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).

\[ S \quad O \quad Br \]

\[ O \quad S \quad Br \]

\[ 1 \quad \rightarrow \quad MW (2450 \text{ Hz}) \quad 12 \text{ min} \quad 30 \% \quad 2 \]

Scheme 1

The precursor of intramolecular Diels-Alder (IMDA) cycloadditon, 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 take place over facile exo transition state and is promoted by Thorpe-Ingold (Scissor) effect as previously show 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 of 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), Rf:0.28; δH (300 MHz, CDCl3): 6.55 (dd, 1H, J1 5.8 Hz, J2 1.8 Hz), 6.46 (d, 1H, J 5.8 Hz), 5.10 (dd, 1H, J1 1.8 Hz, J2 4.6 Hz), 3.44 (d, 2H, J 12.5 Hz), 3.38 (d, 2H, J 12.5 Hz), 2.56 (dd, 1H, J1 4.8 Hz, J2 12.5 Hz), 1.90 (d, 1H, J 12.5 Hz). δC (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+(81Br), 10%], 232 [M+(79Br), 8%], 93 [M+(81Br+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 \( \pi \) 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 sulphur 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 \( P1 \), 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) Å\(^3\). 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-ene 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 ° (A(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  | 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 |
| r          | 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(10,8,18) | 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 |
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 | Exp. | Unscal. | Scal$^b$ | Scal$^d$ | Abs. | Rel. | Red mass | Force Const. | PED (%)$^d$ | Assignments, PED (%)$^d$ |
|----|------|---------|----------|----------|------|------|----------|-------------|-----------|-------------------------|
| 1  | 3140 | 3261    | 3115     | 3135     | 4    | 12   | 1.11     | 6.93        |           | $\nu_{CH}$, C10,12, sym (98) |
| 2  | 3077 | 3233    | 3088     | 3109     | 2    | 8    | 1.09     | 6.71        |           | $\nu_{CH}$, C10,12, asym (100) |
| 3  | 3008 | 3156    | 3015     | 3035     | 3    | 11   | 1.11     | 6.49        |           | $\nu_{CH}$, C1, asym (88) |
| 4  | 3008 | 3153    | 3011     | 3031     | 8    | 26   | 1.10     | 6.46        |           | $\nu_{CH}$, C5, asym (82) |
| 5  | 2983 | 3149    | 3007     | 3027     | 1    | 5    | 1.11     | 6.48        |           | $\nu_{CH}$, C15, asym (100) |
| 6  | 2983 | 3148    | 3007     | 3026     | 30   | 99   | 1.09     | 6.37        |           | $\nu_{CH}$, C8, (92) |
| 7  | 2948 | 3093    | 2954     | 2973     | 12   | 40   | 1.06     | 5.96        |           | $\nu_{CH}$, C15, sym (100) |
| 8  | 2948 | 3091    | 2952     | 2971     | 29   | 95   | 1.06     | 5.98        |           | $\nu_{CH}$, C1.5, sym (90) |
| 9  | 2933 | 3084    | 2946     | 2965     | 1    | 4    | 1.06     | 5.95        |           | $\nu_{CH}$, C1.5, sym (93) |
| 10 | 1568 | 1657    | 1583     | 1593     | 2    | 8    | 6.40     | 10.36       |           | $\nu_{C=C}$ (83) |
| 11 | 1447 | 1503    | 1435     | 1445     | 5    | 15   | 1.09     | 1.45        |           | $\delta_{CH2}$, scis, C5 (92) |
| 12 | 1439 | 1486    | 1420     | 1429     | 11   | 37   | 1.10     | 1.44        |           | $\delta_{CH2}$, scis, C15 (74) |
| 13 | 1418 | 1476    | 1410     | 1419     | 5    | 16   | 1.09     | 1.40        |           | $\delta_{CH2}$, scis, C1 (78) |
Table 2. Cont.

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

| 46 | -     | 402 | 384 | 387 | 2 | 8 | 2.57 | 0.25 | \(\delta_{CCO}, (11) + \tau_{CO}, (13)\) |
| 47 | -     | 387 | 370 | 372 | 1 | 3 | 5.34 | 0.47 | \(\delta_{SCC}, (13) + \nu_{CS} (10) + \nu_{CO} (13)\) |
| 48 | -     | 345 | 329 | 331 | 1 | 4 | 4.19 | 0.29 | \(\tau_{CC}, (27) + \gamma_{C} (10)\) |
| 49 | -     | 325 | 311 | 313 | 1 | 5 | 3.55 | 0.22 | \(\nu_{CB} (44) + \delta_{CCO}, (18)\) |
| 50 | -     | 282 | 269 | 271 | 1 | 4 | 2.44 | 0.11 | \(\gamma_{C}, C4 (43) + \delta_{CCC}, (17)\) |
| 51 | -     | 262 | 250 | 252 | 2 | 8 | 3.93 | 0.16 | \(\nu_{CB} (27) + \delta_{CCC}, (12)\) |
| 52 | -     | 144 | 138 | 139 | 2 | 6 | 5.71 | 0.07 | \(\delta_{CCB}, (25) + \gamma_{C}, C4 (36)\) |
| 53 | -     | 116 | 110 | 111 | 1 | 3 | 5.97 | 0.05 | \(\delta_{CCB}, (28) + \tau_{CC} (43)\) |
| 54 | -     | 78  | 75  | 75  | 2 | 6 | 5.11 | 0.02 | \(\tau_{CC} (52)\) |

\[ r \]
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<sub>2</sub>
78.8 14.6 65.3

RMS<sub>2</sub>
71.1 13.2 58.9

Sca. Factor
1.0000 0.9552 0.9614

- Harmonic frequencies (in cm<sup>-1</sup>), IR intensities (km mol<sup>-1</sup>), reduced masses (amu) and force constants (m dyn Å<sup>-1</sup>).
- Scaling Factor calculated in this research.
- Scaling factor obtained from Ref. [38].
- \(\nu\), stretching; \(\delta\), bending; ipb, in-plane bending; \(\gamma\), out-of-plane bending; \(\tau\), 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<sup>a</sup>.

| Number | Wave number Exp. | Wave number Unscaled | Wave number Scaled<sup>b</sup> | IR intensityScaled<sup>e</sup> Abs. | IR intensityScaled<sup>e</sup> Rel. | Red Mass | Force Constant |
|--------|-----------------|----------------------|------------------------|----------------|----------------|---------|----------------|
| 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
- \( \text{RMS}_{\text{in}} \) = 196.0 34.0 169.6
- \( \text{RMS}_{\text{over}} \) = 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 |
| \( \text{RMS}_{\text{mol}} \) | 84.6 | 16.4 | 72.3 |
| \( \text{RMS}_{\text{over}} \) | 76.4 | 14.8 | 65.2 |
| Scaling Factor | 1.0000 | 0.9520 | 0.9573 |

\(^a\) Harmonic frequencies (in \( \text{cm}^{-1} \)), IR intensities (km \( \text{mol}^{-1} \)), 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        | 3019         | 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 |
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 \(\nu_{\text{CH}}\) stretching fundamentals of C10 and C12 atoms, respectively [51,52]. The wavenumbers corresponding to the aliphatic \(\nu_{\text{CH}}\) 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
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\text{CH} stretching region and are evident overlap between the different C-H stretching modes. Seven bands at 3015, 3011, 3007, 2954, 2952 and 2946 cm\(^{-1}\) were calculated in this research. First three is asymmetric ν\text{C-H} stretching band and the last three bands symmetric ν\text{C-H} stretching band for –CH\textsubscript{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 -C(5)H\textsubscript{2}, -C(15)H\textsubscript{2} and -C(1)H\textsubscript{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 -CH\textsubscript{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\text{CH}_2. The rocking -CH\textsubscript{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 -CH\textsubscript{2} group is bonded. The -CH\textsubscript{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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