	1618		1619	$\nu C{=}C_{(Bz)}$
6		1588	1591	νC=C/Bz
7	1525	1519	1537	$\nu C{=}N_{(Im)}$,ν $C{=}C_{(Bz)}$
8	1456	1449	1457	$\beta CH_{Met)}$, β CH_{BZ}
9	1401		1399	$\gamma CH_{Met)}$
10		1378	1380	$\gamma CH_{Met)}$
11	1334	1328	1341	γCH_2
12		1281	1293	βCH_{BZ},ν C—$N_{(Im)}$, γ CH_2
13		1256	1270	βCH_2
14	1234	1230	1245	βCH_{BZ},ν C—$N_{(Im)}$
15	1170		1167	βCH_{BZ}
16		1145	1148	βCH_{BZ}
17		1104	1110	βCH_{BZ}
18	1055		1053	$\gamma CH_{Met)}$
19	1017	1010	1019	$\gamma CH_{Met)}$
20	932		933	γH_2C=
21		887	884	$\beta def_{(BZ+Im)}$, βCH_2
22	814	855	825	$\gamma CH_{BZ,}$ rg $_{breathing}$
23		776	786	γH_2C=
24	721		740	γCH_{BZ}
25		670	678	$\beta def_{(BZ+Im)}$, γH_2C=
26		618	619	$\beta def_{(BZ+Im)}$, γH_2C=
27		500	502	$\beta def_{(BZ)}$

[a] Calculated with B3LYP/6-311+G**; scaled according to correlation equation $\nu_{obs.}/\nu_{calc.} = 1.0087(9) - 0.0000163$ $(\nu_{calc.}/cm^{-1})$ [16].
[b] Vibrational modes: ν, stretching, β, in-plane bending; γ, out-of-plane bending; rg, ring; def, deformation; superscript *s*, symmetric; superscript *as*, asymmetric; Bz, benzene; Im, imidazole; Met, methyl.
[c] Estimated graphical representation.

using the wavenumber-linear scaling method (WLS) performed by Yoshida et al. with the following relationship:

$$\nu_{obs.}/\nu_{calc.} = 1.0087(9) - 0.0000163(6)(\nu_{calc.}/cm^{-1}) \quad (1)$$

Combining the results of experimental FT-IR and FT-Raman data with the theoretical calculations, vibrational frequency assignments were made with a high degree of confidence. The calculated and scaled frequencies are very close to the corresponding experimental values.

In the higher frequency region, the ν_{C-H} asymmetric mode of vibration associated with the benzene ring (1) is observed at 3046 and 3061 cm^{-1} in the FT-IR and FT-Raman spectra, respectively. A weak Raman band at 3006 cm^{-1} (2) is assigned to a sp^2C—H stretching mode. The C—H alkyl stretching vibrations (ν_{C-H}) of the title compound have been assigned to the signals observed at 2974 cm^{-1} in the FT-IR spectrum and at 2926 cm^{-1} in the FT-Raman spectrum (3). The weak IR and Raman bands at 1681 and 1657 cm^{-1}, respectively, are assigned to a stretching mode of the C=C double bond (4). In the FT-IR and FT-Raman spectra of 1-propenyl-2-methylbenzimidazole, the C=C stretching bands appear at 1658 and 1662 cm^{-1}, respectively [11]. The aromatic ring stretching modes were observed in the region between 1618 and 1588 cm^{-1} (5, 6). Complete analogies can also be found in the case of 1-propenyl-2-methylbenzimidazole. The $\nu_{C=N}$ mode was found at 1525 and 1519 cm^{-1} (8). In addition, the ν_{C-N} stretching in the imidazole ring was identified at 1281 cm^{-1} (12) in combination with other in-plane and out-of-plane bending modes. A group of four bands (modes 9, 10, 18 and 19) have been assigned as out-of-plane bending modes (γ_{C-H}) of the methyl groups. In the spectra

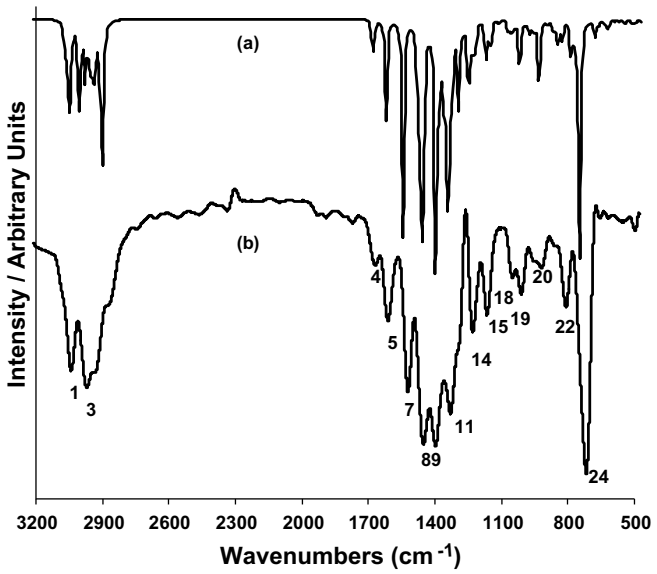

Fig. 1. Theoretical and experimental FT-IR spectra from 500 to 3200 cm^{-1} for isomers mix of 1-(2-methylpropenyl)-2-methylbenzimidazole: (a) calculated and scaled and (b) experimental. Labeled peaks are explained in Table 4.

of 1-(2-methylpropenyl)-2-methylbenzimidazole, the C—H in-plane modes (β_{C-H} of benzene appear as a series of bands (modes 14,15,16,17) in the spectral range 1100–1240 cm^{-1}, while in 1-propenyl-2-methylbenzimidazole these modes appear in the 1006–1284 cm^{-1} region. In the FT-IR spectrum, the presence of out-of-plane C—H bending mode in benzene ring (24) was observed at 721 cm^{-1}. This band is shifted in the FT-IR spectrum of 1-propenyl-2-methylbenzimidazole to 711 cm^{-1}. A medium intensity Raman band located at 1256 cm^{-1} is assigned to an in-plane bending mode of CH_2 in vinyl group (13); the corresponding out-of-plane IR (20) and Raman (23) band was observed at 932 and 776 cm^{-1}, respectively.

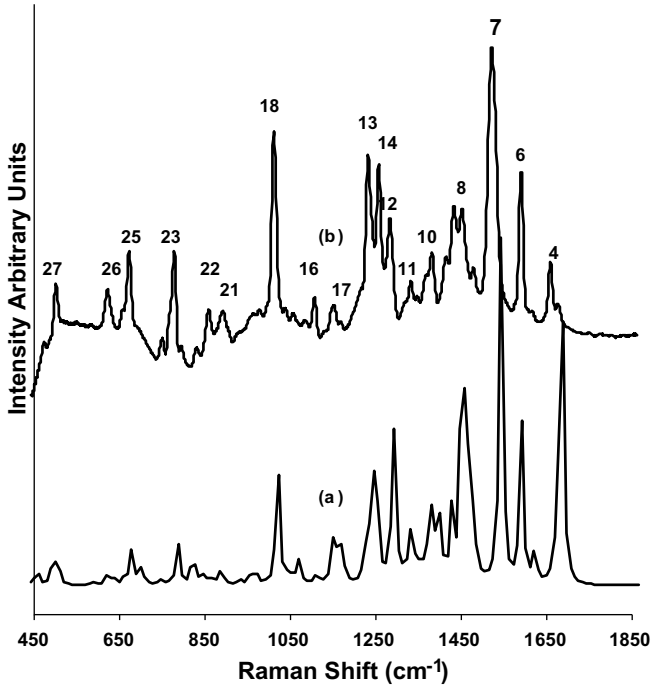

Fig. 2. Theoretical and experimental FT-Raman spectra from 450 to 1850 cm^{-1} for isomers mix of 1-(2-methylpropenyl)-2-methylbenzimidazole: (a) calculated and scaled and (b) experimental. Labeled peaks are explained in Table 4.

The C—C ring breathing mode is readily assigned to the band at 814 and 855 cm^{-1} in the IR and Raman spectrum, respectively. The remaining modes (25, 26 and 27) in the 700–500 cm^{-1} region can be associated with the deformations of the benzene and imidazole rings. These correspond to a mix of vibration modes such as ring breathing, C—H out-of-plane modes (γ_{C-H}) and ring skeletal in plane and out-of-plane deformations (β_{C-C-C} and γ_{C-C-C}). The same assignment can be done for 1-propenyl-2-methylbenzimidazole in modes below 700 cm^{-1}. All assignments and vibrational frequencies are in agreement with typical values recently reported for the benzimidazole ring [22,23].

The NMR chemical shifts of two possible structures were calculated by B3LYP/6-311+G** hybrid functional using GIAO approximation. The ^1H and ^{13}C shieldings were converted into the predicted chemical shifts using δTMS values, calculated at the same level of theory ($\delta C = 191.77$ ppm and $\delta H = 31.76$ ppm). The comparison of calculated chemical shifts in 1-(2-methylpropenyl)-2-methylbenzimidazole structures with the experimental data is given in Table 5. The calculations reported here were performed in DMSO solution, rather than in the gas phase, using IEF-PCM model. These are in agreement with experimental chemical shifts obtained in DMSO solutions. Results of linear regression fits between experimental and calculated chemical shifts (^1H and ^{13}C) performed for the two structures tested are included in Table 5. The regression coefficients between the calculated and experimental chemical shifts range from a low of 0.9958 for ^{13}C NMR data of (2-propenyl) structure to a high of 0.9980 for ^{13}C NMR data of (1-propenyl) structure in the worst case (see Table 5).

Table 5
The experimental and theoretical ^1H and ^{13}C NMR chemical shifts δ(ppm) from TMS for studied compounds

Atom	1-(2-Methyl-1-propenyl) 2-methylBZM		1-(2-Methyl-2-propenyl) 2-methylBZM	
	δ(exp.)	δ(calc.)	δ(exp.)	δ(calc.)
$C_{1\alpha}$	135	142	135	142
C_2	151	156	151	156
$C_{3\alpha}$	140	150	140	150
C_4	121	125	121	125
C_5	121	125	121	125
C_6	121	125	121	125
C_7	110	112	109	110
C_8	14	16	13	15
C_9	118	124	48	52
C_{10}	138	149	142	154
C_{11}	21	24	19	21
C_{12}	18	19	118	117
a[a]		0.95		0.96
b[b]		−0.6		−0.3
R^{2c}		0.998		0.996
Av.[d]		−4.9		−4.5
S_r[e]		2.3		3.2
H_4	7.6	7.9	7.6	7.9
$H_{5,6}$	7.2	7.3	7.2	7.4
H_7	7.2	7.1	7.2	7.4
H_8	2.6	2.4	2.6	2.4
H_9	6.5	6.5	4.4	4.6
H_{11}	1.7	1.6	1.4	1.5
H_{12}	2.0	2.1	4.9	5.1
H_{12}			4.8	5.2
a[a]		0.96		0.95
b[b]		−0.1		0.1
R^{2} [c]		0.997		0.996
Av.[d]		−0.01		−0.2
S_r[e]		0.1		0.2

For numbering of atoms refer to Scheme 1.
[a] Slope.
[b] Intercept.
[c] Correlation coefficient.
[d] Average differences between experimental and calculated chemical shifts.
[e] Standard error of the estimate; BZM, benzimidazole.

The experimental and calculated ^{1}H and ^{13}C chemical shifts show no significant difference in the benzimidazole ring between the investigated structures. ^{1}H NMR resonances at 6.5 and 4.9/4.8 ppm were observed and assigned to vinyl protons (H_9 and H_{12}) of structures 1-propenyl and 2-propenyl of 1-(2-methylpropenyl)-2-methylbenzimidazole, respectively. In the ^{1}H NMR spectrum of 1-propenyl-2-methylbenzimidazole, the chemical shift associated to vinyl protons of *E* and *Z* structures are observed at 6.95/6.05 and 6.75/5.95 ppm. The vinyl protons in 1-(2-propenyl)-2-methylbenzimidazole were found at 490 and 5.15 ppm. The resonances at 118 and 138 ppm correspond to vinyl carbons (C_9 and C_{10}) for structure (a) according to Scheme 1. In structure (b), these signals were found at 118 and 142 ppm for carbons C_{10} and C_{12}. The resonances at 117, 134 and 118 ppm correspond to the vinyl carbon in *E*, *Z* and 2-propenyl isomers of 1-(propenyl)-2-methylbenzimidazole. Based on the ^{1}H and ^{13}C chemical shifts, data presented in Table 5 and the fits (Figs. 3 and 4), one can deduce that the selected DFT method combined with the basis set represent a good compromise between accuracy and computational time, and yielded proton and carbon chemical shifts in agreement with experimental values.

4. Conclusions

In this work, the 1-(2-methylpropenyl)-2-methylbenzimidazole and its isomers have been synthesized and characterized by elemental analysis, $^{1}H/^{13}C$ NMR, UV, IR and Raman spectroscopy. The energies, geometric parameters, vibrational frequencies and $^{13}C/^{1}H$ chemical shift values of title compounds were calculated by using B3LYP with the standard 6-311+G** basis sets. For the isomers studied, the 1-propenyl structure is thermodynamically favored by 3.2 kcal/mol. Comparison between the calculated geometric parameters and the X-ray structure by the 2-methylbenzimidazole ring does not show major discrepancies except for some small differences in the imidazole ring. The experimental infrared and Raman spectra for the isomeric mixture of 1-(2-methylpropenyl)-2-methylbenzimidazole have been assigned and were supported by the calculated (scaled) vibrational spectra. The typical vibrations in the benzimidazole ring and the stretching $\nu_{C=C}$ mode of the propenyl group have been very accurately predicted by the selected computational method. Correlations between the proton and carbon-13 experimental chemical shifts and the GIAO NMR calculations are in good agreement and these values have been used for definitive signal assignments to the corresponding structural isomers.

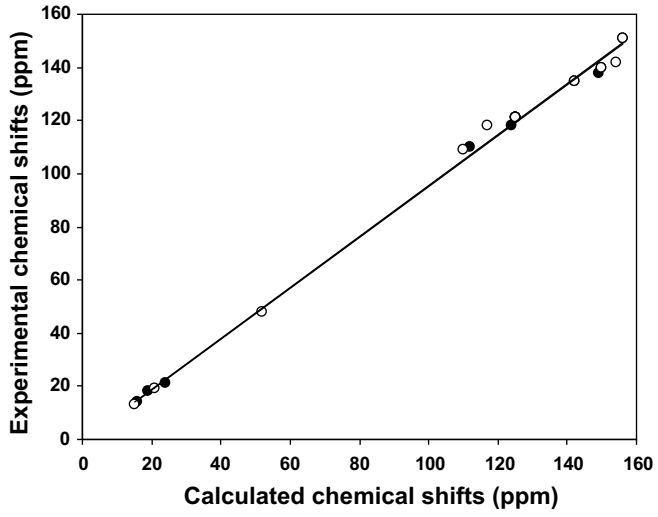

Fig. 3. The linear regression between experimental and theoretical DFT predicted ^{13}C NMR chemical shifts for the investigated structures using 6-311+G** basis set; ○ structure (a), ● structure (b).

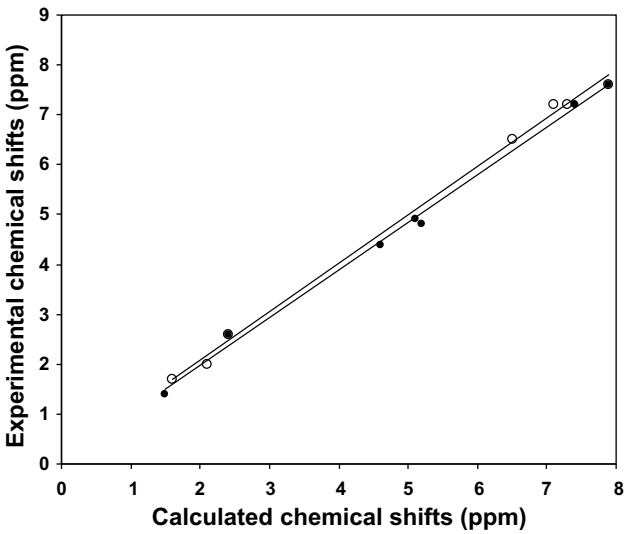

Fig. 4. The linear regression between experimental and theoretical DFT predicted ^{1}H NMR chemical shifts for investigated structures using 6-311+G** basis set; ○ structure (a), ● structure (b).

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