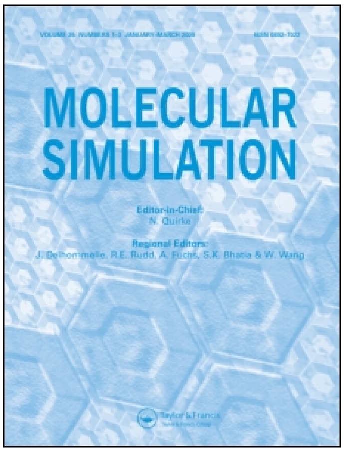

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Structure and vibrational frequencies of 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene: density functional theory study

H. Arslan[a]; A. Demircan[b]
[a] Department of Chemistry, Mersin University, Mersin, Turkey [b] Department of Chemistry, University of Nigde, Nigde, Turkey

To cite this Article Arslan, H. and Demircan, A.(2008) 'Structure and vibrational frequencies of 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene: density functional theory study', Molecular Simulation, 34: 5, 567 — 574

To link to this Article: DOI: 10.1080/08927020701632862

URL: http://dx.doi.org/10.1080/08927020701632862

Molecular Simulation
Vol. 34, No. 5, April 2008, 567–574

Taylor & Francis
Taylor & Francis Group

Structure and vibrational frequencies of 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene: density functional theory study

H. Arslan[a]* and A. Demircan[b]

[a]*Department of Chemistry, Faculty of Arts and Science, Mersin University, Mersin, Turkey;* [b]*Department of Chemistry, Faculty of Liberal Arts and Sciences, University of Nigde, Nigde, Turkey*

(*Received 12 June 2007; final version received 14 August 2007*)

The Fourier transform infrared (FT-IR) spectrum of 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene has been recorded in the region 4000–525 cm^{-1}. The optimised geometry, frequency and intensity of the vibrational bands of the title compound have been calculated using the *ab initio* Hartree–Fock and the density functional theory method with 6-31G(d,p) and 6-311G(d,p) basis set levels. The harmonic vibrational frequencies were calculated and the scaled values have been compared with experimental FT-IR spectrum. The observed and the calculated frequencies are found to be in good agreement. The theoretical vibrational spectrum of the title compound were interpreted by means of potential energy distributions using VEDA 4 program.

Keywords: FT-IR spectrum; DFT; vibrational analysis; furan; IMDA cycloaddition

1. Introduction

The intramolecular Diels–Alder (IMDA) reaction of furans with different donated dienophiles constitutes a powerful tool for the synthesis of complex molecules [1,2]. IMDA cycloadducts derived from heteroatoms in tether of furans have recently been of great interest [3,4] since they involve in ring formation for natural product synthesis such as Azadirachtin [5], Fraquinocin E [6], Isoquinolin Alkoloids [7], (±)-Bathrachotoxinin A [8], Chatancin [9], etc. Additionally, the cycloadducts from IMDA reaction of furans are versatile intermediate in the preperation of carbohydrates and other biologically active compounds [10]. However, aromatic character and low reactivity of furan make the Diels–Alder reaction one of the most difficult cycloadditon process [11]. In view of these context, we have been studying on synthesis of hetero-tricyclicfused compounds [12,13]. Sulphure containing rigid tricycle **2** was obtained from 2-{[(2-chloroprop-2-en-1-yl)thio]methyl}, **1** under solvent free condition in a commercial microwave by irradiating (Scheme 1).

The preqursor of IMDA cyloadditon, **1** was obtained from the treatment of furfurylmercaptanol with 2,3-dichloropropene by employing Williamson ether synthesis method [14]. The IMDA cycloaddition reaction of **1** was carried out in a commercially available microwave oven (2450 MHz) for 12 min irradiation. This stereoselective cycloaddition process take place over facile exo process and is promoted by Thorpe–Ingold (Scissor) effect as previously similar studies [15]. Aromatic furan rings and inactivated diene and dienophile sides make the cycloaddition process reversible and give reasonable low yield [16]. The amenity of this reaction is the separation of residue, that the polarity of **1** and **2** absolutely different from each other. Therefore, starting material, **1** can easily be recovered after purification by crystallisation.

For the design and characterisation of a new organic compound, high accuracy quantum chemical calculations using density functional theory (DFT) method are helpful tools. They allow determination of the molecular structure, the calculation of the charge distribution in a molecule and related properties such as dipole and quadrupole moments with reasonable accuracy. Their hyperpolarisability tensor can also obtain as a by-product of the calculation of the normal vibrations of the molecules.

The literature search has revealed that *ab initio* Hartree–Fock (HF) and DFT calculations and vibrational analysis have not been reported so far on 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene (6ClTEB). Therefore, the present investigation was undertaken to study the vibrational spectrum of this molecule completely and to identify the various normal modes with greater wavenumber accuracy. The *ab initio* HF and DFT calculations have been performed to support our wavenumber assignments.

2. Experimental

2.1. *Synthesis of 6ClTEB*

2-{[(2-chloroprop-2-en-1-yl)thio]methyl}, **1** (0.94 g, 5 mmol) was placed in a 5 mL vial and irradiated in a commercial microwave (2450 MHz) for 12 min. Resulting,

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*Corresponding author. Email: arslanh@mersin.edu.tr

ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020701632862
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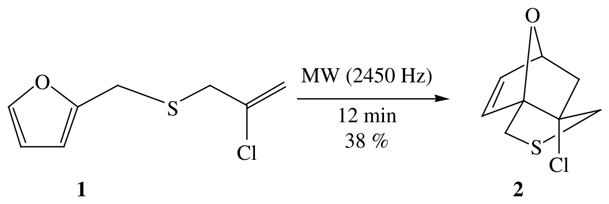

Scheme 1.

cyclic and acyclic mixture was subjected to flash column chromatography to afford the title compound as yellow crystal, 0.36 g (38%): m.p.: 77–78°C. TLC, (Hexane: Ethyl acetate (9:1)), R_f: 0.44 υ_{max} (thin film)/cm^{-1}: 2856 (s, C—H), 1218 (s, C—O), 720 (w, C—Cl). δ_H (400 MHz CDCl$_3$): 6.52 (dd, 1H, J_1 1.8 Hz, J_2 5.7 Hz, *AB*), 6.37 (d, 1H, *J* 5.7 Hz, *AB*), 5.01 (dd, 1H, J_1 1.8 Hz, J_2 4.8 Hz), 3.46 (d, 1H, *J* 12.3 Hz, *AB*), 3.31 (d, 1H, *J* 12.2 Hz, *AB*), 3.21 (d, 1H, *J* 12.3 Hz, *AB*), 3.20 (d, 1H, *J* 12.2 Hz, *AB*), 2.51 (dd, 1H, J_1 12.4 Hz, J_2 4.8 Hz, *AB*), 1.74 (d, 1H, *J* 12.4 Hz, *AB*). δ_C (100 MHz CDCl$_3$):137.7, 135.0, 101.1 (*q*), 80.7, 77.7, 64.5, 44.3, 29.9. *m/z* (EI, 70 ev): 189 [M$^+$, %5], 153 [M$^+$-(Cl), %12], 149 [M$^+$- (CH$_2$—CCH$_2$), %5] 113 [M$^+$-(Cl, CH$_2$CHCH$_2$), %10], 81 [(C$_5$H$_5$O)$^+$, %100]. Elemental Analysis (C$_8$H$_9$ClOS) (%): Calculated (Found) C, 50.93 (50.94); H, 4.81 (4.86).

2.2. *Instrumentation*

The room temperature attenuated total reflection Fourier transform infrared spectrum of the 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene was registered using Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism (4000–525 cm^{-1}; number of scans: 250; resolution: 1 cm^{-1}). The observed experimental FT-IR spectrum is shown in Figure 1.

2.3. *Calculations*

The molecular structure of the 6ClTEB was optimised by HF and DFT using Becke's three-parameter hybrid exchange functional (B3) and the Lee, Yang, and Parr (LYP) correlation functional with the standard 6-31G(d,p) and 6-311G(d,p) basis sets. The vibrational frequencies were also calculated with this method. These calculations were carried out using Gaussian 03W program package on a double Xeon/3.2 GHz processor with 4 GB Ram [17]. The frequency values computed at these levels contain known systematic errors [18]. Therefore, we have used the scaling factor values of 0.9089 for calculated wavenumbers lower than 800 cm^{-1} and the scale factor of 0.8992 for larger wavenumbers for HF and 1.0013 for calculated wavenumbers lower than 800 cm^{-1} and the scale factor of 0.9613 for larger wavenumbers for B3LYP method [19]. The assignment of the calculated wavenumbers is aided by the animation option of GaussView 3.0 graphical interface for Gaussian programs, which gives a visual presentation of the shape of the vibrational modes [20]. Furthermore, theoretical vibrational spectrum of the title compound was interpreted by means of potential energy distributions (PEDs) using VEDA 4 program [21]. The VEDA program does not scale the elements of force constant matrix as proposed by Pulay et al. [22]. The analysis was repeated few hundred-times to achieve the highest values of the PED contributions for definition of internal coordinates restricted to express pure carbon atoms motions [23].

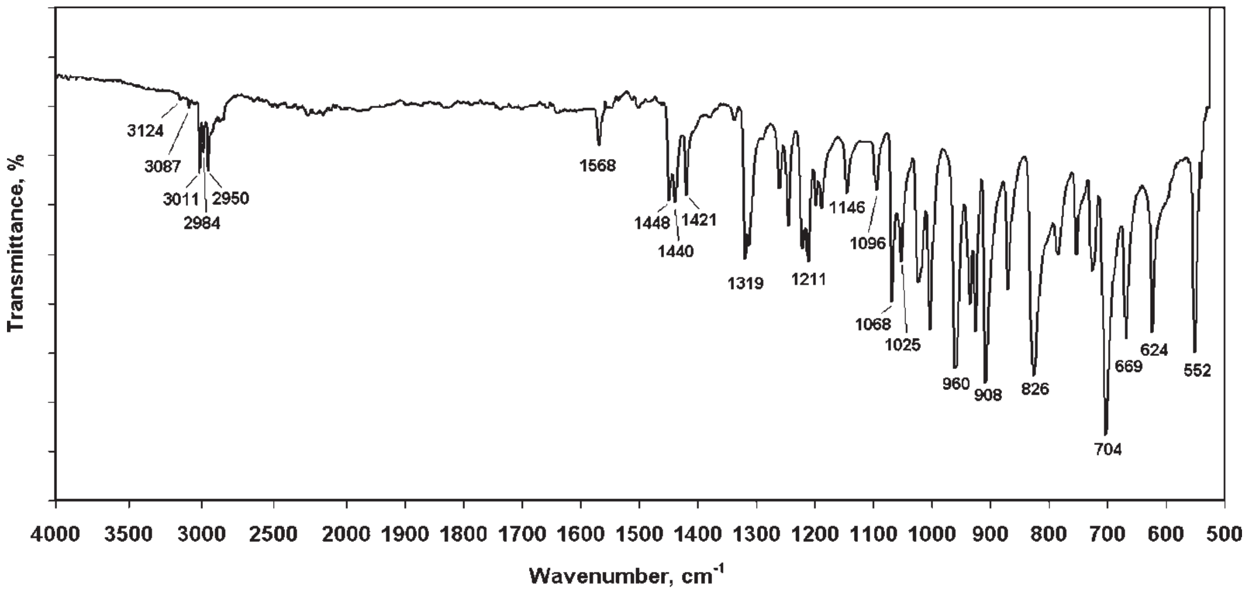

Figure 1. FT-IR spectrum of 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene.

3. Results and discussion

3.1. *Molecular geometry*

The crystal and molecular structure of 6ClTEB have been reported [24]. The geometric structure is triclinic, space group *P*1, with the cell dimensions $a = 6.651$ (3) Å, $b = 7.971$ (3) Å, $c = 8.048$ (3) Å, $\alpha = 80.33$ (3)°, $\beta = 89.07$ (3) °, $\gamma = 81.43$ (3) ° and $V = 415.9$ (3) Å^3. In this work, we performed full geometry optimisation of the title compound. The optimised structure of 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene with the labelling of atoms is given in Figure 2. The optimised geometrical parameters (bond length and angles) by HF and DFT/B3LYP with 6-31G(d,p) and 6-311G(d,p) as basis sets are listed in Table 1. The largest discrepancies between the calculated and experimental geometrical parameters are observed for C—H. The large deviation from experimental C—H bond lengths may arise from the low-scattering factors of hydrogen atoms in the X-ray diffraction experiment. In the intermolecular hydrogen bond distances for a Donor-Hydrogen-Acceptor system, D-H distance is typically ~1.1 Å, whereas H–A distance is ~ 1.6-2.0 Å. The crystaline form of the title compound has two intermolecular interactions (C7-H12–O9^i, with H–O = 2.52(4) Å ($i = 1 - x$, $1 - y$, $1 - z$) and C8-H18–O9^{ii}, with H–O = 2.54(3) Å ($ii = -x$, $1 - y$, $1 - z$)). According to these crystalline geometrical parameters, we can say the title compound has weak molecular interactions. Table 1 compares the calculated geometrical parameters with the experimental data. As follows from this comparison, the bond lengths and angles calculated for the title compound show quite good agreement with experimental values. All these results agree with weak intermolecular interactions. The largest difference between experimental and calculated (DFT) bond length and angle is about 0.032 Å and 1.3°, except C—H bond lengths. As a result, the optimised bond lengths and angles by DFT-B3LYP/6-311G(d,p) method show the best agreement with the experimental values.

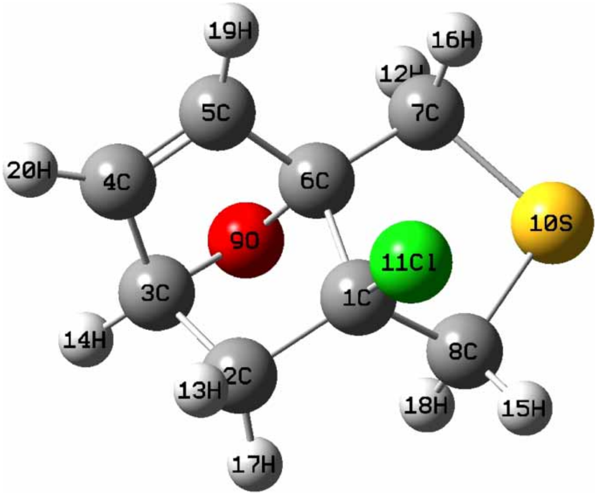

Figure 2. View of the optimised structure of the title compound.

3.2. *Vibrational assignments*

The harmonic vibrational frequencies for the title compound were calculated at HF and DFT/B3LYP level using 6-31G(d,p) (valence-split basis set with d,p-polarisation functions) and 6-311G(d,p) (triply split valence basis sets with d,p-polarisation functions). Table 2 lists the wavenumbers and the theoretical infrared intensities of the bands observed in the FT-IR spectrum of 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene. The last column of Table 2 shows the detailed vibrational assignment obtained from the calculation PED.

Comparison of the frequencies calculated at HF and DFT/B3LYP with experimental values reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in DFT to a certain extend makes the frequency values smaller in comparison with the HF frequency data. Reduction in the computed harmonic vibrations, though basis set sensitive are only marginal as observed in the DFT values using 6-311G(d,p) and 6-31G(d,p). Anyway not withstanding the level of calculations, it is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experiment. Therefore, in our study, we have used the scaling factor values of 0.9089 for calculated wavenumbers lower than 800 cm^{-1} and the scale factor of 0.8992 for larger wavenumbers for HF and 1.0013 for calculated wavenumbers lower than 800 cm^{-1} and the scale factor of 0.9613 for larger wavenumbers for B3LYP method [19].

In order to investigate the performance and vibrational frequencies for the title compound, mean absolute deviation, standard deviation (SD), root mean square (RMS) value and correlation coefficient between the calculated harmonic and observed fundamental vibrational frequencies for each method and basis set were also calculated and given in Table 3. The RMS values were obtained in this study using the following expression [25],

$$\mathrm{RMS} = \sqrt{\frac{1}{n-1}\sum_{i}^{n}(\nu_i^{\mathrm{calc}} - \nu_i^{\mathrm{exp}})^2}$$

These results indicate that the fundamental frequencies calculated (DFT) for the title compound show quite good agreement with experimental values. Furthermore, the 6-311G(d,p) basis set calculations approximate the observed fundamental frequencies much better than the 6-31G(d,p) basis set results. The small difference between experimental and calculated vibrational modes is observed.

Table 1. Optimised and experimental geometrical parameters of 6-chloro-8-thia-1,4-epoxybicyclo [4.3.0]non-2-ene in the ground state.

		HF		DFT/B3LYP	
Parameters	Experimental	6-31G(d,p)	6-311G(d,p)	6-31G(d,p)	6-311G(d,p)
Bond lengths (Å)					
R(1,2)	1.529(4)	1.549	1.548	1.554	1.551
R(1,6)	1.558(3)	1.560	1.560	1.580	1.579
R(1,8)	1.512(4)	1.531	1.529	1.532	1.529
R(1,11)	1.805(2)	1.802	1.806	1.828	1.829
R(2,3)	1.555(4)	1.556	1.556	1.568	1.567
R(3,4)	1.502(5)	1.520	1.521	1.522	1.521
R(3,9)	1.441(4)	1.415	1.412	1.442	1.441
R(4,5)	1.307(5)	1.317	1.316	1.335	1.332
R(5,6)	1.507(4)	1.521	1.522	1.524	1.524
R(6,7)	1.495(4)	1.513	1.511	1.515	1.512
R(6,9)	1.432(3)	1.413	1.411	1.442	1.441
R(7,10)	1.823(3)	1.828	1.830	1.851	1.851
R(8,10)	1.812(3)	1.825	1.825	1.846	1.844
r		0.9959	0.9957	0.9990	0.9992
Bond angles (°)					
A(2,1,6)	102.5(2)	101.4	101.4	101.7	101.8
A(2,1,8)	115.8(2)	114.5	114.6	114.8	115.0
A(2,1,11)	112.67(19)	113.1	113.0	112.8	112.7
A(6,1,8)	106.2(2)	105.1	105.2	105.2	105.2
A(6,1,11)	110.64(16)	112.4	112.4	111.9	111.9
A(8,1,11)	108.65(19)	109.9	109.7	109.9	109.8
A(1,2,3)	99.9(2)	99.7	99.7	100.0	100.0
A(2,3,4)	107.3(3)	107.6	107.4	107.4	107.2
A(2,3,9)	100.8(2)	101.1	101.2	101.1	101.1
A(4,3,9)	101.8(2)	101.4	101.4	101.9	101.8
A(3,4,5)	105.7(3)	105.5	105.4	105.6	105.6
A(4,5,6)	106.3(3)	105.3	105.3	105.5	105.6
A(1,6,5)	108.6(2)	110.1	109.9	109.5	109.4
A(1,6,7)	110.9(2)	111.0	111.1	111.1	111.2
A(1,6,9)	97.47(18)	97.8	97.9	97.6	97.6
A(5,6,7)	121.8(2)	120.8	120.7	121.1	121.2
A(5,6,9)	101.8(2)	101.6	101.6	102.1	102.0
A(7,6,9)	113.2(2)	112.8	112.9	112.6	112.6
A(6,7,10)	107.76(19)	107.4	107.4	107.9	107.8
A(1,8,10)	107.43(18)	107.7	107.5	108.0	107.8
A(3,9,6)	96.1(2)	97.4	97.5	96.4	96.5
A(7,10,8)	94.61(13)	94.5	94.5	93.8	93.8
r		0.9914	0.9921	0.9948	0.9955

This discrepancy can come from the formation of intermolecular hydrogen bonding. Also, we note that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

The IR bands at 3124 and 3087 cm^{-1} in FT-IR spectrum of 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene have been assigned to symmetric and asymmetric ν_{CH} stretching fundamentals of C4 and C5 atoms, respectively [26,27]. The corresponding scaled frequencies are calculated at 3113 and 3087 cm^{-1}. The wavenumbers corresponding to the aliphatic ν_{CH} stretching are listed in Table 2. All the calculated values in each method are overestimated, as well known in theoretical quantum mechanic assignment concerning hydrocarbonides compounds. After we applied the scale factor given by Sundaraganesan et al. [19] to all the methods, we observed a good concordance between the experimental and the calculated values. The vibrational spectra show three bands in the aliphatic ν_{CH} stretching region. These bands are evident overlap between the different C—H stretching modes. Six bands at 3018, 3011, 3010, 2961, 2960 and 2954 cm^{-1} were calculated in this research. First three is asymmetric $\nu_{\mathrm{C—H}}$ stretching band and the other bands symmetric $\nu_{\mathrm{C—H}}$ stretching band for -CH_2- group.

The vibrational modes concerning the bond angle bending (HCH): scissoring, wagging, twisting and rocking are well defined in all the calculations. As seen from Table 2, the bands observed at 1448, 1440 and 1421 cm^{-1} in FT-IR spectrum correspond to scissoring deformation of -C(2)H_2-, -C(7)H_2- and -C(8)H_2- group in the title

Table 2. Experimental vibrational frequencies along with the calculated vibrational frequencies (in cm^{-1}) and IR intensities (abs) (km mol^{-1}) for the title compound.

		HF						DFT/B3LYP						
		6-31G(d,p)			6-311G(d,p)			6-31G(d,p)			6-311G(d,p)			
No.	Exp.	Freq.	Freq.[b]	Int.	Freq.	Freq.[b]	Int.	Freq.	Freq.[c]	Int.	Freq.	Freq.[c]	Int.	Assignment, PED (%)[a]
1	3124	3421	3076	13	3393	3051	10	3259	3133	13	3238	3113	8	ν_{CH}, C4,5, sym (99)
2	3087	3392	3050	6	3363	3024	7	3233	3108	6	3211	3087	6	ν_{CH}, C4,5, asym (100)
3	3011	3320	2985	11	3300	2967	17	3158	3036	10	3139	3018	52	ν_{CH}, C3,8, asym (90)
4	3011	3310	2976	100	3297	2964	92	3153	3031	27	3139	3018	29	ν_{CH}, C3,8, asym (99)
5	3011	3308	2974	10	3289	2957	12	3148	3026	3	3132	3011	20	ν_{CH}, C2, asym (89)
6	3011	3304	2971	26	3282	2951	26	3148	3026	89	3131	3010	5	ν_{CH}, C7, asym (98)
7	2984	3261	2932	58	3243	2916	56	3095	2975	71	3080	2961	57	ν_{CH}, C2,8, sym (91)
8	2984	3249	2921	56	3233	2907	57	3092	2972	54	3079	2960	56	ν_{CH}, C7, sym (97)
9	2950	3241	2914	31	3220	2895	37	3089	2969	3	3073	2954	7	ν_{CH}, C2,5,8, sym (93)
10	1568	1815	1632	7	1794	1613	6	1657	1593	7	1639	1576	6	$\nu_{C=C}$ (84)
11	1448	1631	1466	8	1622	1458	11	1503	1445	12	1493	1435	17	δ_{CH2}, scis, C2 (86)
12	1440	1615	1452	27	1608	1446	24	1489	1431	29	1479	1422	29	δ_{CH2}, scis, C7 (72)
13	1421	1610	1448	5	1603	1441	6	1478	1421	14	1467	1410	15	δ_{CH2}, scis, C8 (74)
14	1319	1486	1336	46	1478	1329	41	1353	1301	41	1342	1290	44	ν_{CC}, C6,7, (14) + $\delta_{=CH}$, ipb (53)
15	1312	1481	1332	18	1473	1324	23	1347	1295	17	1339	1287	10	δ_{OCH} (16) + δ_{CH}, ipb (21)
16	1261	1461	1314	1	1454	1307	1	1323	1272	1	1316	1265	0	δ_{OCH} (43) + δ_{CH2}, wagg, C2 (39)
17	1246	1435	1290	24	1429	1285	28	1298	1248	20	1294	1244	18	δ_{CH2}, wagg, C7,8 (57)
18	1223	1409	1267	28	1401	1260	25	1282	1232	36	1276	1227	29	$\delta_{=CH}$, ipb (13) + δ_{CH2}, wagg, C2,7,8 (23)
19	1211	1395	1254	58	1386	1246	51	1254	1205	59	1246	1198	52	δ_{CH2}, wagg, C2 (12) + δ_{OCH} (31)
20	1198	1357	1220	15	1351	1215	14	1239	1191	17	1236	1188	13	ν_{CC}, C6,7, (16) + δ_{OCH} (12) + δ_{CH_2}, wagg, C7 (21)
21	1189	1337	1202	21	1331	1197	14	1217	1170	34	1212	1165	23	δ_{CH2}, twist, C2,7,8 (45)
22	1146	1328	1194	39	1324	1190	40	1209	1162	9	1208	1161	8	δ_{CH2}, twist, C2,7 (51)
23	1096	1278	1149	11	1273	1145	9	1167	1122	9	1168	1123	7	δ_{CH2}, twist, C7,8 (45)
24	1068	1215	1092	11	1209	1087	9	1114	1071	7	1110	1067	5	ν_{CC}, C1,8, (17) + δ_{CH} (37)
25	1054	1206	1084	68	1200	1079	73	1093	1051	33	1087	1045	27	$\delta_{=CH}$, ipb (50)
26	1025	1183	1064	28	1177	1058	31	1071	1030	38	1064	1023	38	ν_{CO}, (15) + ν_{CC}, (11)
27	1003	1162	1045	31	1157	1040	30	1038	998	56	1032	992	46	ν_{CC}, C1,2, (40) + $\delta_{=CH}$, ipb (11)
28	961	1136	1021	90	1130	1016	100	1025	985	57	1017	978	53	δ_{CH2}, rock, C2,7,8 (51)
29	936	1104	993	76	1101	990	73	981	943	92	975	937	100	ν_{CO}, (19) + δ_{CH2}, rock, C7 (24)
30	926	1074	966	5	1069	961	5	953	916	56	952	915	23	$\gamma_{=CH}$, opb (37)
31	908	1047	941	66	1043	938	73	942	906	16	945	908	37	$\gamma_{=CH}$, opb (68)
32	889	1024	921	42	1015	913	38	930	894	65	924	888	77	ν_{CC}, C2,3 (17) + δ_{CCO}, (12) + δ_{CH2}, rock, C8 (13)
33	871	1007	905	35	1001	900	41	918	882	37	913	878	28	ν_{CC}, (43) + δ_{CH2}, rock, C2,8 (11)
34	831	955	859	11	952	856	10	880	846	18	877	843	16	ν_{CO} (11) + δ_{COC}, (14) + δ_{CH2}, rock, C2,8 (13)
35	826	935	841	40	935	841	32	844	811	20	843	810	10	ν_{CO} (22) + δ_{COC}, (13) + δ_{CH2}, rock, C7 (13)
36	804	916	824	5	913	821	6	841	808	32	836	804	38	ν_{CO} (18) + $\delta_{=CC}$, (43)
37	787	868	789	21	866	787	19	788	789	12	786	787	12	δ_{CCC}, (14) + δ_{COC}, (11) + δ_{CCO}, (16)
38	754	833	757	10	827	752	12	760	761	13	758	759	12	ν_{CS} (10) + γ_{C}, C6, (16) + δ_{CH2}, rock, C7,8 (16)
39	729	808	734	70	803	730	66	733	734	5	730	731	7	ν_{CS} (22) + δ_{CCS}, (12) + γ_{CH}, C4,5 (18)

Table 2 – *continued*

		HF						DFT/B3LYP						
		6-31G(d,p)			6-311G(d,p)			6-31G(d,p)			6-311G(d,p)			
No.	Exp.	Freq.	Freq.[b]	Int.	Freq.	Freq.[b]	Int.	Freq.	Freq.[c]	Int.	Freq.	Freq.[c]	Int.	Assignment, PED (%)[a]
40	724	798	725	52	792	720	61	725	726	35	720	721	35	ν_{CS} (25) + δ_{CCC}, (23) + γ_{CH}, C4,5 (16)
41	704	791	719	32	793	721	31	716	717	100	713	714	91	γ_{CH}, C4,5 (35) + ν_{CCl} (37)
42	669	729	663	8	728	662	9	673	674	10	672	673	10	ν_{CC} (21) + γ_{CH} (25)
43	624	688	625	25	687	624	22	630	631	28	629	630	21	δ_{OCC}, (21) + τ_{CO}, (18)
44	552	602	547	21	600	545	20	552	553	21	550	551	18	γ_{CH}, C5 (11)
45	–	559	508	9	556	505	7	514	515	12	512	513	8	ν_{CC} (10) + ν_{CS} (17) + δ_{SCC}, (16)
46	–	461	419	1	458	416	2	419	420	2	417	418	2	ν_{CCl} (29) + δ_{CCC}, (15)
47	–	429	390	14	428	389	16	393	394	13	393	394	15	ν_{CCl} (17) + δ_{SCC}, (13)
48	–	417	379	4	415	377	4	385	385	6	384	384	5	τ_{CC}, (10) + γ_{C} (21)
49	–	378	344	1	377	343	1	350	350	1	350	350	1	δ_{CCC}, (29) + γ_{C} (11)
50	–	326	296	1	327	297	1	298	298	1	301	301	1	δ_{CCCl}, (54) + τ_{CS} (12)
51	–	311	283	5	311	283	5	287	287	6	287	287	5	δ_{CCO}, (34) + δ_{CCC}, (14)
52	–	195	177	7	195	177	6	177	177	8	177	177	6	δ_{CCO}, (21) + γ_{C} (49)
53	–	147	134	6	147	134	5	134	134	5	134	134	4	δ_{CCCl}, (19) + τ_{CC} (48)
54	–	94	85	4	95	86	4	80	80	5	82	82	4	τ_{CS} (11) + τ_{CC} (52)

[a] ν, stretching; δ, bending; ipb, in-plane bending; γ, out-of-plane bending; τ, torsion; sym, symmetric; asym, asymmetric; wagg, wagging; twist, twisting; rock, rocking; sciss; scissoring; PED less than 10% are not shown. [b] The scale factor of 0.9089 for calculated frequencies lower than 800 cm^{-1} and the scale factor of 0.8992 for larger frequencies. [c] The scale factor of 1.0013 for calculated frequencies lower than 800 cm^{-1} and the scale factor of 0.9613 for larger frequencies.

Table 3. Mean absolute deviation, SD, correlation coefficient, and RMS between the calculated and observed fundamental vibrational frequencies for the title compound.

	HF		DFT-B3LYP	
	6-31G(d,p)	6-311G(d,p)	6-31G(d,p)	6-311G(d,p)
Mean absolute deviation	30.54	30.80	10.54	9.07
SD	18.91	18.84	19.21	19.15
RMS	113.10	37.89	12.97	12.37
r	0.9996	0.9996	0.9999	0.9999

compound, respectively [26]. The theoretically computed values of scissoring deformation vibration modes show a good agreement with the experimental values. The wagging, twisting and rocking vibrational modes are distributed in a wide range [26–28]. Twisting and wagging vibrational modes of the -CH_2- groups were assigned in the range of 1250–1100 cm^{-1}. The above result is in close agreement with the literature values [29]. These vibrational modes are described in the Tables by mean of the general symbol δ_{CH2}. The infrared bands in this region are observed with very intense bands. The rocking -CH_2- is assigned in the wavenumber range of 950–750 cm^{-1} and the wavenumber shift of these bands is due to the atom nature in which the -CH_2- group is bonded. The -CH_2- rocking vibrational modes are intensive bands in which can be appreciating the vibrational coupling with other vibrational modes [27]. These bands are assigned using calculated PED.

The ν_{CO} stretch for the C—O—C oscillators is assigned in the spectral region of 1050–950 cm^{-1}, where the ν_{CO} normal mode is very intensive. The calculated DFT/6-311G(d,p) scaled values for the title compound is: 1023 cm^{-1}, these value is in agreement with the experimental wavenumber (1025 cm^{-1}). The bands observed at 754, 729 and 724 cm^{-1} in FT-IR spectrum corresponds to C—S stretching vibrations in the title compound. The corresponding scaled frequencies are calculated at 759, 731, and 724 cm^{-1}. These results were confirmed by Bensebaa et al. [30].

The C—C stretching vibrations in cyclic alkanes appear as weak bands in the region 1200–800 cm^{-1} and consequently are of little importance for structural study [31]. Hence, in the present study, the FT-IR bands observed at 1319 and 1198 cm^{-1} in title compound have been assigned to C—C stretching vibrations. These results were confirmed by Nakkeeran et al. and Gunasekaran [32,33].

The C—Cl stretching vibrations give generally strong bands in the region 710–500 cm^{-1}. For simple organic chlorine compounds, C—Cl absorptions are in the region 750–700 cm^{-1}. Considering these factors, the band observed (calculated) at 704 (714) cm^{-1} in FT-IR spectrum has been assigned to C—Cl stretching vibration in the present investigation. The above result is in close agreement with the literature values [34–36].

4. Conclusion

The frequency assignment for the 6-chloro-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene have been done for the first time from the FT-IR spectrum recorded for this compound. The equilibrium geometries and harmonic frequencies of the title compound were determined and analysed both at HF and DFT level of theories utilising 6-31G(d,p) and 6-311G(d,p) basis sets. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. The IR spectrum of the title compound was interpreted in terms of the PED analysis.

Acknowledgements

This work was supported by the Mersin University Research Fund (Project No: BAP.ECZ.F.TB.(HA).2007-1) and The Scientific & Technological Research Council of Turkey (TUBITAK) (Project no: 2377(103T121).

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