

Scientific paper

Ab Initio Studies on 5-Bromo-10-Oxa-3-Thiatricyclo[5.2.1.0^{1,5}]-Dec-8-Ene 3,3-Dioxide

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Abstract

5-Bromo-10-oxa-3-thiatricyclo[5.2.1.0^{1,5}]-dec-8-ene 3,3-dioxide (BOTCDO) was synthesized from the reaction between 2-(2-bromoallylsulfanyl)methyl-furan and *m*-chloroperbenzoic acid in dichloromethane. The molecular structure and vibrational frequencies of BOTCDO in the ground state have been investigated with ab initio (HF) and density functional theory methods (B3LYP, B3PW91 and MPW1PW91) implementing the standard 6-31G(d) basis set. The optimized geometric bond lengths and bond angles obtained by using HF and DFT methods show the best agreement with the experimental data. Comparison of the observed fundamental vibrational frequencies of title compound and calculated results by HF and DFT methods indicate that MPW1PW91 is superior to the scaled HF approach for molecular problems. Optimal uniform scaling factors calculated for the title compound are 0.8920, 0.9553, 0.9518 and 0.9452 for HF, B3LYP, B3PW91 and MPW1PW91 methods, respectively.

Keywords: HF; DFT; FT-IR spectrum; quantum chemical calculations; furans; sulfoxide.

1. Introduction

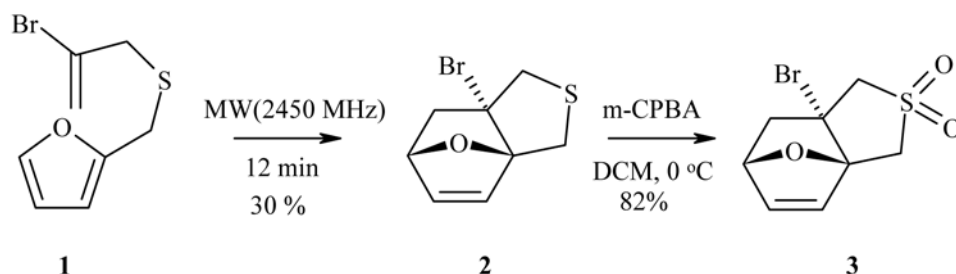
The renewal of interest in cycloaromatization reactions over the last decade has clearly intensified due to the elegant mode of action of the enediyne natural products.^{1,2} In particular, the intramolecular Diels–Alder (IMDA) cycloaddition has been extensively used for assembly of complex molecular architectures of designed or natural products origin.^{3–5} Biosynthetic pathways incorporating IMDA reactions have been recognized and examples of biomimetic total synthesis of natural products by using a key IMDA cycloaddition are known.^{5–7} IMDA reactions between unactivated furans and dienophiles take place generally at lower temperature compared to their intermolecular counterparts,⁸ and thus, they have a much higher scope with respect to the necessary activation of the reaction partners.⁹ Furthermore, success of IMDA cycloaddition critically depends on the length of the tether connecting the furan with the dienophile unit.^{10,11}

The utility of sulfoxide have received great attention in point of chemical and biological properties.^{2,13} The sulfonyl functional group has recently been shown to potentially inhibit a variety of enzymatic processes providing unique properties for drug design and medicinal chem-

istry.^{14,15} Furthermore, alkenyl sulfones are well known for their ability to inhibit many types of cysteine proteases.^{16,1} The alkenyl sulfones are reversible inhibitors of these enzymes through conjugate addition of the thiol of the active site cysteine residue, mimicking the initial covalent adduct in normal proteolytic turnover. Particularly, Hanzlick¹⁸ proposed alkenyl sulfone series as potential cysteine protease inhibitors targeting the plant protease papain.

In the point of chemical properties view, sulfoxides used as dienophiles in a Diels–Alder reaction and their 1,4-cycloaddition have attracted considerable attention¹⁹. The sulfonyl group has versatile functionality in organic synthesis and can be conveniently eliminated resulting in an alkene.^{20,21} Moreover sulfonyl group can also be converted to the corresponding ketone by oxidative desulfonylation.²² From synthetic and medicinal chemistry point of view, tricyclic sulfone, 5-bromo-10-oxa-3-thiatricyclo[5.2.1.0^{1,5}]-dec-8-ene-3,3-dioxide (BOTCDO) might be a convenient route for the development of combinatorial furan chemistry.

In our further systematic studies on IMDA cycloaddition of furans,^{23,24} we have recently synthesized the



Scheme 1

tricyclicsulfones (**3**) by oxidizing the thermal intramolecular Diels-Alder cycloadduct, (**2**)^{25,26} (Scheme 1). 2-[(2-bromoprop-2-en-1-yl)thio]methylfuran (**1**) was derived from furfurylmercaptanol by employing Williamson ether synthesis.²⁷ Irradiation of thioether, 2-[(2-bromoprop-2-en-1-yl)thio]methylfuran in a commercial microwave oven (2450 MHz) in solvent-free condition for 12 min underwent [4+2] cycloaddition and gave 5-bromo-10-oxa-3-thia-tricyclo[5.2.1.0^{1,5}]dec-8-ene, (**2**) with modest yield. The tricyclic cycloadduct, (**2**) was then oxidized to sulfones, 5-bromo-10-oxa-3-thia-tricyclo[5.2.1.0^{1,5}]dec-8-ene-3,3-dioxide (**3**), using *m*-chloroperbenzoic acid (*m*-CPBA) in dichloromethane at 0 °C giving 78% yield.^{25,26}

Several theoretical methods are useful in analyzing vibrational spectra of organic molecules. These methods can be roughly divided into the following groups: classical mechanics, semi-empirical quantum mechanical methods, ab initio quantum mechanical method and ab initio followed by empirical scaling of the force constants. Ab initio molecular orbital calculation is relatively successful approaches to the calculation of vibrational spectrum of closed shell organic molecules. However, raw frequency values computed at the Hartree-Fock level contain known systematic errors due to neglecting electron correlation. Therefore, it is necessary to scale frequencies predicted at the Hartree-Fock level.

DFT methods are gaining popularity recently as a cost-effective general procedure for studying the physical properties of molecules.²⁸ Much effort has been devoted to refining the methodology and exploring the limits of its applicability.^{29,30} In the recent theoretical studies,^{31,32} the harmonic vibrational frequencies for a large number of molecules were computed with Hartree-Fock and Density functional methods. On the basis of a comparison of computed and observed fundamental vibrational frequencies, the scaled DFT methods were found to be reliable.

In the present study, we have, therefore, 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, by using the Hartree-Fock,³³ density functional using Becke's three-parameter hybrid method³¹ with the Lee, Yang, and Parr correlation functional methods,³² the Barone and Adamo's Becke-style one-parameter functional using the modified Perdew-Wang exchange and Perdew-Wang 91 correlation

method,^{34,35} Becke's three parameter exchange functional combined with gradient corrected correlation functional of Perdew and Wang's 1991,^{36,37} with the standard 6-31G(d) basis set. 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) level taking as a test compound 5-bromo-10-oxa-3-thia-tricyclo[5.2.1.0^{1,5}]dec-8-ene 3,3-dioxide.

2. Experimental

2.1. Synthesis of 5-bromo-10-oxa-3-thia-tricyclo[5.2.1.0^{1,5}]dec-8-ene 3,3-dioxide

To a solution of *meta*-chloroperbenzoic acid (*m*-CPBA) (300 mg, 1.2 mmol) which was previously purified and recrystallized in dry diethyl ether, in dichloromethane (10 mL), cooled to 0 °C, was added dropwise a solution of 2-(2-bromo-allylsulfanylmethyl)-furan (140 mg, 0.6 mmol) in dichloromethane (10 mL) over 3 min. The reaction mixture was stirred at room temperature for 4 h and the diluted with cold 4% sodium bicarbonate solution (4 mL). The organic layer was separated, washed with water (20 mL) and concentrated in *vacuo*. The crude solid residue was subjected to flash column chromatography to afford titled compound. EtOAc / *n*-Hexane (3:7) [*R_f*: 0.27] was used as eluent to provide pure dioxide. Off pale yellow crystals (for re-crystallization, 1:1 Ether / DCM): yield 120 mg (78%); m.p. 142–144 °C; δ_H (300 MHz CDCl₃): 6.57 (dd, 1H, *J*₁ 1.8 Hz, *J*₂ 5.7 Hz, AB), 6.35 (d, 1H, *J* 5.7 Hz, AB), 5.13 (dd, 1H, *J*₁ 1.8 Hz, *J*₂ 4.8 Hz), 3.93 (d, 1H, *J* 12.3 Hz, AB), 3.86 (d, 1H, *J* 12.5 Hz, AB), 3.65 (d, 1H, *J* 12.3 Hz, AB), 3.59 (d, 1H, *J* 12.5 Hz, AB), 2.53 (dd, 1H, *J*₁ 4.8 Hz, *J*₂ 12.0 Hz, AB), 1.98 (d, 1H, *J* 12.0 Hz, AB). δ_C (75 MHz CDCl₃): 135.0, 131.1, 128.5, 119.2 (*q*), 76.5 (*q*), 67.4, 52.3, 50.9, 46.7. *m/z*: 266 [M⁺(⁸¹Br), % 16], 264 [M⁺(⁷⁹Br), % 16], 184.9 [M⁺(⁸¹Br)-(C₅H₅O), % 10], 121 [M⁺-(SO₂+Br), % 16], 81 [(C₅H₅O)⁺, % 16], 55 [(C₃H₃O)⁺, % 40]. E. A. Required for C₈H₉O₃SBr: C, 36.24%; H, 3.42%. Found: C, 36.48%; H, 3.21%.

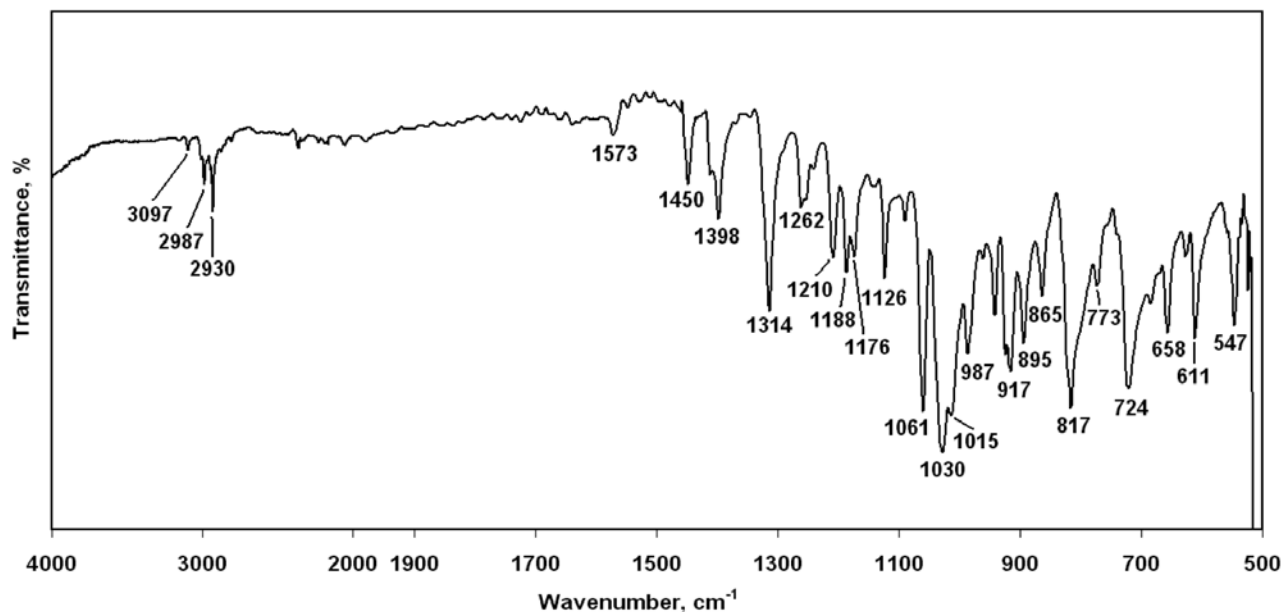


Figure 1: FT-IR spectrum of 5-bromo-10-oxa-3-thiatriacyclo[5.2.1.0^{1,5}]-dec-8-ene 3,3-dioxide recorded at room temperature.

2.2. Instrumentation

The room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) solid state spectrum of the 5-bromo-10-oxa-3-thiatriacyclo[5.2.1.0^{1,5}]-dec-8-ene 3,3-dioxide was registered using Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism (4000–525 cm⁻¹; number of scans: 250; resolution: 1 cm⁻¹) (Fig. 1).

2.3. 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.³⁸ The molecular structure of the BOTCDO, in the ground state are optimized by using the Hartree-Fock (HF),³³ density functional using Becke's three-parameter hybrid method³¹ with the Lee, Yang, and Parr correlation functional methods³² (B3LYP), the Barone and Adamo's Becke-style one-parameter functional using the modified Perdew–Wang exchange and Perdew–Wang 91 correlation method, (mPW1PW91),^{34,35} Becke's three parameter exchange functional combined with gradient corrected correlation functional of Perdew and Wang's 1991 (B3PW91),^{6,37} and 6-31G(d) basis set. The vibrational frequencies were also calculated with these methods. The frequency values computed at these levels contain known systematic errors.³⁹ 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.^{40,41} We have also calculated optimal scaling factors for all investigated methods. The assignment of the calculated wave numbers 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.⁴² Furthermore, theoretical vibrational spectra of the title compound were interpreted by means of PEDs using VEDA 4 program.⁴³

3. Results and Discussion

3.1. Geometry Optimization

The crystal and molecular structure of 5-bromo-10-oxa-3-thiatriacyclo[5.2.1.0^{1,5}]-dec-8-ene 3,3-dioxide have been reported.²⁶ The structure parameters is orthorhombic, the space group *Pbca*, with the cell dimensions $a = 10.1723$ (6) Å, $b = 10.3446$ (9) Å, $c = 17.6278$ (10) Å and $V = 1854.9$ (2) Å³. In this work, we performed full geometry optimization of the title compound. The crystal and optimized structure of BOTCDO with the labelling of atoms is given in Fig. 2. The optimized geometrical parameters (bond length and angles) by HF, B3LYP, B3PW91 and MPW1PW91 methods with 6–31G(d) as basis

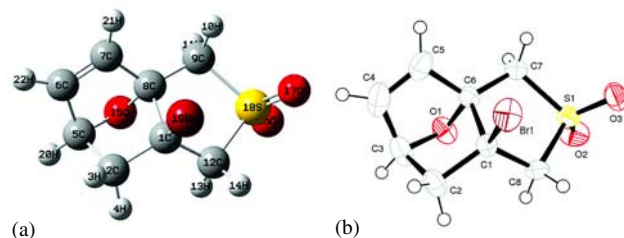


Figure 2: The optimized molecular structure (a) and ORTEP-3 view (50% probability displacement ellipsoids) of the title compound, with the atom numbering scheme (b).

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. However, owing to our calculations, DFT method correlates well for the bond

length and angle in comparison to the HF method. The largest difference between experimental and calculated DFT bond length and angle is about 0.049 Å and 2.8°. In the intermolecular hydrogen bond distances for a Donor-Hydrogen...Acceptor system, D-H distance is typically ~1.1 Å, whereas HA distance is ~1.6 to 2.0 Å. The crys-

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(1,2)	1.542(5)	1.549	1.553	1.547	1.544
R(1,8)	1.478(5)	1.570	1.595	1.588	1.583
R(1,12)	1.517(5)	1.530	1.526	1.522	1.520
R(1,19)	1.961(3)	1.958	1.985	1.964	1.956
R(2,5)	1.554(6)	1.555	1.567	1.562	1.559
R(5,6)	1.487(7)	1.520	1.521	1.517	1.515
R(5,15)	1.463(5)	1.416	1.444	1.436	1.432
R(6,7)	1.318(7)	1.317	1.335	1.334	1.332
R(7,8)	1.504(5)	1.519	1.522	1.518	1.515
R(8,9)	1.492(5)	1.513	1.512	1.508	1.506
R(8,15)	1.440(4)	1.409	1.438	1.429	1.425
R(9,18)	1.785(4)	1.802	1.848	1.835	1.827
R(12,18)	1.797(4)	1.802	1.846	1.833	1.824
R(16,18)	1.433(3)	1.435	1.469	1.465	1.461
R(17,18)	1.437(3)	1.435	1.469	1.465	1.461
<i>r</i>		0.9843	0.9848	0.9837	0.9838
Bond angles (°)					
A(2,1,8)	101.8(3)	101.15	101.32	101.30	101.31
A(2,1,12)	114.6(3)	114.74	115.26	115.08	114.97
A(2,1,19)	113.7(3)	113.12	112.68	112.95	113.09
A(8,1,12)	105.7(3)	105.66	106.46	106.13	105.95
A(8,1,19)	110.8(2)	111.99	111.26	111.18	111.19
A(12,1,19)	109.6(2)	109.68	109.43	109.69	109.80
A(1,2,5)	100.1(3)	99.88	100.33	100.22	100.17
A(2,5,6)	108.3(4)	107.75	107.58	107.18	107.08
A(2,5,15)	100.6(3)	100.97	100.93	101.18	101.23
A(6,5,15)	102.0(3)	101.36	101.87	102.08	102.08
A(5,6,7)	106.5(4)	105.65	105.71	105.56	105.54
A(6,7,8)	105.5(4)	105.12	105.36	105.15	105.09
A(1,8,7)	109.7(3)	109.94	108.97	108.69	108.68
A(1,8,9)	110.8(3)	111.13	111.71	111.48	111.41
A(1,8,15)	97.2(2)	97.80	97.65	97.86	97.92
A(7,8,9)	121.3(3)	121.05	121.21	121.20	121.23
A(7,8,15)	102.5(3)	102.00	102.43	102.67	102.69
A(9,8,15)	112.5(3)	112.12	111.98	112.14	112.13
A(8,9,18)	106.1(2)	106.51	106.84	106.86	106.82
A(1,12,18)	107.3(2)	107.22	107.15	107.12	107.02
A(5,15,8)	95.1(3)	97.43	96.52	96.51	96.57
A(9,18,12)	97.41(17)	96.82	95.71	95.79	95.88
A(9,18,16)	110.6(2)	110.34	110.30	110.34	110.36
A(9,18,17)	109.59(16)	108.80	108.68	108.64	108.58
A(12,18,16)	109.77(19)	108.99	109.00	108.98	109.02
A(12,18,17)	110.00(16)	109.92	109.82	109.85	109.77
A(16,18,17)	117.62(18)	120.59	120.50	120.45	120.44
<i>r</i>		0.9900	0.9903	0.9901	0.9901

Table 2: Vibrational wavenumbers obtained for the title compound at MPW1PW91/6-31G(d) level^a.

Num- ber	Wave number			IR Inten.		Red mass	Force Constant	Assignments, PED (%) ^d	
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.				Rel.
1	3156	3300	3119	3135	2	1	1.11	7.11	ν_{CH} , C6,7, sym (98)
2	3097	3274	3094	3110	1	1	1.09	6.88	ν_{CH} , C6,7, asym (100)
3	3009	3219	3042	3058	2	1	1.11	6.77	ν_{CH} , C9, asym (100)
4	3009	3216	3039	3055	1	1	1.11	6.75	ν_{CH} , C12, asym (99)
5	3005	3196	3020	3036	24	19	1.09	6.57	ν_{CH} , C5 (92)
6	3005	3191	3016	3031	4	3	1.10	6.62	ν_{CH} , C2, asym (93)
7	2987	3145	2973	2988	1	0	1.06	6.17	ν_{CH} , C9, sym (100)
8	2966	3139	2967	2982	0	0	1.06	6.15	ν_{CH} , C12, sym (97)
9	2930	3125	2954	2969	11	9	1.06	6.12	ν_{CH} , C2, sym (97)
10	1573	1683	1591	1599	3	2	6.52	10.89	$\nu_{\text{C=C}}$ (84)
11	1450	1520	1437	1444	6	5	1.09	1.48	δ_{CH_2} , scis, C2 (89)
12	1413	1470	1389	1396	12	9	1.12	1.43	δ_{CH_2} , scis, C9 (72)
13	1398	1467	1386	1393	18	15	1.10	1.40	δ_{CH_2} , scis, C12 (72)
14	1314	1376	1301	1307	32	26	2.80	3.13	$\delta_{=\text{CH}}$, ipb (60)
15	1294	1371	1295	1302	78	63	3.46	3.83	$\nu_{\text{S=O}}$ (54)
16	1262	1367	1292	1299	87	70	2.73	3.01	δ_{OCH} (11) + δ_{CH_2} , wagg, C8 (22)
17	1254	1340	1267	1273	2	1	1.56	1.65	δ_{CH_2} , wagg, C8 (10) + δ_{OCH} (43)
18	1243	1297	1226	1232	24	20	1.54	1.53	δ_{CH_2} , wagg, C12 (26) + δ_{CH} , C5 (17)
19	1210	1292	1221	1227	0	0	1.70	1.67	$\delta_{=\text{CH}}$, ipb, C6,7 (24) + δ_{CH_2} , wagg, C2,12 (28)
20	1203	1264	1195	1201	51	41	1.51	1.42	δ_{CH_2} , wagg, C2,12 (36) + $\delta_{=\text{CH}}$, ipb (24)
21	1188	1246	1178	1184	5	4	1.81	1.66	ν_{CO} (11) + δ_{CH_2} , wagg, C9,12 (43)
22	1176	1232	1164	1170	23	18	1.55	1.39	ν_{CC} (14) + δ_{CH} twist, C2 (50)
23	1146	1214	1147	1153	22	18	1.59	1.38	δ_{CH} twist, C9,12 (60)
24	1126	1169	1105	1111	36	29	1.36	1.09	δ_{CH} twist, C12,9 (65)
25	1092	1144	1082	1087	124	100	5.51	4.25	$\nu_{\text{S=O}}$ (69)
26	1062	1132	1070	1075	6	5	1.59	1.20	ν_{CC} (14) + δ_{CH} twist, C2 (29)
27	1054	1112	1051	1057	39	32	1.83	1.34	$\delta_{=\text{CH}}$, ipb (20) + δ_{CH} twist, C2 (19)
28	1030	1088	1028	1034	11	9	1.80	1.26	$\delta_{=\text{CH}}$, ipb (12) + δ_{CH} twist, C9 (26)
29	1015	1050	992	997	16	13	2.61	1.69	ν_{CC} (27) + $\delta_{=\text{CH}}$, ipb (12)
30	987	1038	981	986	35	28	2.42	1.53	δ_{CCO} (14)
31	963	995	940	945	35	28	2.36	1.37	δ_{CH_2} , rock, C9 (18) + ν_{CO} (20) + δ_{CCO} (22)
32	943	975	921	926	6	5	3.22	1.80	ν_{CC} (29)
33	925	960	907	912	16	13	2.11	1.15	ν_{CC} (54)
34	917	946	894	899	6	5	1.46	0.77	$\gamma_{=\text{CH}}$ (73)
35	895	936	885	889	5	4	2.07	1.07	ν_{CC} (11) + δ_{CH_2} , rock, C12 (14)
36	865	899	850	854	11	9	2.27	1.08	ν_{CC} (20) + δ_{CH_2} , rock, C2 (11)
37	817	863	815	820	11	9	2.92	1.28	ν_{CO} (23) + $\delta_{\text{CC=C}}$ (25)
38	809	856	809	813	9	7	3.19	1.37	ν_{CO} (11) + δ_{COC} (27) + δ_{CH_2} , rock, C9 (14)
39	773	816	771	775	32	26	5.97	2.34	ν_{CS} (22) + γ_{C} , C8 (14)
40	724	793	750	753	2	1	2.96	1.10	δ_{CCC} (10) + δ_{CH_2} , rock, C9,12 (16)
41	712	747	706	710	14	12	2.76	0.91	$\delta_{\text{CC=C}}$ (11) + $\gamma_{=\text{CH}}$ (17)
42	687	725	685	689	25	20	1.99	0.62	$\gamma_{=\text{CH}}$ (24)
43	658	711	672	675	3	3	3.86	1.15	δ_{SCC} (10) + δ_{CCC} (28)
44	628	680	643	646	7	5	4.33	1.18	ν_{CC} (12) + δ_{CCO} (11) + γ_{C} (14)
45	611	643	607	610	6	5	5.00	1.22	δ_{CCO} (21)
46	547	563	532	535	7	6	3.15	0.59	τ_{CC} (16)
47	-	553	523	526	25	20	7.61	1.37	$\delta_{\text{O=S=O}}$ (40)
48	-	481	455	457	25	20	5.36	0.73	$\delta_{\text{O=S=O}}$ (40) + τ_{CO} (20)
49	-	454	429	431	31	25	5.35	0.65	γ_{C} (43) + γ_{C} (15)
50	-	404	382	384	4	3	2.27	0.22	δ_{CCC} (13)
51	-	365	345	346	0	0	2.45	0.19	γ_{S} (34)
52	-	348	329	331	1	1	2.37	0.17	ν_{CBr} (15) + δ_{CCO} (14) + γ_{C} (10)
53	-	316	299	301	5	4	6.31	0.37	ν_{CBr} (14) + ν_{CS} (20) + γ_{C} (10)
54	-	299	283	284	0	0	4.03	0.21	ν_{CBr} (20) + δ_{OSC} (12) + δ_{CCBr} (19)
55	-	289	274	275	2	2	5.47	0.27	δ_{SCC} (22) + $\delta_{\text{O=S=O}}$ (15)
56	-	242	228	230	2	2	5.78	0.20	δ_{CCO} (14) + δ_{CCC} (19) + γ_{S} (17)

Num-ber	Wave number			IR Inten.		Red mass	Force Constant	Assignments, PED (%) ^d	
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.				Rel.
57	-	194	183	184	1	1	9.37	0.21	δ_{OSC} , (12) + δ_{CCBr} , (35)
58	-	138	131	131	2	2	6.93	0.08	γ_{C} , (43) + τ_{CC} , (21)
59	-	100	94	95	1	0	6.49	0.04	τ_{CC} , (21) + γ_{C} , (20)
60	-	53	50	50	3	2	7.44	0.01	τ_{CC} , (58)
<i>r</i>		0.9998	0.9998	0.9998					
Mean deviation		79.44	-2.52	-73.19					
Mean absol. deviation		79.44	13.46	73.19					
Average absol. error		5.46	1.11	5.30					
RMS_{mol}		96.39	16.39	83.52					
RMS_{over}		84.40	14.35	73.13					
Scaling Factor		-	0.9452	0.9500					

^a Harmonic frequencies (in cm^{-1}), IR intensities (km mol^{-1}), reduced masses (amu) and force constants (m dyn \AA^{-1}). ^b Scaling Factor calculated in this research. ^c Scaling factor obtained from Ref.⁴⁰ ^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.

taline form of the title compound has two intermolecular interactions ($\text{C7-H7A}\cdots\text{O2}^i$, with $\text{H}\cdots\text{O} = 2.42 \text{ \AA}$ ($i = 1/2 + x, y, 1/2-z$) and $\text{C8-H8A}\cdots\text{O3}^{ii}$, with $\text{H}\cdots\text{O} = 2.42 \text{ \AA}$ ($ii = -1/2 + x, y, 1/2-z$)). According to these crystalline geometrical parameters, we can say that the title compound has too weak molecular interactions. The good correlation between the experimental and calculated structure parameters confirmed these weak intermolecular interactions. As a result, the optimized bond lengths and angles by DFT method show the best agreement with the experimental values.

3.2. Vibrational Frequencies

The literature search has revealed that DFT calculations and vibrational analysis have not been reported so far on 5-bromo-10-oxa-3-thiatriacyclo[5.2.1.0^{1,5}]-dec-8-ene 3,3-dioxide. Therefore, we have calculated the theoretical vibrational spectra of 5-bromo-10-oxa-3-thiatriacyclo[5.2.1.0^{1,5}]-dec-8-ene 3,3-dioxide by using HF, B3LYP, B3PW91 and MPW1PW91 methods with 6-31G(d) basis set. Theoretical and experimental results of the title compound are shown in Table 2 and supplementary materials as Table S1–S3. The vibrational bands assignments have

been made by using both the animation option of GaussView 3.0 graphical interface for gaussian programs⁴² and VEDA 4 program.⁴³ All the calculated spectra are in a good agreement with the experimental one. All three hybrid functions are superior to HF in terms of realistic reproduction of both band intensity distribution and general spectral features.

The IR bands at 3156 and 3097 cm^{-1} in FT-IR spectrum of the title compound have been designated to symmetric and asymmetric ν_{CH} stretching fundamentals of C6 and C7 atoms, respectively.^{44,45} The wave numbers corresponding to the aliphatic ν_{CH} stretching are listed in and Table 2 and Table S1–S3. A good coincidence of theoretical wave numbers with that of experimental evaluations is found in the symmetric and asymmetric stretching vibrations of the $-\text{CH}_2-$ moieties. The vibrational spectra show five bands in the aliphatic ν_{CH} stretching region and are evident overlap between the different C–H stretching modes. Seven bands at 3042, 3039, 3020, 3016, 2973, 2967 and 2954 cm^{-1} were calculated in this research (MPW1PW91). 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.^{44,46}

Table 3: Mean deviation, mean absolute deviation, correlation coefficient, root mean square and average absolute error between the calculated and observed fundamental vibrational frequencies for the title compound.

Parameters	HF	DFT		
		B3LYP	B3PW91	MPW1PW91
Scaling Factor	0.8920	0.9553	0.9518	0.9452
Mean deviation	12.29	-5.05	-3.87	-2.52
Mean absolute deviation	26.87	14.66	14.42	13.46
Average absolute error	2.21	1.25	1.20	1.11
RMS_{mol}	31.71	17.77	17.16	16.39
RMS_{over}	27.76	15.59	15.02	14.35
<i>r</i>	0.9997	0.9998	0.9998	0.9998

Table S1: Vibrational wavenumbers obtained for the title compound at HF/6-31G(d) level ^a.

Number	Wave number				IR intensity		Red mass	Force Constant
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.	Rel.		
1	3156	3443	3071	3096	2	1	1.11	7.02
2	3097	3415	3046	3071	2	1	1.09	6.79
3	3009	3359	2996	3021	1	1	1.11	6.70
4	3009	3355	2993	3017	1	1	1.11	6.68
5	3005	3344	2983	3007	24	16	1.09	6.49
6	3005	3329	2970	2994	5	3	1.10	6.53
7	2987	3290	2935	2959	0	0	1.06	6.10
8	2966	3286	2931	2954	0	0	1.06	6.08
9	2930	3263	2910	2934	12	8	1.06	6.05
10	1573	1816	1620	1633	3	2	6.50	10.66
11	1450	1647	1469	1481	6	4	1.08	1.46
12	1413	1600	1427	1438	11	7	1.12	1.41
13	1398	1593	1421	1433	18	12	1.10	1.38
14	1314	1493	1331	1342	23	16	2.48	2.72
15	1294	1489	1328	1339	17	11	2.17	2.36
16	1262	1467	1309	1319	148	100	6.00	6.47
17	1254	1461	1303	1314	2	1	1.54	1.60
18	1243	1440	1284	1295	21	14	1.52	1.48
19	1210	1415	1262	1272	0	0	1.72	1.66
20	1203	1397	1246	1257	50	34	1.47	1.36
21	1188	1357	1210	1220	6	4	1.79	1.61
22	1176	1334	1190	1200	22	15	1.54	1.36
23	1146	1324	1181	1191	20	13	1.56	1.33
24	1126	1279	1141	1150	31	21	1.34	1.06
25	1092	1236	1102	1111	128	86	5.62	4.23
26	1062	1216	1085	1094	7	4	1.62	1.20
27	1054	1210	1079	1088	39	26	1.73	1.24
28	1030	1182	1054	1063	11	7	1.90	1.30
29	1015	1151	1027	1035	15	10	2.63	1.67
30	987	1134	1011	1019	35	23	2.44	1.52
31	963	1103	984	992	35	24	2.40	1.37
32	943	1071	956	963	6	4	3.40	1.87
33	925	1060	946	954	16	11	2.14	1.14
34	917	1029	918	926	6	4	1.48	0.76
35	895	1014	905	912	5	4	2.06	1.04
36	865	964	860	867	11	7	2.26	1.06
37	817	940	839	846	11	7	3.08	1.32
38	809	921	822	828	9	6	3.12	1.32
39	773	900	802	809	33	22	6.11	2.33
40	724	867	774	780	2	1	3.02	1.09
41	712	816	728	734	16	11	2.73	0.88
42	687	804	718	723	23	16	1.99	0.60
43	658	793	707	713	4	2	3.95	1.13
44	628	732	653	658	7	5	4.44	1.18
45	611	695	620	625	6	4	5.04	1.20
46	547	614	548	552	7	5	3.12	0.57
47	–	603	538	542	24	16	7.89	1.39
48	–	520	464	468	25	17	5.37	0.72
49	–	504	449	453	30	20	5.35	0.64
50	–	438	391	394	4	3	2.25	0.21
51	–	402	359	362	0	0	2.44	0.19
52	–	377	337	339	1	1	2.40	0.17
53	–	341	304	307	5	3	6.35	0.36
54	–	327	291	294	0	0	4.00	0.21
55	–	318	284	286	2	2	5.70	0.28
56	–	261	233	235	2	1	5.81	0.20
57	–	216	193	194	1	1	9.42	0.20
58	–	149	133	134	2	2	6.95	0.08

Number	Wave number				IR intensity		Red mass	Force Constant
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.	Rel.		
59	–	112	100	101	1	0	6.43	0.04
60	–	55	49	50	3	2	7.52	0.01
r		0.9997	0.9997	0.9997				
Mean deviation		185.28	12.29	–131.67				
Mean absolute deviation		185.28	26.87	131.67				
Average absolute error		14.03	2.21	8.54				
RMS_{mol}		200.90	31.71	168.10				
RMS_{over}		175.91	27.76	147.19				
Scaling Factor		–	0.8920	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. ⁴¹.

Table S2: Vibrational wavenumbers obtained for the title compound at B3LYP/6-31G(d) level^a.

Number	Wave number				IR intensity		Red mass	Force Constant
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.	Rel.		
1	3156	3268	3121	3142	2	2	1.11	6.96
2	3097	3241	3096	3116	2	2	1.09	6.74
3	3009	3188	3045	3065	1	1	1.11	6.64
4	3009	3187	3045	3064	0	0	1.11	6.64
5	3005	3165	3024	3043	27	22	1.09	6.45
6	3005	3160	3019	3038	5	4	1.10	6.49
7	2987	3119	2980	2999	0	0	1.06	6.06
8	2966	3115	2976	2995	1	1	1.06	6.05
9	2930	3097	2959	2978	13	11	1.06	6.02
10	1573	1660	1586	1596	3	2	6.37	10.35
11	1450	1521	1453	1462	5	4	1.08	1.48
12	1413	1470	1404	1413	7	6	1.10	1.40
13	1398	1468	1402	1411	17	14	1.10	1.40
14	1314	1360	1299	1307	10	9	1.87	2.04
15	1294	1352	1292	1300	15	13	2.25	2.43
16	1262	1332	1273	1281	119	100	4.35	4.55
17	1254	1327	1268	1276	28	24	1.68	1.74
18	1243	1286	1228	1236	14	12	1.50	1.46
19	1210	1279	1222	1230	2	2	1.74	1.68
20	1203	1252	1196	1203	42	36	1.39	1.28
21	1188	1229	1174	1181	13	11	1.68	1.49
22	1176	1219	1164	1172	18	15	1.56	1.36
23	1146	1199	1146	1153	13	11	1.52	1.29
24	1126	1161	1109	1116	24	21	1.30	1.03
25	1092	1121	1070	1077	26	22	1.70	1.26
26	1062	1113	1063	1070	112	94	5.11	3.73
27	1054	1096	1047	1054	48	41	1.67	1.18
28	1030	1070	1022	1029	12	10	2.22	1.50
29	1015	1027	981	988	15	13	2.60	1.62
30	987	1014	968	975	32	27	2.49	1.51
31	963	974	931	937	35	30	2.41	1.35
32	943	954	911	917	10	8	3.82	2.05
33	925	941	899	904	9	8	1.91	1.00
34	917	932	890	896	12	10	1.65	0.85
35	895	921	879	885	4	4	2.09	1.04
36	865	885	845	851	11	9	2.42	1.12
37	817	844	806	811	13	11	2.77	1.16
38	809	843	806	811	11	9	3.75	1.57
39	773	791	756	761	33	27	6.32	2.33
40	724	775	740	745	2	1	3.08	1.09

Number	Wave number				IR intensity		Red mass	Force Constant
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.	Rel.		
41	712	736	703	707	16	14	2.72	0.87
42	687	709	677	682	19	16	2.04	0.60
43	658	684	653	658	4	3	3.94	1.09
44	628	662	632	637	8	6	4.70	1.21
45	611	632	604	608	7	6	5.20	1.22
46	547	556	531	535	7	6	3.11	0.57
47	–	543	518	522	23	20	8.19	1.42
48	–	474	453	456	25	21	5.37	0.71
49	–	445	425	428	30	25	5.33	0.62
50	–	403	385	387	4	3	2.22	0.21
51	–	358	342	345	0	0	2.40	0.18
52	–	344	329	331	1	1	2.48	0.17
53	–	307	293	295	5	4	6.15	0.34
54	–	292	279	281	1	0	4.15	0.21
55	–	284	271	273	2	2	6.13	0.29
56	–	239	228	230	2	2	5.94	0.20
57	–	191	183	184	1	1	9.51	0.20
58	–	137	131	132	2	2	7.01	0.08
59	–	99	94	95	1	0	6.34	0.04
60	–	51	49	49	3	2	7.68	0.01
r		0.9998	0.9998	0.9998				
Mean deviation		61.04	–5.05	–59.51				
Mean absolute deviation		61.04	14.66	59.51				
Average absolute error		3.93	1.25	4.56				
RMS_{mol}		78.76	17.77	65.68				
RMS_{over}		68.96	15.56	57.50				
Scaling Factor		–	0.9553	0.9614				

^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. ⁴¹.

Table S3: Vibrational wavenumbers obtained for the title compound at B3PW91/6-31G(d) level ^a.

Number	Wave number				IR intensity		Red mass	Force Constant
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.	Rel.		
1	3156	3280	3122	3140	2	1	1.11	7.02
2	3097	3253	3096	3114	2	1	1.09	6.79
3	3009	3200	3046	3064	1	1	1.11	6.70
4	3009	3198	3043	3061	1	1	1.11	6.68
5	3005	3175	3022	3039	24	16	1.09	6.49
6	3005	3171	3018	3036	5	3	1.10	6.53
7	2987	3128	2977	2994	0	0	1.06	6.10
8	2966	3122	2971	2988	0	0	1.06	6.08
9	2930	3106	2956	2974	12	8	1.06	6.05
10	1573	1669	1589	1598	3	2	6.50	10.66
11	1450	1513	1440	1448	6	4	1.08	1.46
12	1413	1462	1392	1400	11	7	1.12	1.41
13	1398	1459	1389	1397	18	12	1.10	1.38
14	1314	1364	1298	1306	23	16	2.48	2.72
15	1294	1358	1293	1300	17	11	2.17	2.36
16	1262	1353	1288	1295	148	100	6.00	6.47
17	1254	1329	1265	1273	2	1	1.54	1.60
18	1243	1286	1224	1231	21	14	1.52	1.48
19	1210	1281	1219	1227	0	0	1.72	1.66
20	1203	1253	1192	1199	50	34	1.47	1.36
21	1188	1234	1175	1182	6	4	1.79	1.61
22	1176	1222	1163	1170	22	15	1.54	1.36

Number	Wave number				IR intensity		Red mass	Force Constant
	Exp.	Unscaled	Scaled ^b	Scaled ^c	Abs.	Rel.		
23	1146	1204	1145	1152	20	13	1.56	1.33
24	1126	1160	1104	1111	31	21	1.34	1.06
25	1092	1131	1076	1082	128	86	5.62	4.23
26	1062	1123	1069	1075	7	4	1.62	1.20
27	1054	1103	1049	1055	39	26	1.73	1.24
28	1030	1078	1026	1032	11	7	1.90	1.30
29	1015	1038	988	994	15	10	2.63	1.67
30	987	1026	976	982	35	23	2.44	1.52
31	963	983	936	941	35	24	2.40	1.37
32	943	964	918	923	6	4	3.40	1.87
33	925	950	905	910	16	11	2.14	1.14
34	917	936	891	896	6	4	1.48	0.76
35	895	927	882	887	5	4	2.06	1.04
36	865	891	848	853	11	7	2.26	1.06
37	817	854	812	817	11	7	3.08	1.32
38	809	848	807	812	9	6	3.12	1.32
39	773	804	765	769	33	22	6.11	2.33
40	724	784	746	750	2	1	3.02	1.09
41	712	740	704	708	16	11	2.73	0.88
42	687	716	681	685	23	16	1.99	0.60
43	658	698	664	668	4	2	3.95	1.13
44	628	672	640	644	7	5	4.44	1.18
45	611	637	606	609	6	4	5.04	1.20
46	547	559	532	535	7	5	3.12	0.57
47	–	547	521	524	24	16	7.89	1.39
48	–	477	454	456	25	17	5.37	0.72
49	–	449	427	430	30	20	5.35	0.64
50	–	402	383	385	4	3	2.25	0.21
51	–	361	343	345	0	0	2.44	0.19
52	–	345	329	330	1	1	2.40	0.17
53	–	312	297	299	5	3	6.35	0.36
54	–	295	281	283	0	0	4.00	0.21
55	–	287	273	274	2	2	5.70	0.28
56	–	240	229	230	2	1	5.81	0.20
57	–	192	183	184	1	1	9.42	0.20
58	–	138	131	132	2	2	6.95	0.08
59	–	99	94	95	1	0	6.43	0.04
60	–	52	50	50	3	2	7.52	0.01
r		0.9998	0.9998	0.9998				
Mean deviation		67.68	–3.87	–64.16				
Mean absolute deviation		67.68	14.42	64.16				
Average absolute error		4.52	1.20	4.77				
RMS_{mol}		84.76	17.16	72.02				
RMS_{over}		74.22	15.02	63.06				
Scaling Factor		–	0.9518	0.9573				

^a Harmonic frequencies (in cm^{-1}), IR intensities (km mol^{-1}), reduced masses (amu) and force constants ($\text{m dyn } \text{Å}^{-1}$). ^b Scaling Factor calculated in this research. ^c Scaling factor obtained from Ref. ⁴¹.

Calculations of the vibrational spectra of hydrogen bonded systems are extremely demanding since their potential energy hyper surfaces are highly anharmonic; therefore, calculations of the vibrational spectra in the harmonic approximation are of very limited value. Some methods have been developed for solving this problem such as variational solving of the Schrödinger equation⁴⁷. However, according to single crystal X-ray diffraction data, the title compound has not got any strong hydrogen bond. Therefo-

re, we did not focus on the hydrogen bonds for the title compound. The crystalline form of the title compound has two weak molecular interactions (C7-H7A...O2 and C8-H8A...O3). The biggest difference between calculated and experimental $\nu_{\text{C-H}}$ stretching vibrations of the $-\text{CH}_2-$ moieties is 33 and 30 cm^{-1} for $\nu_{\text{C}_9\text{-H}}$ and $\nu_{\text{C}_{12}\text{-H}}$ stretching, respectively. These discrepancies for $\nu_{\text{C}_9\text{-H}}$ and $\nu_{\text{C}_{12}\text{-H}}$ stretching vibrational modes come from the formation of weak intermolecular hydrogen bonding with C-H.

The biological effects are often connected with the capability of contributing into intermolecular interactions during formation of supramolecular compounds with biomacromolecules. Hydrogen bonds are implicated in regulating dioxygen activation in methane monooxygenase,^{48,49} and hydrogen atom abstraction in lipoxygenase.^{50–54} As the inhibition of some enzymes by derivatives of the title compound can be attributed to weak intermolecular interactions, the title compound may itself possess same biological activity due to the presence of these interactions.

The peaks appearing in the region (600–1500 cm⁻¹) are associated with the scissoring, rocking, wagging and twisting modes of methylene groups. The vibrational modes of scissoring, rocking, wagging and twisting are well defined in all the calculations. The bands observed at 1450, 1413 and 1398 cm⁻¹ in FT-IR spectrum correspond to scissoring deformation of –C(2)H₂–, –C(9)H₂– and –C(12)H₂– group in the title compound.^{44,45} The wagging, twisting and rocking vibrational modes are distributed in a wide range.^{44–46,55,56} The rocking –CH₂– is assigned in the wave number range of 950–800 cm⁻¹ and the wave number shift of these bands is due to the atom nature in which the –CH₂– group is bonded. The –CH₂– rocking vibrational modes are intensive bands in which can be appreciating the vibrational coupling with other vibrational modes.^{55,56} All these bands are assigned using calculated potential energy distribution.

The two ν_{S=O} stretching modes were calculated at 1294 and 1092 cm⁻¹ and observed in reasonably good agreement at 1322 and 1106 cm⁻¹ in the infrared spectrum of vinylsulfonamide⁵⁷. The band observed at 773 cm⁻¹ in FT-IR spectrum corresponds to ν_{C–S} stretching vibration in the title compound. The calculated DFT/6–31G(d) scaled value for the title compound is 771 cm⁻¹, this value is well in agreement with the experimental wave number. This result was confirmed by Bensebaa et al.⁵⁸

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 and Table S1–S3. The root mean square (RMS) values were obtained in this study using the equations (12) and (13) from Ref.⁴¹ 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.^{40,59–65}

These results indicate that the DFT calculations approximate the observed fundamental frequencies much better than the HF results. Furthermore, the MPW1PW91 method calculations approximate the observed fundamental frequencies much better than the other investigated DFT methods results. The small difference between experimental and calculated vibrational modes is observed. 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, λ, we employed a least-square procedure using the equation (10) from Ref.⁴¹;

$$\lambda = \frac{\sum_i^{\text{all}} \omega_i^{\text{theor}} \nu_i^{\text{expt}}}{\sum_i^{\text{all}} (\omega_i^{\text{theor}})^2}$$

Where ω_i^{theor} and ν_i^{expt} are the *i*th theoretical harmonic and *i*th experimental fundamental frequencies (in cm⁻¹), respectively. Only single (uniform) scaling factors were calculated, without discrimination for different vibrations. The values obtained are 0.8920, 0.9452, 0.9518 and 0.9553 for HF, MPW1PW91, B3PW91 and B3LYP, respectively. They are very close to those recommended by Scott & Radom and Kuppens et al.^{40,41} for the same levels of theory 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 0.892, 0.945, 0.952 and 0.955 for HF, MPW1PW91, B3PW91 and B3LYP, respectively.

4. Conclusions

The ground state geometries were optimized using the HF, B3LYP, B3PW91 and MPW1PW91 methods with the 6-31G(d) basis set. The vibrational frequencies were also calculated with these methods. IR spectrum of the title compound computed is 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 0.8920, 0.9452, 0.9518 and 0.9553 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 0.892, 0.945, 0.952 and 0.955 for HF, MPW1PW91, B3PW91 and B3LYP, respectively.

5. Acknowledgements

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Povzetek

5-bromo-10-oksa-3-tiatriciklo[5.2.1.0^{1,5}]-dek-8-ene 3,3-dioksid (BOTCDO) je bil sintetiziran na osnovi reakcije med 2-(2-bromoalilsulfanilmetil)-furanom in *m*-kloroperbenzojeve kisline v diklormetanu. Molekularno strukturo in vibracijske frekvence BOTCDO v osnovnem stanju smo raziskovali z metodami *ab initio* (HF) in teorijo gostotnega funkcionala (B3LYP, B3PW91 in MPW1PW91) s pomočjo standardnega 6–31G(d) baznega seta. Dolžine vezi in velikosti kotov geometrije optimirane s HF in DFT kažejo najboljše ujemanje z eksperimentalnimi podatki. Primerjava dejanskih osnovnih vibracijskih frekvenc obravnavanih spojin z izračunanimi (HF in DFT) nakazujejo, da je MPW1PW91 metoda boljša od normalizirane HF metode za molekularne probleme. Najboljši normalizacijski faktorji obravnavanih spojin za metode HF, B3LYP, B3PW91 in MPW1PW91 so 0.8920, 0.9553, 0.9518 in 0.9452.