

Full Research Paper

The Molecular Structure and Vibrational Spectrum of 6-bromo-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene

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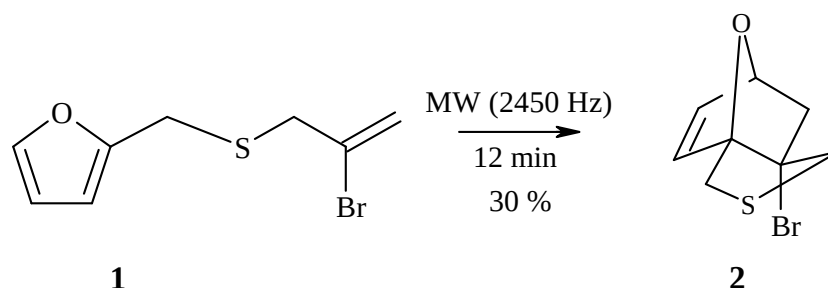
Abstract: Geometric parameters and FT-IR spectrum of 6-bromo-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene were computed by the HF, B3LYP, B3PW91 and mPW1PW91 methods in conjunction with the 6-31G(d,p) basis set. The calculated IR spectra are in a good agreement with the observed FT-IR spectrum. A general better performance of B3LYP, B3PW91 and mPW1PW91 versus HF was quantitatively characterized by using PAVF 1.0 program. Optimal uniform scaling factors calculated for the title compound are 0.8952, 0.9552, 0.9520 and 0.9456 for HF, B3LYP, B3PW91 and MPW1PW91 methods, respectively.

Keywords: Diels-Alder reactions; Intramolecular Cycloaddition; Ab initio calculations; Density functional calculations; IR spectroscopy.

1. Introduction

Heterocycles such as furan, thiophene and pyrrole undergo Diels-Alder reactions despite their stabilized 6π -aromatic electronic configuration [1]. In fact proclivity of furans to undergo [2-4] cycloaddition with various π -bonds has attracted the attention of many research groups, as it allows for the rapid construction of valuable synthetic intermediates [2-4]. In view of furans electron-rich

constitution and electron donor properties they have been involved mostly as the diene component in the cycloaddition process [5,6]. In this context, we have been studying on synthesis of heterotricyclic-fused compounds [7,8]. Sulphure containing rigid tricycle, **2**, was obtained from 2-[(2-bromoprop-2-en-1-yl)thio]methyl}furan, **1**, under solvent free condition in a commercial microwave (Scheme 1).



Scheme 1

The precursor of intramolecular Diels-Alder (IMDA) cycloaddition, **1**, was obtained from the treatment of furfurylmercaptanol with 2,3-dichloropropene by employing Williamson ether synthesis method [9]. 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 takes place over facile exo transition state and is promoted by Thorpe-Ingold (Scissor) effect as previously shown in similar studies [10]. Aromatic furan rings and inactivated diene & dienophile sides make such cycloaddition reaction reversible and could give modest yield [11].

Although semi-empirical methods proved its usefulness in practice to facilitate the IR identifications, the performance of semi-empirical methods can not satisfy modern criteria of theoretical FT-IR spectral predictions. The IR spectra computed with Hartree-Fock (HF) and density functional theory (DFT) methods were in much better agreement with the observed IR spectrum: the correlation between the calculated and experimental vibration frequencies was characterized by the coefficients for all DFT methods higher than HF method [12-24]. The calculated absolute band intensities were satisfactorily matched with the observed relative intensities as well. Also, the new local density functionals (M05, M05-2X, M06 and M06-2X) with a very broad applicability were recently developed by the Truhlar group [25,26]. These new hybrid meta exchange-correlation functionals are parametrized including both nonmetallic and metallic compounds. Also, these functionals give the best overall performance for a combination of main-group thermochemistry, thermochemical kinetics, and organic, organometallic, biological, and noncovalent interactions as well as the other popular functionals (B3LYP, BLYP, and BP86) [25-28].

In the present work, we have calculated the vibrational frequencies and geometric parameters of the title compound in the ground state to distinguish the fundamentals from the experimental vibrational frequencies and geometric parameters. Furthermore, we interpreted the calculated spectra in terms of potential energy distributions (PEDs) and made the assignment of the experimental bands due to PED analysis results. In continuation of our theoretical studies, in the present work we checked the relative performance of B3LYP, B3PW91 and mPW1PW91 methods, as well as of HF for comparison, at the 6-31G(d,p) level taking as a test compound 6-bromo-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene.

2. Experimental

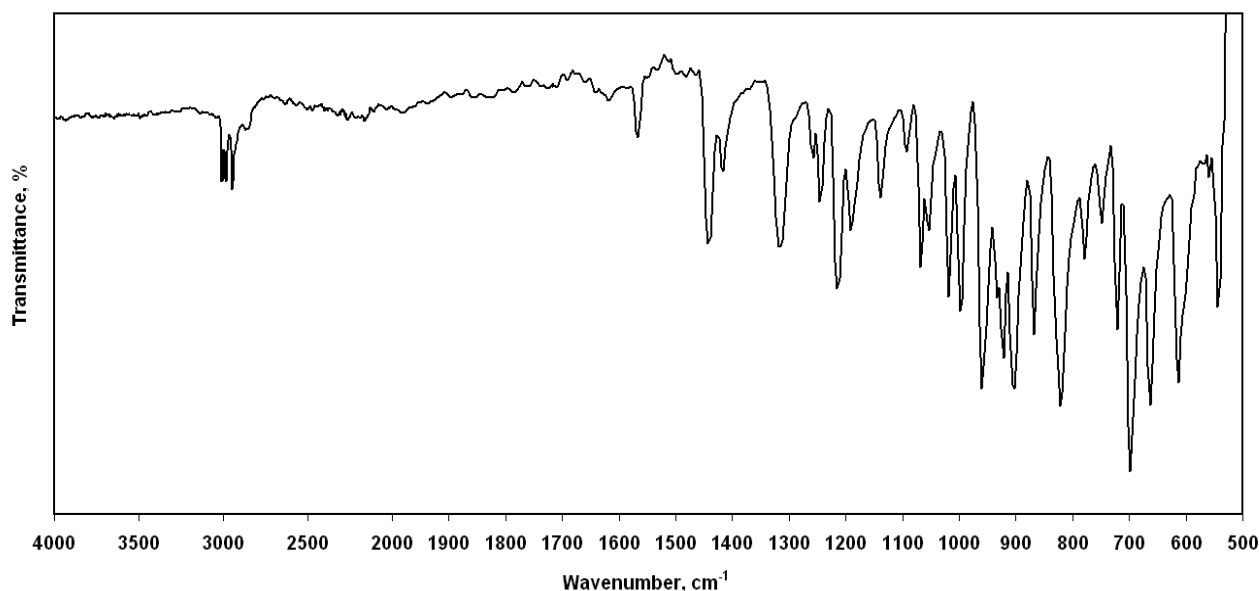
2.1. Synthesis of 6-bromo-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene

2-[[2-bromoprop-2-en-1-yl]thio]methyl}furan, **1**, (1.17 g, 5 mmol) was placed in a 5 mL vial and irradiated in a commercial microwave (2450 MHz) for 12 min. Resulting, cyclic and acyclic mixture was subjected to flash column chromatography to afford the title compound as yellow crystal, 0.36 g (30 %), m.p.: 64–66 °C; TLC, (Hexane:Diethylether; (9 : 1), R_f :0.28; δ_H (300 MHz, $CDCl_3$): 6.55 (dd, 1H, J_1 5.8 Hz, J_2 1.8 Hz), 6.46 (d, 1H, J 5.8 Hz), 5.10 (dd, 1H, J_1 1.8 Hz, J_2 4.6 Hz), 3.44 (d, 2H, J 12.5 Hz), 3.38 (d, 2H, J 12.5 Hz), 2.56 (dd, 1H, J_1 4.8 Hz, J_2 12.5 Hz), 1.90 (d, 1H, J 12.5 Hz). δ_C (75.5 MHz): 139.1, 138.5, 103.8, 82.6, 71.8, 49.9, 46.2, 31.8. m/z (EI, 70 eV): 234 [M^+ (^{81}Br), 10%], 232 [M^+ (^{79}Br), 8%], 93 [M^+ -(^{81}Br +CH₂SCH₂), 100%]. EA (C₈H₉BrOS): Requires: 41.22%, H. 3.89 %, Found: C 41.51, H 3.63 % [11].

2.2. Instrumentation

The room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectrum of the 6-bromo-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) (Figure 1).

Figure 1. FT-IR spectrum of 6-bromo-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene recorded at room temperature.



2.2. Calculations details

All the calculations were performed with the Gaussian 03W program package on a double Xeon/3.2 GHz processor with 8 GB Ram [29]. The molecular structure of the 6-bromo-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene, in the ground state is optimized by using the Hartree-Fock (HF) [30],

density functional using Becke's three-parameter hybrid method [31] with the Lee, Yang, and Parr correlation functional methods [32] (B3LYP), the Barone and Adamo's Becke-style one-parameter functional using the modified Perdew–Wang exchange and Perdew–Wang 91 correlation method, (mPW1PW91) [33,34], Becke's three parameter exchange functional combined with gradient corrected correlation functional of Perdew and Wang's 1991 (B3PW91) [35,36], and 6-31G(d,p) basis set. The vibrational frequencies were also calculated with these methods. The frequency values computed at these levels contain known systematic errors [37]. Therefore, we have used the scaling factor values of 0.8992, 0.9614, 0.9573 and 0.9500 for HF, B3LYP, B3PW91 and mPW1PW91, respectively [23,38]. We have also calculated optimal scaling factors for all investigated methods by PAVF 1.0 program [39]. 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 [40]. Furthermore, theoretical vibrational spectra of the title compound were interpreted by means of PEDs using VEDA 4 program [41].

3. Results and Discussion

Sulfones have always been in interest as a core functional group in both organic and medicinal chemistry because of their versatile synthetic utility and as inhibitors of various types of enzymatic processes [42]. More specifically, alkenyl sulfones are well known for their ability to inhibit many types of cysteine proteases [43,44]. The alkenyl sulfones are reversible inhibitors of these enzymes through conjugated addition of the thiol of the active site cysteine residue. In the synthetic sense, the alkenyl sulfone has come to play important role, acting as an efficient Michael acceptor and as a π donor in cycloaddition reactions [45,46]. We have recently been studying IMDA reaction of furans, since having seen the sulfones are great interest in medicinal chemistry, then we focused onto synthesis of tricyclic sulfones, **2**, as parameter of the compound gave negative charge on sulphure and bromine atoms (Atomic polar tensor: S, -0.137; Br, -0.293) [47]. The issue of the further study is to research the biologic activity test of these sulfones.

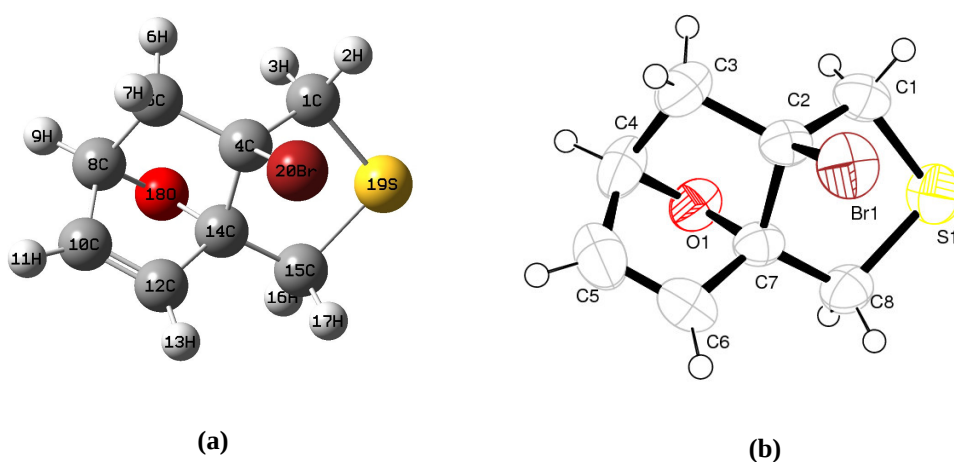
3.1. Geometry optimization

The crystal and molecular structure of 6-bromo-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene have been reported [11]. The structure parameters is triclinic, the space group *P*1, with the cell dimensions $a = 6.6508$ (10) Å, $b = 7.9576$ (12) Å, $c = 8.4012$ (12) Å, $\alpha = 81.030$ (12) °, $\beta = 88.572$ (12) °, $\gamma = 81.179$ (12) ° and $V = 434.00$ (11) Å³. In this work, we performed full geometry optimization of the title compound. The crystal and optimized structure of 6-bromo-8-thia-1,4-epoxybicyclo[4.3.0]non-2-en with the labelling of atoms are given in Figure 2. The optimized geometrical parameters (bond length and angles) by HF, B3LYP, B3PW91 and mPW1PW91 methods with 6–31G(d,p) as basis set are listed in Table 1. Also, 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. Owing to our calculations, DFT/mPW1PW91 method correlates well for the bond length in comparison to the other DFT methods and HF method according to RMS values (RMS = 0.014, 0.018, 0.012 and 0.010 Å for HF, B3LYP, B3PW91 and mPW91PW91 levels, respectively). The largest difference between experimental and calculated DFT/mPW1PW91

bond length and angle is about 0.018 Å ($R(C10-C12)$) and 1.1 ° ($\angle(C5-C8-C10)$). As a result, the optimized bond lengths and angles by DFT/mPW1PW91 method show the best agreement with the experimental values.

The importance of relativistic effects in properly describing the electronic structure of molecules containing heavy atoms is frequently stressed in the literature [25,28,48,49]. The relativistic effects lead to an increase of vibrational frequencies and shortening of bond lengths [48,49]. Although the title compound contains one heavy atom “Br”, we cannot observe this effect in the obtained results. The difference between calculated and experimental C-Br bond length is nearly within the experimental error range of the single crystal X-ray diffraction data.

Figure 2. The optimized molecular structure (a) and ORTEP-3 view (50 % probability displacement ellipsoids) of the title compound, with the atom numbering scheme (b).



3.2. Vibrational frequencies

Vibration frequencies calculated by HF, B3LYP, B3PW91 and mPW1PW91 for the title compounds are listed in Table 2-5, respectively. All the calculated spectra are in a good agreement with the experimental one, including the calculated absolute band intensities that well match the experimental relative intensities. All three hybrid functions are superior to HF in terms of realistic reproduction of both band intensity distribution and general spectral features.

A general better performance of B3LYP, B3PW91 and mPW1PW91 versus HF can be quantitatively characterized by using the mean deviation, mean absolute deviation, average absolute error, root mean square values and coefficients of correlation (cc) between the calculated and observed vibration frequencies and given in Table 2-5. The root mean square (RMS_{mol} and RMS_{over}) values were calculated in this study by PAVF 1.0 program [39] according to Scott and Radom [38]. The cc values for all three DFT methods were bigger than 0.9998, whereas for HF it was 0.9997: these values are very close to those reported for the literature data [12-24].

Table 1. Optimized and experimental geometries of the title compound in the ground state.

Parameters	Experimental	Calculated			
		HF	DFT		
			B3LYP	B3PW91	mPW1PW91
Bond lengths (Å)					
R(1,4)	1.508(6)	1.529	1.529	1.524	1.522
R(1,19)	1.813(4)	1.824	1.844	1.829	1.825
R(4,5)	1.533(5)	1.548	1.551	1.544	1.541
R(4,14)	1.552(5)	1.557	1.575	1.569	1.566
R(4,20)	1.965(3)	1.964	1.989	1.967	1.959
R(5,8)	1.554(6)	1.556	1.570	1.564	1.561
R(8,10)	1.512(8)	1.520	1.522	1.517	1.515
R(8,18)	1.436(5)	1.415	1.443	1.435	1.431
R(10,12)	1.314(7)	1.317	1.335	1.334	1.332
R(12,14)	1.508(6)	1.521	1.524	1.520	1.517
R(14,15)	1.502(5)	1.513	1.515	1.512	1.510
R(14,18)	1.444(4)	1.414	1.443	1.435	1.430
R(15,19)	1.829(4)	1.829	1.852	1.839	1.834
<i>r</i>		0.9971	0.9994	0.9990	0.9988
Bond angles (°)					
A(4,1,19)	107.7(3)	107.53	107.69	107.49	107.44
A(1,4,5)	115.5(3)	115.02	115.45	115.30	115.15
A(1,4,14)	106.5(3)	105.48	105.63	105.26	105.16
A(1,4,20)	109.1(3)	109.46	109.41	109.62	109.72
A(5,4,14)	102.3(3)	101.62	101.98	101.95	101.93
A(5,4,20)	113.0(3)	113.10	112.78	113.15	113.31
A(14,4,20)	109.9(2)	111.68	111.12	111.01	110.97
A(4,5,8)	100.0(3)	99.59	99.87	99.77	99.73
A(5,8,10)	107.1(4)	107.56	107.32	106.98	106.87
A(5,8,18)	100.9(3)	101.13	101.13	101.34	101.41
A(10,8,18)	102.0(4)	101.42	101.89	102.11	102.10
A(8,10,12)	105.9(4)	105.45	105.53	105.39	105.37
A(10,12,14)	105.7(4)	105.38	105.55	105.33	105.28
A(4,14,12)	109.9(3)	110.24	109.59	109.24	109.22
A(4,14,15)	111.0(3)	110.96	111.01	110.77	110.72
A(4,14,18)	97.3(3)	97.64	97.51	97.73	97.79
A(12,14,15)	121.4(3)	120.76	121.16	121.23	121.20
A(12,14,18)	102.1(3)	101.60	102.02	102.27	102.30

Table 1. Cont.

A(15,14,18)	112.3(3)	112.88	112.69	112.81	112.86
A(14,15,19)	107.4(3)	107.52	107.97	107.99	107.94
A(8,18,14)	95.7(3)	97.39	96.37	96.38	96.44
A(1,19,15)	94.58(18)	94.50	93.75	93.81	93.86
<i>r</i>		0.9943	0.9975	0.9965	0.9961

These results indicate that the DFT calculations approximate the observed fundamental frequencies much better than the HF results. The small difference between experimental and calculated vibrational modes is observed. 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.

Finally, one should mention scaling factors, which are crucial for IR spectral predictions. To calculate optimal scaling factors, we used PAVF 1.0 program [39]. Only single (uniform) scaling factors were calculated, without discrimination for different vibrations (as, for example, for CH and non-CH stretching vibrations in Ref. [50]). The values obtained are 0.8952, 0.9456, 0.9520 and 0.9552 for HF, mPW1PW91, B3PW91 and B3LYP, respectively. They are very close to those recommended by Scott and Radom and Kuppens et al. [23,38] for the same levels of theory (0.8992, 0.9500, 0.9573 and 0.9614, respectively) and increase in the same order of HF, mPW1PW91, B3PW91 and B3LYP. Thus, for future IR spectral predictions for unknown derivatives of the title compound, one can recommend scaling factors of 0.895, 0.946, 0.952 and 0.955 for HF, mPW1PW91, B3PW91 and B3LYP, respectively.

Table 2. Vibrational wavenumbers obtained for the title compound at B3LYP/6-31G(d,p) level ^a.

No	Wave number				IR intensity		Red mass	Force Const.	Assignments, PED (%) ^d
	Exp.	Unscal.	Scal ^b	Scal ^c	Abs.	Rel.			
1	3140	3261	3115	3135	4	12	1.11	6.93	ν_{CH} , C10,12, sym (98)
2	3077	3233	3088	3109	2	8	1.09	6.71	ν_{CH} , C10,12, asym (100)
3	3008	3156	3015	3035	3	11	1.11	6.49	ν_{CH} , C1, asym (88)
4	3008	3153	3011	3031	8	26	1.10	6.46	ν_{CH} , C5, asym (82)
5	2983	3149	3007	3027	1	5	1.11	6.48	ν_{CH} , C15, asym (100)
6	2983	3148	3007	3026	30	99	1.09	6.37	ν_{CH} , C8, (92)
7	2948	3093	2954	2973	12	40	1.06	5.96	ν_{CH} , C15, sym (100)
8	2948	3091	2952	2971	29	95	1.06	5.98	ν_{CH} , C1,5, sym (90)
9	2933	3084	2946	2965	1	4	1.06	5.95	ν_{CH} , C1,5, sym (93)
10	1568	1657	1583	1593	2	8	6.40	10.36	$\nu_{\text{C=C}}$ (83)
11	1447	1503	1435	1445	5	15	1.09	1.45	δ_{CH_2} , scis, C5 (92)
12	1439	1486	1420	1429	11	37	1.10	1.44	δ_{CH_2} , scis, C15 (74)
13	1418	1476	1410	1419	5	16	1.09	1.40	δ_{CH_2} , scis, C1 (78)

Table 2. Cont.

14	1318	1352	1292	1300	12	40	1.97	2.13	δ_{CH} , ipb (64)
15	1310	1346	1285	1294	6	20	2.04	2.18	$\delta_{\text{OCH}}(22) + \delta_{\text{CH}}$, ipb (11) + ν_{CC} , C14,15(13)
16	1259	1320	1260	1269	0	1	1.49	1.53	δ_{OCH} (40) + δ_{CH_2} , wagg, C5 (34)
17	1246	1294	1236	1244	6	19	1.34	1.33	δ_{CH_2} , wagg, C1,15 (59)
18	1218	1279	1222	1230	14	47	1.46	1.40	δ_{CH} , ipb (12) + δ_{CH_2} , wagg, C1,15 (27)
19	1211	1250	1194	1202	18	59	1.49	1.37	δ_{CH_2} , wagg, C5 (42) + δ_{OCH} (12)
20	1193	1237	1182	1190	5	17	1.67	1.51	ν_{CC} , C14,15 (14) + δ_{CH_2} , wagg, C15 (20)
21	1189	1213	1158	1166	13	44	1.57	1.36	δ_{CH_2} , twist, C1,5 (36) + ν_{CC} , C1,4 (14)
22	1140	1207	1152	1160	3	9	1.39	1.19	δ_{CH_2} , twist, C15 (45)
23	1094	1162	1110	1118	5	15	1.23	0.98	δ_{CH_2} , twist, C1 (34)
24	1068	1114	1064	1071	2	8	1.67	1.22	ν_{CC} (25) + δ_{CH} (37)
25	1055	1094	1045	1052	9	30	1.48	1.04	δ_{CH} , ipb (47)
26	1019	1071	1023	1030	12	38	2.61	1.76	ν_{CC} , (21) + δ_{CCC} (12)
27	998	1037	991	997	19	62	2.96	1.88	ν_{CC} , C4,5 (28) + δ_{CH} , ipb (28)
28	962	1021	975	981	19	61	2.25	1.38	δ_{CH_2} , rock, C1,5,15 (24)
29	934	981	937	943	30	100	2.30	1.30	δ_{CH_2} , rock, C15 (23) + δ_{COC} (13)
30	923	952	910	915	20	67	2.96	1.58	δ_{CH_2} , rock, C1 (34)
31	909	938	895	901	5	17	1.53	0.79	δ_{CH_2} , opb (71)
32	903	928	886	892	22	73	2.11	1.07	ν_{CC} , (47) + δ_{CC} , opb (33)
33	870	912	871	877	11	36	2.09	1.02	ν_{CC} , (19) + δ_{CH_2} , rock, C1,5 (42)
34	830	880	841	846	6	21	2.37	1.08	$\nu_{\text{CC}}(16) + \delta_{\text{COC}}(20)$ + $\delta_{\text{CH}_2, \text{rock}}$, C1,5 (10)
35	822	840	803	808	3	11	2.58	1.07	$\nu_{\text{CC}}(10) + \delta_{\text{COC}}(27)$ + $\delta_{\text{CH}_2, \text{rock}}$, C15 (41)
36	780	836	799	804	15	50	3.57	1.47	ν_{CO} (25) + δ_{CC} , (33)
37	750	786	751	756	3	11	3.55	1.29	δ_{CCC} , (26) + ν_{CC} (10)
38	722	752	718	723	5	15	4.21	1.40	ν_{CS} (28) + γ_{C} , C14, (15)
39	701	730	698	702	3	11	2.74	0.86	ν_{CS} (10) + δ_{CCS} , (10) + γ_{CH} , C10,12 (26)
40	688	723	690	695	9	29	4.80	1.48	ν_{CS} (14) + δ_{CCC} , (24) + γ_{CH} , C14 (28)
41	666	709	677	681	30	97	2.21	0.65	γ_{CH} , C10,12 (35)
42	650	672	641	646	5	17	4.11	1.09	ν_{CC} (17) + γ_{CH} (13) + δ_{CCO} , (16)
43	617	621	593	597	13	43	4.77	1.08	δ_{OCC} , (21) + τ_{CO} , (14)
44	543	544	520	523	6	21	2.96	0.52	τ_{CH} (39)
45	-	505	482	485	3	9	4.79	0.72	ν_{CC} (11) + ν_{CS} (14) + δ_{SCC} , (16)

Table 2. Cont.

46	-	402	384	387	2	8	2.57	0.25	$\delta_{\text{CCO}}, (11) + \tau_{\text{CO}}, (13)$
47	-	387	370	372	1	3	5.34	0.47	$\delta_{\text{SCC}}, (13) + \nu_{\text{CS}} (10) + \nu_{\text{CO}} (13)$
48	-	345	329	331	1	4	4.19	0.29	$\tau_{\text{CC}}, (27) + \gamma_{\text{C}} (10)$
49	-	325	311	313	1	5	3.55	0.22	$\nu_{\text{CBr}}, (44) + \delta_{\text{CCO}}, (18)$
50	-	282	269	271	1	4	2.44	0.11	$\gamma_{\text{C}}, \text{C4} (43) + \delta_{\text{CCC}}, (17)$
51	-	262	250	252	2	8	3.93	0.16	$\nu_{\text{CBr}}, (27) + \delta_{\text{CCC}}, (12)$
52	-	144	138	139	2	6	5.71	0.07	$\delta_{\text{CCBr}}, (25) + \gamma_{\text{C}}, \text{C4} (36)$
53	-	116	110	111	1	3	5.97	0.05	$\delta_{\text{CCBr}}, (28) + \tau_{\text{CC}} (43)$
54	-	78	75	75	2	6	5.11	0.02	$\tau_{\text{CC}} (52)$
r		0.9999	0.9999	0.9999					
Mean dev.		63.71	-2.83	-57.54					
Mean abs. deviation		63.71	12.22	57.54					
Ave. absolute error		4.27	1.09	4.25					
RMS_{mol}		78.8	14.6	65.3					
RMS_{over}		71.1	13.2	58.9					
Sca. Factor		1.0000	0.9552	0.9614					

^a Harmonic frequencies (in cm^{-1}), IR intensities (km mol^{-1}), reduced masses (amu) and force constants ($\text{m dyn } \text{\AA}^{-1}$).

^b Scaling Factor calculated in this research.

^c Scaling factor obtained from Ref. [38].

^d 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.

Table 3. Vibrational wavenumbers obtained for the title compound at HF/6-31G(d,p) level ^a.

Number	Wave number				IR intensity		Red Mass	Force Constant
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.	Rel.		
1	3140	3423	3064	3078	4	11	1.11	7.66
2	3077	3393	3037	3051	3	7	1.09	7.39
3	3008	3319	2971	2984	4	9	1.11	7.20
4	3008	3312	2964	2978	42	100	1.09	7.06
5	2983	3309	2962	2976	4	10	1.11	7.16
6	2983	3307	2960	2973	9	22	1.10	7.10
7	2948	3257	2916	2929	25	59	1.06	6.62
8	2948	3251	2910	2923	22	53	1.06	6.60
9	2933	3239	2900	2913	12	28	1.07	6.59
10	1568	1816	1625	1633	3	7	6.28	12.19
11	1447	1630	1459	1466	4	9	1.09	1.71

Table 3. Cont.

12	1439	1615	1445	1452	12	30	1.11	1.71
13	1418	1610	1442	1448	2	6	1.10	1.68
14	1318	1486	1330	1336	18	43	2.24	2.91
15	1310	1481	1326	1332	7	16	1.83	2.36
16	1259	1458	1305	1311	1	2	1.55	1.94
17	1246	1432	1282	1287	11	26	1.39	1.68
18	1218	1409	1261	1267	12	29	1.46	1.71
19	1211	1392	1246	1252	23	55	1.56	1.78
20	1193	1355	1213	1219	5	13	1.93	2.09
21	1189	1331	1192	1197	4	11	1.42	1.48
22	1140	1327	1188	1193	22	54	1.62	1.67
23	1094	1274	1141	1146	7	16	1.24	1.19
24	1068	1214	1087	1092	5	13	1.66	1.44
25	1055	1205	1079	1084	26	62	2.27	1.94
26	1019	1182	1058	1063	9	22	2.52	2.08
27	998	1160	1039	1043	15	37	1.83	1.45
28	962	1130	1012	1016	38	91	2.46	1.85
29	934	1103	987	991	28	68	2.05	1.47
30	923	1070	958	963	2	5	1.39	0.94
31	909	1045	935	939	27	66	2.54	1.63
32	903	1023	916	920	20	47	2.18	1.34
33	870	1000	895	899	14	33	2.01	1.18
34	830	955	855	859	5	11	2.51	1.35
35	822	932	835	838	17	41	2.19	1.12
36	780	914	818	822	2	4	3.10	1.53
37	750	871	780	783	7	17	3.51	1.57
38	722	837	749	753	3	8	4.72	1.95
39	701	815	729	733	27	65	1.69	0.66
40	688	801	717	720	10	25	4.43	1.67
41	666	794	711	714	26	62	3.75	1.39
42	650	728	652	655	4	10	4.25	1.33
43	617	681	609	612	14	33	4.77	1.30
44	543	593	531	533	8	19	2.89	0.60
45	-	548	491	493	3	6	4.92	0.87
46	-	440	394	396	2	5	2.61	0.30
47	-	418	375	376	1	3	5.31	0.55
48	-	373	334	335	2	4	4.06	0.33
49	-	355	318	319	2	5	3.53	0.26
50	-	307	275	276	1	3	2.51	0.14
51	-	288	258	259	3	7	3.92	0.19

Table 3. Cont.

52	-	160	143	144	2	5	5.46	0.08
53	-	128	114	115	1	3	5.38	0.05
54	-	89	80	80	2	4	6.01	0.03
r		0.9997	0.9997	0.9997				
Mean deviation		181.57	13.64	-130.89				
Mean absolute deviation		181.57	30.20	130.89				
Average absolute error		13.83	2.57	8.38				
RMS_{mol}		196.0	34.0	169.6				
RMS_{over}		177.0	30.7	153.1				
Scaling Factor		1.0000	0.8952	0.8992				

^a Harmonic frequencies (in cm⁻¹), IR intensities (km mol⁻¹), reduced masses (amu) and force constants (m dyn Å⁻¹).

^b Scaling Factor calculated in this research.

^c Scaling factor obtained from Ref. [38].

Table 4. Vibrational wavenumbers obtained for the title compound at B3PW91/6-31G(d,p) level ^a.

Number	Wave number				IR intensity		Red mass	Force Constant
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.	Rel.		
1	3140	3274	3117	3134	3	8	1.11	6.99
2	3077	3246	3090	3107	2	6	1.09	6.76
3	3008	3167	3015	3031	6	17	1.11	6.53
4	3008	3164	3013	3029	2	7	1.11	6.52
5	2983	3161	3010	3026	1	3	1.11	6.53
6	2983	3159	3007	3024	29	83	1.09	6.41
7	2948	3101	2952	2969	13	36	1.06	6.00
8	2948	3099	2950	2966	21	61	1.06	6.01
9	2933	3091	2943	2959	5	15	1.06	5.97
10	1568	1666	1586	1595	3	7	6.53	10.67
11	1447	1493	1421	1429	6	17	1.09	1.43
12	1439	1478	1407	1415	13	38	1.11	1.43
13	1418	1466	1395	1403	7	19	1.09	1.38
14	1318	1356	1291	1299	16	47	2.53	2.75
15	1310	1350	1285	1292	4	12	1.87	2.01
16	1259	1320	1257	1264	0	0	1.57	1.61
17	1246	1293	1231	1238	4	12	1.39	1.37
18	1218	1277	1216	1223	12	34	1.46	1.41
19	1211	1252	1192	1198	19	55	1.65	1.52
20	1193	1239	1179	1186	4	12	1.54	1.39
21	1189	1216	1158	1164	15	43	1.64	1.43

Table 4. Cont.

22	1140	1209	1151	1157	3	9	1.41	1.21
23	1094	1161	1105	1111	5	15	1.24	0.98
24	1068	1118	1065	1071	1	3	1.69	1.24
25	1055	1098	1045	1051	16	44	1.61	1.14
26	1019	1080	1028	1034	9	25	2.27	1.56
27	998	1047	997	1002	17	49	2.57	1.66
28	962	1030	981	986	24	70	2.34	1.47
29	934	993	945	950	27	78	2.31	1.34
30	923	961	915	920	20	57	2.80	1.52
31	909	943	898	903	17	49	1.93	1.01
32	903	934	889	894	11	33	1.57	0.81
33	870	919	875	880	12	35	2.15	1.07
34	830	886	843	848	6	16	2.17	1.00
35	822	847	807	811	12	35	2.62	1.11
36	780	845	805	809	1	2	3.13	1.32
37	750	794	756	760	2	7	3.42	1.27
38	722	767	730	734	4	11	4.73	1.64
39	701	743	707	711	8	23	4.87	1.58
40	688	737	701	705	3	10	2.85	0.91
41	666	715	681	684	35	100	1.98	0.60
42	650	676	644	647	6	17	4.05	1.09
43	617	625	595	598	10	30	4.60	1.06
44	543	546	520	522	6	17	2.93	0.51
45	-	508	484	487	3	7	4.81	0.73
46	-	402	382	385	3	7	2.67	0.25
47	-	389	370	372	1	3	5.23	0.47
48	-	348	331	333	2	5	4.25	0.30
49	-	329	313	315	1	3	3.37	0.21
50	-	282	268	270	1	3	2.40	0.11
51	-	264	251	253	2	6	3.79	0.16
52	-	144	137	138	2	5	5.69	0.07
53	-	115	110	110	1	2	6.47	0.05
54	-	76	72	73	2	6	4.75	0.02
r		0.9998	0.9998	0.9998				
Mean deviation		69.36	-2.08	-62.63				
Mean absolute deviation		69.36	13.98	62.63				
Average absolute error		4.79	1.26	4.50				
RMS_{mol}		84.6	16.4	72.3				
RMS_{over}		76.4	14.8	65.2				
Scaling Factor		1.0000	0.9520	0.9573				

^a Harmonic frequencies (in cm⁻¹), IR intensities (km mol⁻¹), reduced masses (amu) and force constants (m dyn Å⁻¹).

^b Scaling Factor calculated in this research.

^c Scaling factor obtained from Ref. [38].

Table 5. Vibrational wavenumbers obtained for the title compound at mPW1PW91/6-31G(d,p) level ^a.

Number	Wave number				IR intensity		Red mass	Force Constant
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.	Rel.		
1	3140	3293	3114	3129	2	6	1.11	7.08
2	3077	3266	3088	3102	2	4	1.09	6.84
3	3008	3185	3012	3026	6	17	1.11	6.61
4	3008	3183	3010	3024	2	6	1.11	6.60
5	2983	3181	3008	3022	1	2	1.11	6.61
6	2983	3179	3006	3020	27	74	1.09	6.50
7	2948	3119	2949	2963	12	33	1.06	6.07
8	2948	3117	2947	2961	20	56	1.06	6.08
9	2933	3109	2940	2953	5	14	1.06	6.04
10	1568	1680	1589	1596	3	7	6.55	10.90
11	1447	1500	1418	1425	6	17	1.09	1.44
12	1439	1486	1406	1412	14	38	1.11	1.44
13	1418	1474	1394	1400	7	19	1.09	1.40
14	1318	1369	1294	1300	17	47	2.73	3.02
15	1310	1360	1286	1292	4	12	1.83	2.00
16	1259	1331	1259	1265	0	0	1.60	1.67
17	1246	1303	1232	1238	4	12	1.40	1.40
18	1218	1287	1217	1222	11	30	1.48	1.44
19	1211	1263	1195	1200	19	53	1.69	1.59
20	1193	1248	1180	1186	4	12	1.52	1.40
21	1189	1226	1159	1165	16	44	1.65	1.46
22	1140	1219	1152	1158	3	9	1.42	1.25
23	1094	1169	1106	1111	5	15	1.24	1.00
24	1068	1127	1066	1071	1	2	1.68	1.26
25	1055	1107	1047	1052	19	52	1.76	1.27
26	1019	1091	1032	1037	7	18	2.15	1.51
27	998	1058	1001	1005	17	45	2.36	1.56
28	962	1041	985	989	26	72	2.37	1.52
29	934	1005	950	954	26	71	2.25	1.34
30	923	970	917	921	20	54	2.72	1.51
31	909	953	901	905	17	47	1.91	1.02

Table 5. Cont.

32	903	944	893	897	11	31	1.56	0.82
33	870	928	878	882	13	34	2.15	1.09
34	830	893	844	848	5	15	2.14	1.00
35	822	856	810	814	11	29	2.67	1.15
36	780	852	806	810	1	2	2.94	1.26
37	750	803	759	763	2	6	3.33	1.27
38	722	777	735	738	3	9	4.81	1.71
39	701	754	713	716	8	22	4.79	1.60
40	688	744	703	707	3	9	2.88	0.94
41	666	723	684	687	37	100	1.95	0.60
42	650	682	645	648	6	16	4.07	1.11
43	617	631	597	599	10	26	4.57	1.07
44	543	550	520	523	6	16	2.92	0.52
45	-	513	485	487	3	7	4.83	0.75
46	-	405	383	385	3	7	2.70	0.26
47	-	392	371	372	1	3	5.18	0.47
48	-	350	331	333	2	5	4.24	0.31
49	-	332	314	315	1	3	3.33	0.22
50	-	283	268	269	1	3	2.40	0.11
51	-	266	252	253	2	6	3.74	0.16
52	-	146	138	138	2	5	5.65	0.07
53	-	116	110	110	1	2	6.48	0.05
54	-	77	72	73	2	6	4.76	0.02
r		0.9998	0.9998	0.9998				
Mean deviation		80.69	-0.93	-71.89				
Mean absolute deviation		80.69	14.00	71.89				
Average absolute error		5.68	1.30	5.06				
RMS_{mol}		96.2	16.6	84.1				
RMS_{over}		86.9	14.9	75.9				
Scaling Factor		1.0000	0.9456	0.9500				

^a Harmonic frequencies (in cm⁻¹), IR intensities (km mol⁻¹), reduced masses (amu) and force constants (m dyn Å⁻¹).

^b Scaling Factor calculated in this research.

^c Scaling factor obtained from Ref. [23].

The IR bands at 3140 and 3077 cm⁻¹ in FT-IR spectrum of 6-bromo-8-thia-1,4-epoxybicyclo[4.3.0]non-2-ene have been designated to symmetric and asymmetric ν_{CH} stretching fundamentals of C10 and C12 atoms, respectively [51,52]. 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 hydrocarbons. After we were applied the scale factor both calculated in this research and given by Scott and Radom

[38] and Kuppens et al. [23] for all the methods, we observed a good concordance between the experimental and the calculated values. The vibrational spectra show four bands in the aliphatic ν_{CH} stretching region and are evident overlap between the different C-H stretching modes. Seven bands at 3015, 3011, 3007, 3007, 2954, 2952 and 2946 cm^{-1} were calculated in this research. First three is asymmetric $\nu_{\text{C-H}}$ stretching band and the last three bands symmetric $\nu_{\text{C-H}}$ stretching band for $-\text{CH}_2-$ group. These assignments were also supported by the literature [51].

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 1447, 1439 and 1418 cm^{-1} in FT-IR spectrum correspond to scissoring deformation of $-\text{C}(5)\text{H}_2-$, $-\text{C}(15)\text{H}_2-$ and $-\text{C}(1)\text{H}_2-$ group in the title compound [51,52]. 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 [51-54]. Twisting and wagging vibrational modes of the $-\text{CH}_2-$ groups were assigned in the range of 1250–1100 cm^{-1} . The above result is in close agreement with the literature values [55]. These vibrational modes are described in the tables by mean of the general symbol δ_{CH_2} . The rocking $-\text{CH}_2-$ is assigned in the wavenumber range of 950–800 cm^{-1} and the wavenumber shift of these bands is due to the atom nature in which the $-\text{CH}_2-$ group is bonded. The $-\text{CH}_2-$ rocking vibrational modes are intensive bands in which can be appreciating the vibrational coupling with other vibrational modes [52,53]. These bands are assigned using calculated potential energy distribution.

The bands observed at 722, 701 and 688 cm^{-1} in FT-IR spectrum corresponds to C-S stretching vibrations in the title compound. The calculated DFT/B3LYP/6-31G(d,p) scaled values for the title compound are: 718, 698 and 690 cm^{-1} , these values are in agreement with the experimental wavenumbers. These results were confirmed by Bensebaa et al. [56].

The C–C stretching vibrations in cyclic alkanes appeared as weak bands in the region 1200–800 cm^{-1} and consequently are of little importance for structural study [57]. Hence, in the present study, the FT-IR bands observed at 1193 and 1189 cm^{-1} in title compound have been assigned to C–C stretching vibrations. These results were confirmed by Gunasekaran et al. [58].

4. Conclusions

The IR spectrum of the title compound computed by the HF, B3LYP, B3PW91 and mPW1PW91 methods in conjunction with the 6-31G(d) basis set are in a good agreement with its observed FT-IR spectrum. The correlation between the calculated and experimental vibration frequencies is characterized by the coefficients of bigger than 0.9998 for all three DFT methods and 0.9997 for HF. Optimal uniform scaling factors calculated for the title compound are 0.8952, 0.9456, 0.9520 and 0.9552 for HF, mPW1PW91, B3PW91 and B3LYP, respectively. For IR spectrum predictions for the title compound type derivatives, any of the three hybrid functions can be equally successfully used. Taking into account small variations of the scaling factors for the derivatives of the title compound, for future IR spectral predictions for unknown compounds of this class, one can recommend scaling factors of 0.895, 0.946, 0.952 and 0.955 for HF, mPW1PW91, B3PW91 and B3LYP, respectively.

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