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MOLECULAR STRUCTURE AND VIBRATIONAL AND CHEMICAL SHIFT ASSIGNMENTS OF (4R)-5-ENO-4,7-EPIDIOXY-3,7-O-METHYL-1,2-O-(S)-TRICHLOROETHYLIDENE-5,6,8-TRIDEOXY- α -D-THREO-1,4-FURANO-4,7-DIULO-OCTOSE BY DFT AND *AB INITIO* HF CALCULATIONS**T. Karakurt¹, M. Dinçer², F. Çetin³**¹*Department of Chemical Engineering, Faculty of Engineering and Architecture, Ahi Evran University, Kırşehir, Turkey*

E-mail: tuncaykarakurt@gmail.com

²*Department of Physics, Faculty of Sciences, Ondokuz Mayıs University, Samsun, Turkey*³*Department of Chemistry, Faculty of Arts and Sciences, Ege University, İzmir, Turkey*

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Elemental analyses, single crystal X-ray diffraction method, and ¹H and ¹³C NMR spectral techniques are used to synthesize and characterize the crystal structure of 4-diethylamino-2- $\{[4-(3\text{-methyl-3-phenyl-cyclobutyl})\text{-thiazol-2-yl}]\text{-hydrazonomethyl}\}$ -phenol. In order to calculate the molecular geometry along with vibrational frequencies and the gauge including atomic orbital (GIAO) ¹H and ¹³C NMR chemical shift values of the title crystal structure in the ground state, the Hartree—Fock (HF) and density functional theory (DFT) methods with 6-311G(*d,p*) basis sets are utilized. The assignments of the vibrational frequencies are calculated with the help of the potential energy distribution (PED) analysis using the VEDA 4 software. Experimental data are used for comparison. The molecule contains C—H \cdots O intra—inter—molecular interactions.

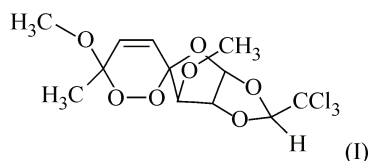
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Keywords: X-ray structure determination, DFT, HF, GIAO, ¹H and ¹³C NMR, IR spectra, vibrational assignment.

INTRODUCTION

Malaria is a principal parasitic illness in many areas of South America, Asia, and Africa. While four types of malarial parasite infect humans, the majority of malaria cases are caused by *Plasmodium falciparum*, and its tenacity to many modern antimalarial drugs has entangled the problem of illness control [1]. Some of the actual combination therapies in clinical exercise for malaria cure rest up on endoperoxide-based compounds [2].

On the whole, the endoperoxides have some advantages over present antimalarial meds. First, there is cross-resistance with other antimalarial meds. Second, the endoperoxides clear the environmental blood of parasites more swiftly than other present meds do. Finally, resistance to the endoperoxides has not yet improved despite extensive clinical use [3]. Besides all these, there are some downsides. The endoperoxides have short half-lives, and effective levels in plasma are undamped for a just relatively curt revolution. As a result, a short period cure (less than 5 days) with the endoperoxides is generally integrated with an unacceptably high ratio (>10 %) of recrudescence infections [4].



This paper reports the molecular and crystal structure of (4R)-5-eno-4,7-epidioxy-3,7-O-methyl-1,2-O-(S)-trichloroethylidene-5,6,8-trideoxy- α -D-threo-1,4-furano-4,7-diulo-octose ($C_{12}H_{15}Cl_3O_7$) (I) determined by the single crystal X-ray diffraction study.

Hartree—Fock (HF) and DFT (B3LYP) methods with the 6-311G(*d,p*) basis set were used in order to calculate the geometrical parameters, harmonic vibrational frequencies, and 1H and ^{13}C NMR chemical shift values of the title crystal structure in the ground state. All ($C_{12}H_{15}Cl_3O_7$) parameters were calculated at the HF/6-311G(*d,p*) and B3LYP/6-311G(*d,p*) levels of theory with optimized geometries. These calculations are significant since they offer an insight into molecular parameters as well as IR and NMR spectra. The purpose of this study is to investigate the molecular and structural parameters of the chemical behavior of the title compound and to compare theoretical approximations with experimental investigations.

COMPUTATIONAL DETAILS

Hartree—Fock (HF) and DFT(B3LYP) [5, 6] with the 6-311G(*d,p*) [7] basis set were utilized to optimize the molecular structure of the title crystal structure in the ground state (*in vacuo*). For modeling purposes, the initial prediction of the title crystal structure was taken from X-ray data. Following this, these methods were used to calculate the vibrational frequencies of the optimized molecular structures and scaled by 0.8929 and 0.9613 [8] respectively. 1H and ^{13}C NMR spectra were calculated within the GIAO approach [9, 10] with the same methods and basis set as those utilized for the geometry optimization. The ^{13}C and 1H NMR chemical shifts were converted to the TMS scale. This was reached by subtracting the calculated absolute chemical shielding of TMS ($\delta = \Sigma_0 - \Sigma$, where δ is the chemical shift, Σ is the absolute shielding, and Σ_0 is the absolute shielding of TMS) with the following values, respectively: 32.60 ppm and 200.01 ppm for HF/6-311G(*d,p*) and 32.10 ppm and 189.40 ppm for B3LYP/6-311G(*d,p*). The calculations were carried out using the Gauss View Molecular Visualization [11, 12], the Gaussian 03 package [13], and the VEDA 4 program [14] for the crystal structure. The effects that the solvent had on theoretical NMR parameters were subsumed using the default model IEF-PCM [15] supplied by Gaussian 03. $CDCl_3$ with a dielectric constant (ϵ) of 4.81 was used as the solvent.

EXPERIMENTAL

Synthesis. (4R)-5-eno-4,7-epidioxy-3-O-methyl-1,2-O-(S)-trichloroethylidene-5,6,8-trideoxy- α -D-threo-1,4-furano-4,7-diulo-octose (100 mg, 0.276 mmol) was dissolved in anhydrous methanol (25 ml). Dimethyl sulphite (2.58 ml, 0.552 mmol) was added to the solution and the reaction mixture was refluxed for 3 h. Solution was neutralized with diluted $NaHCO_3$, and the solvent was removed at $50^\circ C$. The syrupy residue was purified on a silica gel column, eluting with hexane-ethyl acetate (20:1). The solvent was removed to obtain the title product and it was crystallized from diethyl ether and light petroleum (Fig. 1). White crystals, yield 30 % (0.32 mg), mp $147\text{--}148^\circ C$, $[\alpha]_D^{19} -99.0$ (*c* 0.70, $CHCl_3$). IR (KBr, v, cm^{-1}): 2963 (aliphatics), 1716 ($-C=C-$), 1361 ($-C-H$), 1156—1103 ($-O-C-$), 1038—983—811 ($-O-O-$), 619 ($C-Cl$). 1H NMR ($CDCl_3$, TMS, δ ppm): 1.45 (s, 3H, $-CH_3$), 3.43 (s, 3H, $-OCH_3$), 3.48 (s, 3H, $-OCH_3$), 3.72 (s, 1H, $-H-3$), 4.88 (d, 1H, H-2, $J_{H2,3} = 10.0$ Hz), 5.73 (s, 1H, $HCCl_3$), 5.98 (d, 1H, H-5, $J_{H5,6} = 10.0$ Hz), 6.06 (d, 1H, H-6, $J_{H5,6} = 10.0$ Hz), 6.25 (d, 1H, H-1, $J_{H1,2} = 4.00$ Hz). ^{13}C NMR ($CDCl_3$, TMS, δ ppm): 134.3, 123.4, 112.7, 104.8, 104.3, 97.8, 95.6, 89.0, 87.2, 59.2, 59.4, 23.2. The negative polarity APCI MS spectrum in methanol—chloroform produced ($M + Cl^-$) peaks at m/z 411, 413 (100 %), 415, 417 (four chlorine isotope pattern), as the base peak group. Anal. Calcd. (%) for $C_{12}H_{15}Cl_3O_7$: C 38.30, H 3.98. Found: C 38.41, H 3.93.

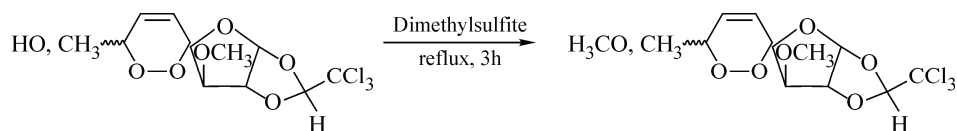


Fig. 1. Chemical structure of the title crystal structure

Crystallographic analysis. All diffraction measurements were performed on the goniometer of a STOE diffractometer with an IPDS(II) image plate detector using graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature (296 K). Data collections: Stoe X-AREA [16]. Cell refinement: Stoe X-AREA [16]. Data reduction: Stoe X-RED [18]. The structure was solved using direct methods with SHELXS-97 [19] and all non-hydrogen atoms were refined anisotropically by the full-matrix least squares procedure based on F^2 using SHELXL97 [17]. Molecular designs were acquired using ORTEP-III [18].

RESULTS AND DISCUSSION

The title crystal structure, an ORTEP-III view of which can be seen in Fig. 2, crystallizes in the monoclinic space group $P2_1$ with two molecules in the unit cell. Additional information on the structure determinations is given in Table 1. The atomic numbering diagram for the title crystal structure (C₁₂H₁₅Cl₃O₇) and the theoretical geometric structure are shown in Fig. 2, *a*, *b*.

The title molecule is built from planar fragments, *viz.* an endoperoxide ring $A(C6/C8/C9/C10/O5/O6)$, a furan ring $B(C3/C4/C6/C7/O4)$, and an acetal group. The endoperoxide ring forms a dihedral angle of $82.93(12)^\circ$ with the furan ring. This dihedral angle was calculated as 80.40° at the HF/6-311G(*d,p*) level and as 80.60° at the B3LYP/6-311G(*d,p*) level. These experimental and theoretical results have shown that the title molecule is non-planar.

The molecule is stabilized by two intermolecular C2—H2 \cdots O3 and C11—H11A \cdots O2, one intramolecular C12—H12C \cdots O5, and one X—H \cdots Cg (π -ring) intermolecular interactions (Fig. 3) whose characteristics are presented in Table 2. In the molecule, the C2 atom at (*x*, *y*, *z*) is doubled as a hydrogen-bond donor *via* the H2 atom to the O3 ring atom ($-1+x$, *y*, *z*), characterized by a C(10) motif, and the C11 atom at (*x*, *y*, *z*) acting as a hydrogen-bond donor *via* the H11A atom to the O2 ring atom at ($-x$, $+y-1/2$, $-z+1/2$) characterized by a C(10) motif [19], and the C12 carbon atom in the molecule acts as a hydrogen-bond donor *via* the H12C atom to the O5 ring atom in the molecule characterized by a S(6) motif [19] (Fig. 3). Crystal molecules are packed by normal van der Waals forces and π — π stacking interactions. The packing diagram of the title crystal structure is shown in the *bc*

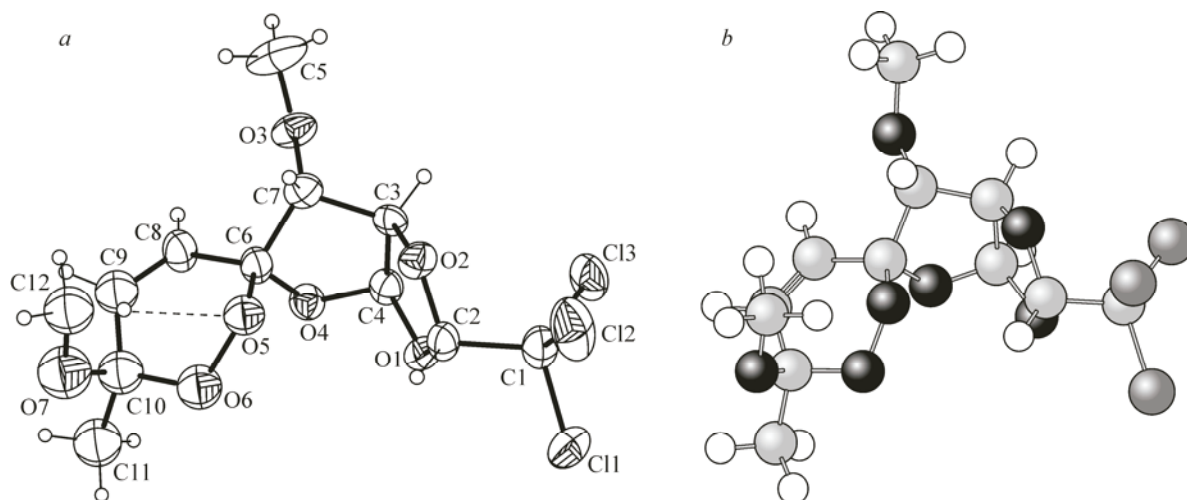


Fig. 2. Experimental geometric structure (*a*); theoretical geometric structure of the title crystal structure (*b*)

Table 1

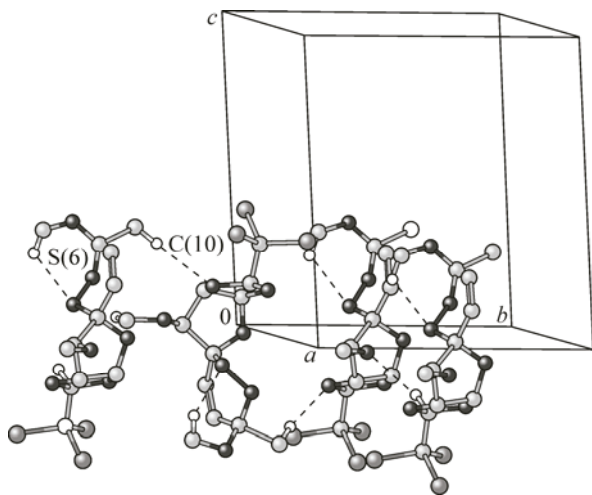
Crystallographic data for title crystal structure

Formula	$C_{12}H_{15}Cl_3O_7$
Formula weight	361.60 (a.k.b)
Temperature, K	293
Wavelength, Å	MoK_{α} , 0.71073
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell: a, b, c , Å; β , deg.	6.5324(4), 11.2550(10), 11.4266(6); 103.759(4)
V , Å ³	816.00(9)
Z	2
D_{calc} , g/cm ³	1.472
$F(000)$	388
Crystal size, mm	0.76×0.44×0.08
h, k, l range	$-8 \leq h \leq 8, -14 \leq k \leq 14, -14 \leq l \leq 14$
Reflections collected	16713
Independent reflections	3770
Reflections observed [$I \geq 2\sigma(I)$]	3126
R_{int}	0.0468
R [$I > 2\sigma(I)$]	0.0610
Rw [$I > 2\sigma(I)$]	0.1801
Goodness-of-fit on indicator	1.044
Structure determination	SHELXL97 (Sheldrick, 1997)
Extinction factor	0.001(2)
$(\Delta\sigma)_{max}, (\Delta\sigma)_{min}$, e/Å ³	0.790, -0.251

plane in Fig. 4, and the details of the hydrogen bond are presented in Table 2. The endoperoxide ring is planar with a maximum deviation of 0.006(3) Å for the C8 atom.

The dihedral angles between the endoperoxide plane, the furan plane, and the acetal group were as follows: 82.93(12)° (*AIB*) and 42.8(3)° (*AIC*). In light of all this, it can be argued that the compound is non-planar. These dihedral angles have been found to be 80.40° at the HF/6-311G(*d,p*) level and 80.60° at the B3LYP/6-311G(*d,p*) level. The theoretical and experimental results have shown that the title crystal structure is non-planar.

Different substituents depending on the endoperoxide ring are defined by the experimental bond



lengths C8=C9 (1.30(7) Å), O6—C10 (1.42(6) Å), O5—C6 (1.43(5) Å), O5—O6 (1.44(5) Å). These bond lengths have been calculated as 1.33 Å, 1.45 Å, 1.42 Å, and 1.28 Å (for HF/6-311G(*d,p*)) respectively, and 1.31 Å, 1.41 Å, 1.39 Å, and 1.39 Å (for B3LYP/6-311G(*d,p*)) respectively. In the previous experimental work, the O—O and O—C bond lengths were found to be 1.47(13) Å and 1.41(15)—1.43(15) Å [20]. When the O5—C6—

Fig. 3. Part of the crystal structure of the title crystal structure, showing C—H...O stacking interactions. For the sake of clarity, H atoms not involved in the motifs shown have been omitted

Table 2

Hydrogen bonding geometry (Å, deg.) for the title crystal structure

D—H...A	D—H	H...A	D...A	D—H...A
C2—H2...O3 ⁱ	1.01(2)	2.45(2)	3.44(2)	165(12)
C11—H11A...O2 ⁱⁱ	0.96(2)	2.57(3)	3.53(3)	173(3)
C12—H12C...O5	0.96(2)	2.37(3)	2.97(3)	120(13)

Symmetry code: ⁱ $-1+x, y, z$; ⁱⁱ $1-x, 1/2+y, z$.

O4—C4—O1—C2—O2—C3 oxygen-carbon chain is considered, the bond distances commencing with C4—O1 are in sequence: short, long, short, long [21]. These distances are all within the ranges of a normal single bond or a partial double bond. It is possible that this pattern is caused by the delocalization of lone pairs on the oxygen atoms. If this is the case, it may have a stabilizing effect on the molecule. This is consistent with its high thermal stability. In the furan ring, the bond lengths of O4—C4 and C3—C4 were obtained to be 1.39(5) Å and 1.51(6) Å. These lengths were calculated as 1.41 Å and 1.54 Å using the HF/6-311G(*d,p*) method, and 1.38 Å and 1.53 Å using the B3LYP/6-311G(*d,p*) method, and the data are shown in Table 3 for the optimized geometric parameters. In our study, according to the HF and B3LYP methods, the optimized geometric parameters are much closer to the experimental data.

A rational method of a global comparison of the structures obtained by theoretical calculations is to superimpose the molecular framework with the one acquired from X-ray diffraction, which results in a RMSE of 0.172 Å for HF and 0.194 Å for B3LYP calculations (Fig. 5). Hence, the B3LYP method correlates better than the HF one for the calculated values.

Assignments of the vibrational modes. A Mattson 1000 Fourier transform (FT)-IR spectrophotometer with KBr pellets was used to measure IR spectra. To be able to reach the spectroscopic signing of the compounds, a frequency calculation assay was made. The harmonic vibrational frequencies were calculated for the crystal structures with the help of HF/6-311G(*d,p*) and B3LYP/6-311G(*d,p*) methods, and detailed PED assignments are shown in Table 4. The experimental and calculated frequencies and IR intensities of the structure can be seen in Table 4. The table also lists the

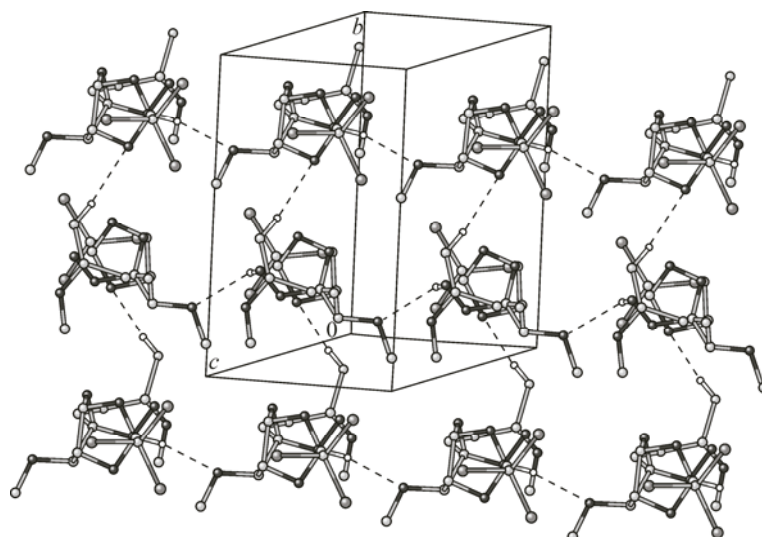


Fig. 4. Crystal packing of the title crystal structure projected on the *bc* plane. The dashed lines indicate the intermolecular hydrogen bonds

Table 3

Selected optimized and experimental geometric parameters in the ground state

Bond lengths, Å	Experimental	HF	DFT	Bond lengths, Å	Experimental	HF	DFT
C2—C1	1.54(5)	1.55	1.54	O5—O6	1.44(5)	1.28	1.39
C4—O1	1.42(5)	1.42	1.38	C10—O6	1.41(6)	1.45	1.41
C4—C3	1.52(6)	1.54	1.53	C9—C8	1.30(7)	1.33	1.31
C3—O2	1.43(4)	1.42	1.40	C9—C10	1.48(8)	1.50	1.51
C5—O3	1.36(7)	1.42	1.40	C8—C6	1.50(5)	1.49	1.49
O4—C4	1.39(5)	1.41	1.38	C10—O7	1.29(10)	1.41	1.38
O5—C6	1.43(5)	1.42	1.39	C1—C11	1.75(4)	1.76	1.76
O3—C7	1.40(4)	1.41	1.39	RMS		0.0632	0.0476
Bond angles, deg.	Experimental	HF	DFT	Torsion angles, deg.	Experimental	HF	DFT
C12—C1—C11	108.72(3)	109.39	109.86	O1—C2—C1—C11	60.12(6)	59.39	59.45
O1—C2—C1	109.33(4)	110.36	109.52	C4—O1—C2—C1	-118.42(4)	-130.37	-134.54
O2—C2—O1	109.23(3)	107.23	107.88	C3—O2—C2—O1	-8.50(4)	4.31	7.75
C4—C3—C7	104.55(4)	105.37	104.06	C5—O3—C7—C6	132.98(7)	159.30	161.21
O3—C7—C6	108.94(4)	108.57	108.35	C5—O3—C7—C3	-116.56(7)	-90.05	-87.51
O4—C4—C3	108.59(3)	109.08	106.87	C10—O6—O5—C6	-69.27(6)	-73.69	-72.18
C5—O3—C7	115.88(5)	113.13	115.35				
O7—C10—C11	106.88(5)	106.72	105.99				
C9—C8—C6	119.33(4)	119.37	119.31				
RMS		1.2761	0.9453				

harmonic vibrational frequencies in the range region $4000\text{--}400\text{ cm}^{-1}$. Any variety between the calculated and observed frequencies can be attributed to two facts: that the experimental results appertain to the solid phase while theoretical calculations appertain to the gaseous one; and that the calculations were actually made on a single molecule while experimental values were obtained in relation to intermolecular interactions.

The 105 normal vibrational modes of the title crystal structure composed of 37 atoms, spanning in irreducible renditions as 105A under the C1 point group symmetry, were designated based on the motion of singular atoms. The calculated IR intensity (Rel. intensity) enables the identification of the strength of the transition. It should be remembered that experimental IR spectra are often reported in either percent transmission or absorbance units. Fig. 6 displays the simulated IR spectra where the intensity is plotted against the harmonic vibrational frequencies and also the experimental IR spectra.

The C—H stretching vibration of the methoxy group band observed in the FT-IR spectrum at 2963 cm^{-1} is assigned to CH_3 asymmetric stretching vibrations. The theoretical values scaled by the B3LYP/6-311G(*d,p*) method at 3023 cm^{-1} are also in good accordance with the experimental values. The O— CH_3 vibrational mode at $\sim 40\text{ cm}^{-1}$ is assigned to anisole [22] and in the range $100\text{--}1000\text{ cm}^{-1}$ to anisole and its derivatives [23—26]. This mode at 1026 cm^{-1} , 909 cm^{-1} , and 995 cm^{-1} is

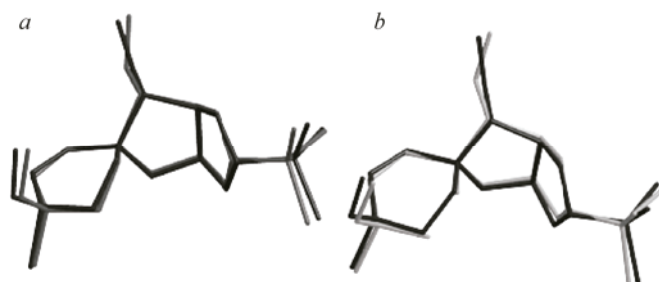


Fig. 5. Atom-by-atom superimposition of the calculated structures (*a* = HF; *b* = B3LYP with 6-311G(*d,p*)) over the X-ray structure (black) for the title crystal structure. Hydrogen atoms are omitted for clarity

Table 4

Comparison of the experimental and calculated vibrational spectra of the title crystal structure

Mode Nos.	Experimental FT-IR, cm ⁻¹	HF/6-311G(d,p)			B3LYP/6-311G(d,p)			Assignments with PED, % (≥10 %)
		Unscaled	Scaled	I _{IR}	Unscaled	Scaled	I _{IR}	
1	2	3	4	5	6	7	8	9
1	–	3428	3061	0	3240	3115	0	v _{CH} (98)
2	–	3374	3012	0	3193	3069	0	v _{CH} (96)
3	–	3361	3001	1	3170	3047	0	v _{CH} (94)
4	–	3324	2968	1	3157	3035	1	v _{CH} (98)
5	–	3320	2965	0	3156	3033	0	v _{CH} (96)
6	–	3320	2964	1	3153	3031	1	v _{CH} (92)
7	2963	3319	2963	1	3145	3023	0	v _{CH} (97), asym, CH ₃
8	–	3313	2958	2	3112	2992	1	v _{CH} (97)
9	–	3312	2957	6	3111	2990	6	v _{CH} (92)
10	–	3297	2944	1	3087	2967	1	v _{CH} (100)
11	–	3282	2931	0	3081	2961	0	v _{CH} (97)
12	–	3256	2908	1	3078	2959	0	v _{CH} (96)
13	–	3235	2888	1	3067	2949	1	v _{CH} (97)
14	–	3224	2879	1	3041	2923	1	v _{CH} (14)+v _{CH} (81)
15	–	3200	2857	2	3015	2898	1	v _{CH} (92)
16	1716	1902	1698	1	1738	1671	0	v _{CC} (65)
17	–	1662	1484	3	1538	1478	1	δ _{HCH} (66)
18	–	1660	1482	2	1537	1477	3	δ _{HCH} (71)+τ _{HCO} (15)
19	–	1650	1473	3	1522	1463	1	τ _{HCO} (15)
20	–	1647	1471	4	1519	1460	3	δ _{HCH} (69)+τ _{HCO} (23)
21	–	1639	1464	1	1517	1458	1	δ _{HCH} (68)+τ _{HCC} (22)
22	–	1636	1461	5	1511	1453	5	τ _{HCC} (21)+δ _{HCH} (71)
23	–	1631	1456	2	1504	1446	2	δ _{HCH} (79)
24	–	1629	1454	2	1500	1442	2	δ _{HCH} (86)
25	–	1566	1398	5	1431	1375	4	δ _{HCC} (83)
26	–	1565	1397	7	1423	1368	4	–
27	–	1564	1396	6	1417	1362	4	δ _{HCO} (51)+δ _{HCO} (14)
28	–	1555	1388	10	1402	1348	8	δ _{HCO} (44)+δ _{HCO} (18)
29	–	1540	1375	4	1387	1334	4	δ _{HCO} (16)+δ _{HCO} (24)+τ _{HCO} (36)
30	1361	1523	1360	3	1372	1319	3	τ _{HCO} (27)+δ _{HCO} (33)
31	–	1508	1347	3	1353	1301	3	δ _{HCO} (17)+δ _{HCO} (11)+τ _{HCO} (35)
32	–	1457	1301	11	1327	1275	10	τ _{HCO} (34)+δ _{HCO} (21)+δ _{HCO} (15)
33	–	1455	1299	4	1319	1268	6	δ _{HCO} (53)
34	–	1435	1281	5	1287	1237	6	v _{CC} (13)+τ _{HCO} (11)
35	–	1400	1250	4	1267	1218	96	τ _{HCO} (20)
36	–	1380	1232	107	1250	1202	10	τ _{HCO} (18)+δ _{HCC} (19)
37	–	1366	1219	10	1232	1184	21	τ _{HCO} (39)
38	–	1355	1210	2	1213	1166	2	–
39	–	1352	1207	7	1201	1155	10	τ _{HCO} (29)+v _{CC} (11)
40	–	1332	1189	18	1196	1150	6	τ _{HCO} (27)
41	–	1312	1172	138	1192	1146	192	δ _{HCH} (16)+τ _{HCO} (49)

Continued Table 4

1	2	3	4	5	6	7	8	9
42	–	1305	1166	69	1187	1141	102	$\tau_{\text{HCOC}}(23)+v_{\text{OC}}(12)$
43	–	1298	1159	72	1181	1135	38	$\tau_{\text{HCOC}}(10)+\tau_{\text{HCOC}}(28)+$ $+v_{\text{OC}}(10)+\delta_{\text{HCH}}(12)$
44	1156	1295	1156	29	1164	1119	15	$v_{\text{OC}}(19)+v_{\text{OC}}(15)$
45	1103	1271	1135	22	1148	1103	14	$v_{\text{OC}}(13)+v_{\text{OC}}(20)+\tau_{\text{HCCC}}(16)$
46	–	1266	1130	12	1128	1085	6	$v_{\text{OC}}(21)$
47	–	1238	1106	32	1102	1059	22	$v_{\text{OC}}(12)+v_{\text{OC}}(41)$
48	–	1221	1090	15	1088	1046	41	$v_{\text{OC}}(11)$
49	–	1216	1086	41	1071	1030	4	$v_{\text{CC}}(45)$
50	1038	1209	1080	26	1048	1008	142	$v_{\text{OC}}(32)+v_{\text{OO}}(45)$
51	–	1188	1060	10	1043	1002	26	$v_{\text{CC}}(35)$
52	–	1154	1030	17	1028	988	6	$v_{\text{OC}}(10)+v_{\text{OC}}(14)$
53	–	1152	1029	52	1012	972	226	$v_{\text{OC}}(37)$
54	1013	1135	1013	9	1000	962	22	$\tau_{\text{HCCC}}(77)$
55	–	1131	1010	78	998	960	5	$v_{\text{OC}}(12)+v_{\text{OC}}(10)+v_{\text{OC}}(13)+$ $+v_{\text{CC}}(22)+\gamma_{\text{COOC}}(11)+$
56	983	1106	987	88	987	948	127	$v_{\text{OO}}(24)v_{\text{OC}}(10)+v_{\text{OC}}(14)$
57	950	1095	978	196	940	903	30	$v_{\text{OC}}(17)+\tau_{\text{HCCC}}(20)+v_{\text{OO}}(15)$
58	–	1026	917	72	916	881	38	$v_{\text{OC}}(26)+\tau_{\text{HCCC}}(10)$
59	–	1006	898	60	905	870	60	$\tau_{\text{COCO}}(12)+\delta_{\text{COC}}(19)$
60	–	995	889	267	892	858	200	$\tau_{\text{HCOC}}(12)+\gamma_{\text{CCOC}}(10)$
61	888	982	877	170	880	846	166	$v_{\text{OO}}(50)$
62	853	965	861	8	860	827	37	$v_{\text{OC}}(20)+\delta_{\text{COC}}(11)$
63	–	946	844	9	845	812	116	$\delta_{\text{COC}}(17)$
64	–	937	837	82	820	788	218	$\gamma_{\text{CICCCI}}(12)+\gamma_{\text{COOC}}(16)+$ $+v_{\text{OC}}(13)+v_{\text{CIC}}(20)+$
65	811	926	826	81	790	760	107	$\delta_{\text{CCO}}(12)+v_{\text{OO}}(13)+\gamma_{\text{CICCCI}}(12)+$ $+v_{\text{CIC}}(55)+\delta_{\text{CCO}}(12)$
66	756	869	776	143	777	747	69	$\tau_{\text{HCCC}}(77)$
67	748	840	750	268	755	726	77	$v_{\text{OC}}(21)+v_{\text{CIC}}(11)+\delta_{\text{OCO}}(46)$
68	–	820	733	369	745	716	9	$v_{\text{OC}}(14)+\delta_{\text{CCO}}(20)+\delta_{\text{CCC}}(17)$
69	–	726	648	16	657	632	25	$\delta_{\text{COO}}(14)+\delta_{\text{COC}}(15)$
70	–	703	627	45	638	613	8	$v_{\text{CC}}(31)$
71	619	695	621	77	623	599	34	$v_{\text{CIC}}(44)+\gamma_{\text{COOC}}(21)$
72	–	669	597	5	611	588	10	$\delta_{\text{COC}}(18)+v_{\text{CC}}(21)$
73	–	649	579	10	589	566	7	$\delta_{\text{OCO}}(13)+\delta_{\text{COO}}(39)$
74	–	617	551	18	558	536	5	$\delta_{\text{OCO}}(15)+\delta_{\text{CCC}}(11)$
75	–	575	513	6	523	503	5	$\delta_{\text{OCO}}(35)$
76	–	543	485	22	490	471	5	$\delta_{\text{OCO}}(18)+\tau_{\text{CCCO}}(11)$
77	–	528	471	51	481	462	25	$\delta_{\text{CCO}}(10)$
78	–	498	445	27	456	438	16	$\delta_{\text{CCO}}(10)$
79	–	452	403	24	413	397	2	$v_{\text{CIC}}(18)$
80	–	426	381	15	389	374	23	$v_{\text{CIC}}(26)$
81	–	415	370	15	381	366	11	$\delta_{\text{CCO}}(18)+\gamma_{\text{CCOC}}(15)$

Continued Table 4

1	2	3	4	5	6	7	8	9
82	—	391	350	0	353	340	1	$\delta_{\text{CCO}}(16)+\nu_{\text{CIC}}(25)$
83	—	365	326	2	337	324	2	$\delta_{\text{COC}}(14)+\delta_{\text{COC}}(17)$
84	—	334	298	2	303	292	2	
85	—	321	287	1	292	281	1	$\delta_{\text{CICCI}}(11)+\delta_{\text{CICCI}}(12)+$ $+\gamma_{\text{CICCI}}(31)+\nu_{\text{CIC}}(15)$
86	—	319	285	4	289	277	4	$\gamma_{\text{CICCI}}(18)$
87	—	300	268	3	275	265	5	$\delta_{\text{OCC}}(12)+\delta_{\text{COC}}(11)+$ $+\delta_{\text{COC}}(13)+\tau_{\text{HCOC}}(12)$
88	—	269	240	10	244	234	12	$\tau_{\text{HCOC}}(13)+\tau_{\text{COOC}}(13)$
89	—	261	233	7	236	227	9	$\delta_{\text{CICCI}}(11)+\delta_{\text{CICCI}}(20)$
90	—	259	231	4	227	218	3	$\tau_{\text{HCCC}}(87)$
91	—	232	207	51	220	212	52	$\tau_{\text{HCOC}}(77)$
92	—	225	201	40	204	196	36	$\gamma_{\text{CICCI}}(10)+\delta_{\text{CICCI}}(46)$
93	—	220	196	14	199	191	49	$\delta_{\text{CICCI}}(12)+\delta_{\text{CICCI}}(10)+\delta_{\text{CICCI}}(10)$
94	—	199	178	56	183	176	8	$\tau_{\text{HCOC}}(11)+\tau_{\text{CCCO}}(16)+\gamma_{\text{CICCI}}(10)$
95	—	183	164	13	166	160	10	$\gamma_{\text{COOC}}(12)+\delta_{\text{CICCI}}(22)$
96	—	167	149	50	160	154	18	$\delta_{\text{OCC}}(18)+\tau_{\text{HCOC}}(45)$
97	—	133	119	16	127	122	32	—
98	—	120	107	29	107	103	22	$\tau_{\text{COCO}}(55)$
99	—	105	94	15	98	94	36	—
100	—	92	82	37	88	85	23	$\tau_{\text{COOC}}(49)$
101	—	80	71	28	75	72	9	$\tau_{\text{CCCO}}(35)$
102	—	64	58	33	59	57	24	$\tau_{\text{COCO}}(11)+\gamma_{\text{OCOC}}(12)+\delta_{\text{COC}}(12)$
103	—	53	47	31	48	46	10	—
104	—	30	27	9	27	26	8	—
105	—	27	24	2	22	22	3	$\tau_{\text{COCO}}(60)$

v: stretching, δ : in-plane bending, γ : out-of-plane bending, τ : torsion, asym: asymmetric stretching; I_{IR} : IR intensity ($\text{K} \cdot \text{mmol}^{-1}$).

assigned to *o*-, *m*-, and *p*-methoxy benzaldehydes respectively. In our study, the O—CH₃ stretching mode is observed at 1038 cm⁻¹. The theoretically computed value is found at 1080 cm⁻¹ (HF/6-311G(*d,p*)) and 1008 cm⁻¹ (B3LYP/6-311G(*d,p*)). The C—O—CH₃ angle bending mode was designated close to 300 cm⁻¹ by Owen and Hester [27] and at 421 cm⁻¹ by Campagnaro and Wood [28]. Rao et al. [29—32] have recommended an assignment for this mode in the range 300—670 cm⁻¹. Singh and Yadav [33] assigned the C—O—CH₃ angle bending mode at 341 cm⁻¹, 382 cm⁻¹, and 430 cm⁻¹ to *o*-, *m*-, and *p*-methoxy benzaldehydes respectively. By the B3LYP/6-311G(*d,p*) method we have calculated the C—O—CH₃ angle bending mode to be at 324 cm⁻¹.

The asymmetric C—O—C stretching vibration produces a strong band at 1261 cm⁻¹ in the IR spectrum [34, 35]. The symmetric C—O—C stretching vibration looks like a weak band at 1076 cm⁻¹ in the IR spectrum [34, 35]. Fukukawa and Ueda [36] reported the symmetric C—O—C stretch at 1045 cm⁻¹ for benzoxazole. In our study, the DFT calculation gives 1046 cm⁻¹ for the symmetric C—O—C mode, 1119 cm⁻¹ for asymmetric C—O—C modes of the title crystal structure. The asymmetric and symmetric C—O—C modes of the title crystal structure are listed in Table 4. Every refracting of the calculated wavenumber for this mode can be ascribed to the underestimation of a high degree of π -electron delocalization based on the formation of hydrogen bonds or conjugation [37].

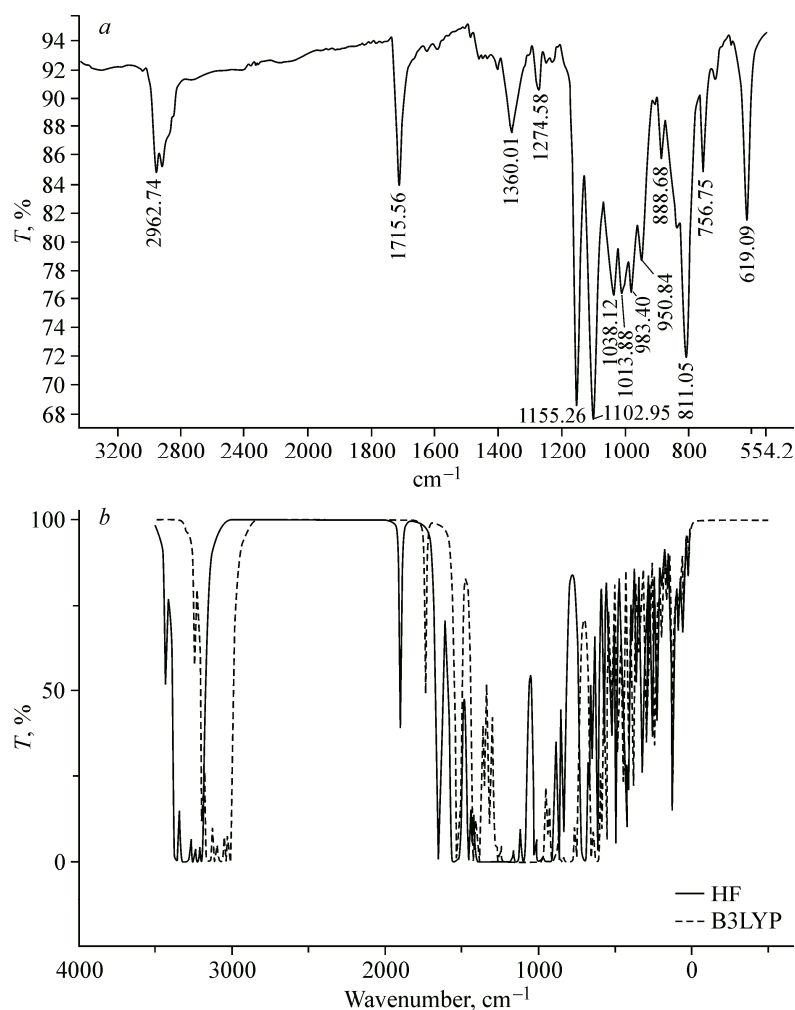


Fig. 6. FT-IR spectrum of the title crystal structure (a), simulated (HF and B3LYP levels) IR spectra of the title crystal structure (b)

Vibrational modes of methoxy groups are known to be due to a diversity of interesting interactions, for instance, electronic effects, Fermi resonance, and intermolecular hydrogen bonding [38]. Electronic effects mostly caused by the presence of the oxygen atom adjacent to the CH₃ group can recast the position of C—H stretching and bending modes [39–41].

The aromatic C—H in-plane bending vibration is observed in the range 1300–1000 cm⁻¹. Although the bands are strong, they have a weak to medium intensity [42]. This shows great accordance with the theoretically scaled frequency values at 1347 cm⁻¹ (HF/6-311G(*d,p*)) and at 1301 cm⁻¹ (B3LYP/6-311G(*d,p*)).

Table 4 presents the theoretical and experimental results for the title crystal structure. The vibrational frequencies were obtained using the Gauss—View software.

Assignments of the chemical shift values. The ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury spectrometer using tetramethylsilane (TMS) as the internal reference (Fig. 7, *a* and *b*). GIAO ¹H and ¹³C chemical shift calculations were made using the HF and B3LYP methods with the 6-311G(*d,p*) basis set for the optimized geometry. The results are listed in Table 5. We included the average values for the CH₃ group of the experimental ¹H chemical shift values. Due to deshielding by the electronegative property of the O atom, the chemical shift values of C6 and C2 are greater than the others and are observed at 134.3 ppm and 123.4 ppm, which is consistent with the values reported previously (104.7 ppm and 114.7 ppm, [43]). Similarly, endoperoxide carbon peaks are observed at

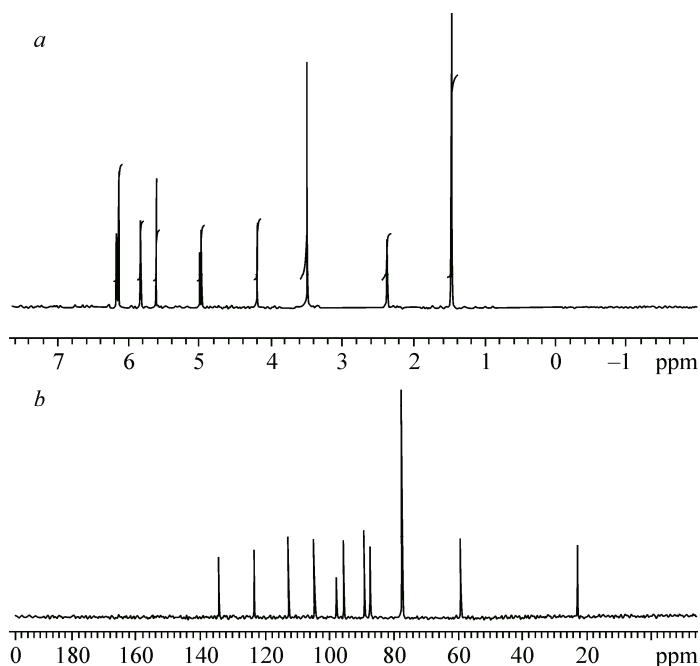


Fig. 7. ^1H NMR spectrum (a); ^{13}C NMR spectrum of the title crystal structure (b)

112.7 ppm and 97.8 ppm. In addition, the chemical shift values of C5, C11, and C12 atoms are lower than the other carbon peaks because of the shielding effect that is the non-electronegative characteristic of the hydrogen atom. It is important to mention that the electron emitting atom or group enhances the shielding and moves the resonance to lower frequencies. Conversely, the electronegative atom or the nearby electron-withdrawing atom or group can reduce the shielding, and move the resonance of the attached proton to higher frequencies. The chemical shifts obtained and computed for the hydrogen atoms of methyl groups are rather low. All values are ≤ 3 ppm [44] due to the shielding effect. The data of this study show that the methyl protons at C5/C11/C12 appear as a singlet with a three-proton integral at 1.45 ppm and is in good agreement with the computed chemical shift values shown in Table 5. In order to compare the theoretical and experimental data, we studied the relativity between the

Table 5

Theoretical and experimental ^{13}C and ^1H isotropic chemical shifts (with respect to TMS, all values in ppm)

Atom	Experimental, ppm (CDCl_3)	HF	DFT	Atom	Experimental, ppm (CDCl_3)	HF	DFT
C1	104.3	100.40	98.84	H(C2—H)	5.73	5.28	5.72
C2	123.4	93.02	122.4	H(Methyl)	1.45	1.1—3.56	1.3—2.99
C3	104.8	68.81	102.14	H(C4—H)	6.25	5.7	6.19
C4	87.20	91.31	90.62	H(C3—H)	4.80	4.33	4.32
C5	59.20	45.40	52.11	H(C7—H)	3.72	3.21	3.45
C6	134.3	127.29	95.88	H(C8—H)	6.10	6.09	6.85
C7	89.10	73.67	76.12	H(C9—H)	6.2	6.4	6.1
C8	112.7	124.64	121.55				
C9	97.80	92.79	131.5				
C10	95.6	86.79	91.33				
C11	23.2	20.12	21.55				
C12	47.4	41.53	44.55				

calculation and the experiments and concluded that the linear function formula is $y = 0.934x - 0.32$ for HF; where R^2 is 0.9940, $y = 1.202x + 0.2631$ for B3LYP; where R^2 is 0.9981. The results suggest that the B3LYP method has better fit with the experimental values than HF in evaluating the ^1H and ^{13}C chemical shifts.

CONCLUSIONS

The current study computed, compared, and reported the experimental geometric parameters, vibrational frequencies, and chemical shifts of the title crystal structure in an attempt to test the HF and DFT levels. The B3LYP level of theory including the electron correlation effects is found to have better fit with the experimental geometric parameters, chemical shifts, and vibrational frequencies than the HF method. We hope this article will be useful in the design and synthesis of new materials.

CCDC-889093 contains the supplementary crystallographic data for the compound reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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