Research Article

Vibrational Spectroscopy Investigation Using Ab Initio and Density Functional Theory Analysis on the Structure of *tert*-Butyl 3a-Chloroperhydro-2,6a-epoxyoxireno[*e*]isoindole-5-carboxylate

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The molecular structure, vibrational frequencies, and infrared intensities of the *tert*-butyl 3a-chloroperhydro-2,6a-epoxyoxireno[*e*]isoindole-5-carboxylate were calculated by the HF and DFT (BLYP and B3LYP) methods using 6-31G(d) and 6-31G(d,p) basis sets. The FT infrared spectrum of the solid sample was measured under standard condition. We obtained two stable conformers for the title compound; however Conformer 1 is approximately 0.2 kcal/mol more stable than the Conformer 2. The comparison of the theoretical and experimental geometry of the title compound shows that the X-ray parameters fairly well reproduce the geometry of Conformer 2. Comparison of the observed fundamental vibrational frequencies of the title molecule and calculated results by HF and DFT methods indicates that B3LYP is superior for molecular vibrational problems. The harmonic vibrations computed by the B3LYP/6-31G(d,p) method are in a good agreement with the observed IR spectral data. Theoretical vibrational spectra of the title compound were interpreted by means of potential energy distributions (PEDs) using VEDA 4 program.

1. Introduction

Epoxides are used as an important intermediate tool in organic synthesis of fine chemicals and pharmaceuticals [1]. Intramolecular Diels-Alder (IMDA) reactions and epoxidation of its cycloadduct have also been of great interest in synthetic pathway of natural products, like conduritols [2], *z*-isomeric insect sex pheromone components [3], dihydrophenanthroline derivatives [4], vitamin D total synthesis [5], and so on. We have previously prepared a variety of key precursors to the intramolecular Diels-Alder reaction of furan (IMDAF) diene via facile alkylation of furan compounds and its protection. Subsequently IMDAF reaction carried out under thermal condition provided five- and six-membered heterocycles fused to an easily cleavable oxabicycloheptene moiety [6–9].

In this study, *tert*-butyl 3a-chloroperhydro-2,6a-epoxyoxireno[*e*]isoindole-5-carboxylate, **3**, was prepared from 5-chloro-10-oxa-3-aza-tricyclo[5.2.1.0^{1,5}]dec-8-en-3-carboxylic acid *tert*-butyl ester, **1**, using metachloroperbenzoic acid, **2**, in dry dichloromethane which was previously recrystallized in dry diethyl ether at 0°C. The product **3** was analyzed by X-ray diffractometer [10], ¹H and ¹³C NMR, IR, mass spectrometer, and elemental analysis. The goal of this project is to transferring chloro-cycloadduct, **3**, to highly substituted tetrahydroisoindole derivative, **4**. We are currently researching this stage by opening epoxy bridges on compound **3** (Scheme 1).

The crystal structure of *tert*-butyl 3a-chloroperhydro-2,6a-epoxyoxireno[*e*]isoindole-5-carboxylate (TBCEIC) has been determined by X-ray diffraction [10], however so far no ab initio studies have been made on the conformation and

SCHEME 1: Synthesis of the *tert*-butyl 3a-chloroperhydro-2,6a-epoxyxireno[e]isoindole-5-carboxylate.

vibrational spectra of the title compound in the gas phase. In the present study, we have synthesized and calculated the vibrational frequencies and geometric parameters of TBCEIC in the ground state to distinguish the fundamentals from the experimental vibrational frequencies and geometric parameters, by using the Hartree-Fock [11] and density functional using B3LYP [12, 13] and Becke's exchange functional in combination with the Lee, Yang, and Parr correlation functional methods [13, 14] (BLYP) with the standard 6-31G(d) and 6-31G(d,p) basis sets. In continuation of our theoretical studies, in the present work, we checked the relative performance of B3LYP and BLYP methods, as well as of HF for comparison, at the 6-31G(d) and 6-31G(d,p) levels taking as a test compound *tert*-butyl 3a-chloroperhydro-2,6a-epoxyxireno[e]isoindole-5-carboxylate.

2. Results and Discussion

2.1. Conformational Stability. We performed full geometry optimization of the title compound. To establish the most stable conformation as the initial point for further calculations, the molecule was submitted to a rigorous conformation analysis around all bonds having free rotation. This study was performed with the software Spartan 06 [15, 16]. The structure of the title compound has two conformations which are shown in Figure 1. For comparison, the total energy and the relative energies of both conformer of the title compound are given in Table 1. Energetics show that Conformer 1 is the most stable. But comparison of the theoretical and experimental geometry of the title compound shows that the X-ray parameters fairly well reproduce the geometry of Conformer 2. Therefore, we will focus on this particular form (Conformer 2) of the title compound in this paper.

2.2. Molecular Geometry. The optimized structure parameters of the title compound calculated by ab initio and DFT method listed in Table 2 are in accordance with atom numbering scheme given in Figure 2(a). The crystal and molecular structure of the title compound have been reported previously [10]. The geometric structure is monoclinic, the space group $P2_1/c$, with the cell dimensions: $a = 18.7133(15) \text{ \AA}$, $b = 8.3800(8) \text{ \AA}$, $c = 9.2123(7) \text{ \AA}$, $\beta = 90.134(7)^\circ$, and $V = 1444.6(2) \text{ \AA}^3$ (Figure 2(b)). The structure parameters obtained by X-ray single-crystal diffraction method are given in Table 2. Also, Table 2 compares the calculated geometric parameters with the experimental data.

Based on this comparison, the bond lengths and angles calculated for the title compound show good agreement

TABLE 1: Energies B3LYP/6-31G(d,p) of the different conformations of the title compound.

Conformer	E (au)	ΔE (kcal/mol)	Dipole (debye)
Conformer 1	-1322.05349	0.0	1.5
Conformer 2	-1322.05323	0.2	3.9

Conformer 1

(a)

Conformer 2

(b)

FIGURE 1: Two stable conformers of the title compound calculated at B3LYP/6-31G(d,p) level. The torsion angles, C22-N13-C15=O11, for Conformer 1 and 2 are -4.74° and 175.65° , respectively.

with experiment. However, according to our calculations, the optimized both bond lengths and bond angles obtained by DFT methods show the best agreement with the experimental values. The large difference between experimental and calculated DFT/B3LYP-6-31G(d,p) bond length and bond angle is $0.065 \text{ \AA}$ and 1.65° , respectively.

2.3. Vibrational Assignments. Table 3 lists the wavenumbers of the bands observed in the FT-IR spectra of the *tert*-butyl 3a-chloroperhydro-2,6a-epoxyxireno[e]isoindole-5-carboxylate. The theoretical frequencies and infrared intensities calculated by HF, BLYP, and B3LYP methods of the title

TABLE 2: Optimized and experimental geometries of the title compound in the ground state.

Parameters ^{a,b}	Experimental ^c	Calculated					
		HF	BLYP		B3LYP		
		6-31G(d)	6-31G(d,p)	6-31G(d)	6-31G(d,p)	6-31G(d)	6-31G(d,p)
Bond lengths (Å)							
R (10,16)	1.800 (2)	1.806	1.807	1.865	1.865	1.834	1.834
R (11,15)	1.210 (3)	1.199	1.200	1.235	1.235	1.222	1.223
R (12,19)	1.446 (3)	1.411	1.410	1.459	1.459	1.438	1.439
R (12,21)	1.432 (2)	1.409	1.409	1.457	1.458	1.436	1.437
R (13,15)	1.339 (3)	1.351	1.349	1.378	1.379	1.364	1.365
R (13,18)	1.459 (3)	1.456	1.458	1.479	1.481	1.467	1.466
R (13,22)	1.453 (3)	1.454	1.455	1.476	1.477	1.462	1.463
R (14,20)	1.442 (3)	1.401	1.401	1.453	1.454	1.433	1.432
R (14,25)	1.440 (3)	1.401	1.401	1.452	1.452	1.431	1.431
R (15,17)	1.342 (3)	1.325	1.325	1.378	1.378	1.357	1.356
R (16,21)	1.548 (3)	1.549	1.550	1.580	1.579	1.566	1.566
R (16,22)	1.514 (3)	1.532	1.530	1.547	1.547	1.536	1.535
R (16,24)	1.538 (3)	1.550	1.549	1.566	1.566	1.553	1.554
R (17,23)	1.463 (3)	1.448	1.449	1.495	1.496	1.472	1.472
R (18,21)	1.501 (3)	1.512	1.512	1.525	1.526	1.516	1.517
R (19,24)	1.536 (4)	1.547	1.547	1.567	1.568	1.556	1.556
R (19,25)	1.509 (4)	1.527	1.526	1.547	1.548	1.535	1.536
R (20,21)	1.516 (3)	1.526	1.524	1.545	1.545	1.533	1.532
R (20,25)	1.450 (3)	1.449	1.449	1.480	1.480	1.467	1.468
R (23,26)	1.508 (4)	1.526	1.525	1.543	1.541	1.531	1.531
R (23,30)	1.502 (4)	1.527	1.526	1.543	1.543	1.531	1.531
R (23,34)	1.502 (4)	1.527	1.527	1.544	1.542	1.532	1.532
<i>r</i>		0.9868	0.9871	0.9961	0.9962	0.9951	0.9950
Bond angles (°)							
A (19,12,21)	96.88 (15)	99.0	99.0	97.6	97.6	98.0	98.0
A (15,13,18)	120.21 (17)	120.1	120.1	120.0	119.7	120.0	119.9
A (15,13,22)	127.19 (17)	125.5	125.6	126.1	126.3	126.0	126.3
A (18,13,22)	112.59 (16)	114.1	114.0	113.8	113.3	113.8	113.6
A (11,15,13)	123.6 (2)	122.9	122.9	123.0	122.9	123.1	122.9
A (11,15,17)	125.62 (19)	125.7	125.7	127.1	127.0	126.6	126.5
A (13,15,17)	110.82 (18)	111.3	111.4	109.9	110.1	110.4	110.6
A (10,16,21)	110.36 (14)	112.7	112.7	112.2	112.0	112.2	112.1
A (10,16,22)	108.77 (16)	109.5	109.6	109.2	109.1	109.4	109.3
A (10,16,24)	113.45 (17)	113.0	112.9	112.4	112.4	112.7	112.8
A (21,16,22)	101.95 (16)	101.7	101.7	102.0	101.8	101.8	101.6
A (21,16,24)	102.96 (17)	102.2	102.2	102.7	102.7	102.5	102.5
A (22,16,24)	118.4 (2)	117.0	117.0	117.8	118.1	117.4	117.8
A (15,17,23)	120.50 (18)	122.7	122.7	120.2	120.1	120.8	120.7
A (13,18,21)	103.57 (16)	102.8	102.8	103.3	103.5	103.2	103.3
A (12,19,24)	102.19 (18)	101.7	101.7	101.9	101.8	101.9	101.9
A (12,19,25)	101.94 (19)	101.9	101.9	102.1	102.1	102.0	102.1
A (24,19,25)	107.8 (2)	107.2	107.2	107.6	107.4	107.3	107.2
A (14,20,21)	114.0 (2)	113.1	113.1	113.7	113.6	113.5	113.5
A (21,20,25)	102.9 (2)	102.8	102.8	103.0	103.0	102.8	102.9
A (12,21,16)	99.80 (15)	98.7	98.6	98.5	98.4	98.8	98.7
A (12,21,18)	112.54 (17)	112.2	112.2	111.6	111.7	111.8	111.9
A (12,21,20)	102.24 (16)	102.2	102.3	102.4	102.5	102.5	102.5
A (16,21,18)	106.95 (16)	106.7	106.7	106.8	106.8	106.7	106.7

TABLE 2: Continued.

Parameters ^{a,b}	Experimental ^c	HF		Calculated BLYP		B3LYP	
		6-31G(d)	6-31G(d,p)	6-31G(d)	6-31G(d,p)	6-31G(d)	6-31G(d,p)
A (16,21,20)	108.39 (16)	109.9	109.9	109.6	109.7	109.4	109.5
A (18,21,20)	124.24 (19)	124.3	124.2	124.8	124.7	124.7	124.5
A (13,22,16)	103.32 (17)	103.2	103.2	103.7	103.7	103.6	103.5
A (17,23,26)	102.1 (2)	102.6	102.6	102.1	102.1	102.4	102.5
A (17,23,30)	110.0 (2)	110.3	110.3	109.8	110.0	109.9	110.1
A (17,23,34)	110.0 (2)	110.3	110.2	110.1	109.7	110.2	109.9
A (26,23,30)	111.1 (3)	110.4	110.5	111.0	110.9	110.8	110.8
A (26,23,34)	110.5 (3)	110.5	110.6	110.8	111.0	110.7	110.8
A (30,23,34)	112.7 (3)	112.3	112.3	112.6	112.5	112.4	112.3
A (16,24,19)	100.05 (3)	99.8	99.9	100.2	100.3	100.2	100.2
A (19,25,20)	104.00 (19)	103.6	103.6	103.7	103.7	103.6	103.6
<i>r</i>		0.9929	0.9929	0.9961	0.9966	0.9964	0.9969

^a The atom numbering scheme of the molecular structure is given in Figure 2(a).

^b *r*: correlation coefficient between optimized and experimental geometrical parameters.

^c From [10].

FIGURE 2: The optimized molecular structure (Conformer 2) of the title compound (a), the single crystal structure of the title compound. Thermal ellipsoids are shown at the 50% probability level (b).

compound are gathered in Table 3. The last column of Table 3 shows the detailed vibrational assignment obtained from the calculated potential energy distribution (PED).

Comparison of the frequencies calculated at HF, BLYP, and B3LYP with experimental values reveals the overestimation of the calculated vibrational modes due to neglect

of anharmonicity in real system. Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values lower in comparison with the Hartree-Fock frequency data [17–20]. Reductions in the computed harmonic vibrations, though basis set sensitives are only marginal as observed in the DFT values using 6-31G(d) and 6-31G(d,p). Any way notwithstanding the level of calculations, it is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experiment [17–20]. Therefore, the scaling factor values of 0.8953/0.8992, 0.9614/0.9614, and 0.9945/1.0072 for HF, B3LYP, and BLYP (6-31G (d)/6-31G(d,p)), respectively, are used in our study [17, 21–25]. Experimental fundamentals are in better agreement with the scaled fundamentals which are found to have a good correlation for DFT/B3LYP/6-31G(d,p) ($r = 0.9999$) than HF method. The calculated frequencies (scaled) do not differ so much from the experimental ones that the maximum difference between two spectra is not more than 27 cm^{-1} for DFT/B3LYP/6-31G(d,p) method. Also, the average absolute error of the calculated frequencies was found less than 0.86% for DFT/B3LYP/6-31G(d,p) method.

A general better performance of B3LYP and BLYP 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 (r) between the calculated and observed vibration frequencies and given in Table 3. All these values were calculated in this study by the PAVF 1.0 program [26] according to Scott and Radom [21]. The root mean square (RMS) values were obtained in this study using the following expression [21]:

$$\text{RMS} = \sqrt{\frac{1}{n-1} \sum_i^n (v_i^{\text{calc}} - v_i^{\text{exp}})^2} \quad (1)$$

The r values for both DFT methods were greater than 0.9998, whereas for HF it was 0.9997. These values are very

TABLE 3: Vibrational wavenumbers obtained for the title compound^a.

Number	Exp.	HF						BLYP						B3LYP						IR intensity		Assignments, PED (%) ^b	
		6-31G(d)			6-31G(d,p)			6-31G(d)			6-31G(d,p)			6-31G(d)			6-31G(d,p)						
		Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Abs.	Rel.				
1	3082	3418	3067	3060	3397	3065	3055	3134	3100	3117	3131	3102	3154	3226	3093	3101	3218	3093	3094	3	0	ν_{CH^+} , C20, 96	
2	3067	3386	3038	3031	3363	3035	3024	3100	3066	3083	3095	3066	3117	3194	3062	3071	3184	3060	3061	14	2	ν_{CH^+} , C25, 95	
3	3067	3342	2999	2992	3323	2999	2988	3090	3056	3073	3094	3065	3116	3174	3043	3051	3173	3050	3051	7	1	ν_{CH3} , asym, C30, C34, 88	
4	3067	3337	2995	2988	3320	2996	2985	3086	3052	3069	3089	3060	3111	3170	3039	3048	3168	3045	3046	3	0	ν_{CH3} , asym, C30, C34, 90	
5	3010	3336	2994	2987	3316	2992	2982	3073	3039	3056	3081	3052	3103	3158	3027	3036	3159	3036	3037	3	0	ν_{CH2} , a sym, C22, 94	
6	3010	3334	2992	2985	3311	2988	2977	3068	3034	3051	3066	3037	3088	3155	3025	3033	3149	3027	3027	26	4	ν_{CH^+} , C19, 92	
7	3010	3310	2970	2963	3294	2972	2962	3057	3024	3040	3060	3031	3082	3143	3013	3022	3142	3020	3021	6	1	ν_{CH2} , asym, C24, 91	
8	3003	3309	2969	2963	3290	2969	2958	3052	3019	3035	3054	3025	3076	3136	3006	3015	3134	3012	3013	50	7	ν_{CH3} , asym, C26, 92	
9	3003	3288	2951	2944	3272	2953	2942	3051	3018	3034	3052	3023	3074	3133	3003	3012	3131	3009	3010	30	4	ν_{CH3} , asym, C26, 95	
10	3003	3286	2949	2942	3271	2952	2941	3036	3003	3019	3041	3012	3063	3120	2991	3000	3120	2999	3000	18	3	ν_{CH3} , asym, C26, C30, C34, 92	
11	3003	3271	2935	2929	3256	2938	2928	3034	3001	3017	3039	3010	3061	3118	2989	2998	3118	2997	2998	7	1	ν_{CH3} , asym, C30, C34, 97	
12	3003	3269	2933	2927	3254	2936	2926	3025	2992	3008	3023	2995	3045	3116	2987	2996	3110	2989	2990	7	1	ν_{CH2} , asym, C18, 96	
13	2972	3261	2926	2920	3243	2926	2916	3011	2978	2994	3011	2983	3033	3094	2966	2975	3089	2969	2970	15	2	ν_{CH2} , sym, C24, 97	
14	2964	3256	2922	2915	3235	2919	2909	2985	2952	2969	2987	2959	3009	3072	2945	2953	3069	2950	2951	15	2	ν_{CH2} , sym, C18, 95	
15	2928	3241	2908	2902	3220	2906	2895	2984	2951	2968	2985	2957	3006	3064	2937	2946	3060	2941	2942	23	3	ν_{CH3} , sym, C26, C30, C34, 91	
16	2928	3223	2892	2886	3203	2890	2880	2978	2945	2962	2978	2950	2999	3057	2931	2939	3052	2933	2934	23	3	ν_{CH3} , sym, C30, C34, 90	
17	2928	3213	2883	2877	3193	2881	2871	2976	2943	2960	2976	2948	2997	3056	2930	2938	3051	2933	2933	10	1	ν_{CH3} , sym, C26, C30, C34, 89	
18	2928	3212	2882	2876	3192	2880	2870	2952	2920	2936	2955	2927	2976	3045	2919	2927	3042	2924	2925	30	4	ν_{CH2} , sym, C22, 95	
19	1686	1941	1742	1738	1939	1750	1744	1704	1685	1695	1700	1684	1712	1784	1710	1715	1781	1712	1712	384	57	$\nu_{C=O}$, C15-O11, 82	
20	1474	1672	1500	1497	1657	1495	1490	1519	1502	1511	1507	1493	1518	1557	1493	1497	1543	1483	1483	17	2	δ_{CH3} , deform., C26, C30, C34, 64	
21	1460	1669	1498	1494	1653	1492	1486	1497	1481	1489	1483	1469	1494	1538	1474	1479	1519	1460	1460	1	0	δ_{CH2} , sciss., C18, C22, 51	
22	1460	1659	1489	1485	1643	1483	1477	1496	1480	1488	1477	1463	1488	1534	1471	1475	1519	1460	1460	4	1	δ_{CH2} , sciss., C18, C22, 66	
23	1451	1652	1482	1479	1636	1476	1471	1487	1471	1479	1471	1457	1482	1527	1464	1468	1511	1452	1453	3	0	δ_{CH2} , sciss., C18, C22, 56	
24	1451	1645	1476	1473	1629	1470	1465	1485	1469	1477	1471	1457	1482	1524	1461	1465	1508	1449	1450	16	2	δ_{CH3} , deform., C30, C34, 58	
25	1451	1637	1474	1471	1626	1467	1462	1484	1468	1476	1469	1455	1480	1521	1458	1462	1507	1448	1449	3	0	δ_{CH3} , deform., C26, C30, 68	
26	1431	1637	1469	1466	1620	1462	1457	1482	1466	1474	1467	1453	1478	1519	1456	1460	1501	1443	1443	0	0	δ_{CH3} , deform., C26, C34, 70	
27	1431	1636	1468	1465	1619	1461	1456	1475	1459	1467	1459	1445	1470	1515	1452	1457	1499	1441	1441	8	1	δ_{CH2} , sciss., C24, 76	
28	1427	1619	1453	1449	1601	1445	1440	1462	1446	1454	1447	1433	1457	1499	1437	1441	1483	1425	1426	1	0	δ_{CH3} , deform., C26, C30, C34, 81	
29	1409	1597	1433	1430	1594	1438	1433	1416	1401	1408	1398	1385	1408	1455	1395	1399	1445	1389	1389	674	100	ν_{NC} , N13-C15, 53	
30	1392	1585	1422	1419	1583	1428	1423	1387	1372	1379	1374	1361	1384	1443	1383	1387	1438	1382	1382	14	2	δ_{CH3} , umbrell., C26, C30, C34, 51	
31	1360	1584	1421	1418	1569	1416	1411	1380	1365	1372	1366	1353	1376	1435	1376	1380	1431	1375	1376	21	3	ν_{CC} , RI, R2, 40 + δ_{CCH^+} , RI, 17	
32	1360	1560	1400	1397	1545	1394	1389	1366	1351	1358	1364	1351	1374	1427	1368	1372	1412	1357	1357	14	2	δ_{CH3} , umbrell., C26, C30, C34, 51	

TABLE 3: Continued.

Number	Exp.	HF						BLYP						B3LYP						IR intensity		Assignments, PED (%) ^b
		6-31G(d)		6-31G(d,p)		6-31G(d)		6-31G(d,p)		6-31G(d)		6-31G(d,p)		6-31G(d)		6-31G(d,p)						
		Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Abs.	Rel.			
33	1350	1559	1399	1396	1544	1393	1388	1362	1347	1355	1361	1348	1371	1422	1363	1367	1408	1353	1354	18	3	δ_{CH_3} , umbrella, C26, C30, C34, 64
34	1350	1546	1387	1384	1538	1388	1383	1350	1335	1343	1339	1326	1349	1403	1345	1349	1394	1340	1340	23	3	δ_{CH_2} , wagg., C18, 52
35	1327	1521	1365	1362	1513	1365	1360	1335	1320	1328	1328	1316	1338	1383	1326	1330	1376	1323	1323	10	1	δ_{CH_2} , wagg., C22, 40
36	1305	1483	1331	1328	1477	1333	1328	1292	1278	1285	1290	1278	1299	1340	1285	1288	1337	1285	1285	2	0	δ_{CH_3} , R1, R2, 62
37	1282	1472	1321	1318	1464	1321	1316	1280	1266	1273	1277	1265	1286	1332	1277	1281	1328	1276	1277	6	1	δ_{CH_2} , twist, C18, 60 + ν_{CN} , C8-N13, 10
38	1259	1454	1305	1302	1449	1308	1303	1268	1254	1261	1262	1250	1271	1321	1266	1270	1315	1264	1264	5	1	δ_{CH_3} , R1, R2, R3, 33
39	1247	1420	1274	1271	1414	1276	1271	1246	1232	1239	1243	1231	1252	1293	1240	1243	1288	1238	1238	26	4	ν_{CC} , C23-C26, 26
40	1228	1408	1263	1261	1401	1264	1260	1236	1222	1229	1230	1218	1239	1283	1230	1233	1278	1228	1229	15	2	δ_{CH_3} , deform., 27 + δ_{CH_2} , wagg., C24, 27
41	1222	1395	1252	1249	1387	1252	1247	1233	1220	1226	1229	1217	1238	1282	1229	1233	1275	1225	1226	15	2	ν_{CC} , C23-C30, 17 + ν_{CC} , C23-C34, 18
42	1211	1391	1248	1245	1387	1252	1247	1211	1198	1204	1209	1198	1218	1264	1212	1215	1262	1213	1213	9	1	ν_{CC} , R1, R2, R3, 25 + ν_{NC} , 53
43	1211	1374	1233	1230	1367	1234	1229	1210	1197	1203	1205	1194	1214	1256	1204	1208	1250	1201	1202	22	3	δ_{CH_2} , twist, C22, C24, 60
44	1180	1366	1226	1223	1362	1229	1225	1198	1185	1191	1191	1180	1200	1246	1194	1198	1242	1194	1194	27	4	δ_{CH_2} , twist, C22, 19 + δ_{CCH} , C20, C25, 10
45	1180	1364	1224	1221	1358	1225	1221	1193	1180	1186	1189	1178	1198	1241	1190	1193	1234	1186	1186	4	1	δ_{CH_2} , twist, C18, 46 + ν_{CO} , R1, 23
46	1180	1354	1215	1212	1349	1217	1213	1178	1165	1172	1170	1159	1178	1229	1178	1182	1224	1176	1177	9	1	ν_{CC} , 25 + $\nu_{\text{C-O}}$, C23, 45 + δ_{CH_2} , twist, C18, 10
47	1163	1336	1199	1196	1329	1199	1195	1171	1158	1165	1167	1156	1175	1218	1168	1171	1213	1166	1166	34	5	ν_{CC} , 30 + δ_{CH_2} , twist, C24, 30
48	1163	1330	1193	1191	1324	1195	1191	1161	1148	1155	1154	1143	1162	1210	1160	1163	1204	1157	1158	372	55	δ_{CCH} , 31 + δ_{CH_2} , twist, C18, C24, C22, 30
49	1128	1289	1157	1154	1287	1161	1157	1100	1088	1094	1093	1083	1101	1152	1104	1108	1150	1105	1106	112	17	ν_{CC} , C16-C21, 12 + $\nu_{\text{C-O}}$, C15-O17, 12
50	1109	1269	1139	1136	1266	1142	1138	1089	1077	1083	1087	1077	1095	1144	1097	1100	1138	1094	1094	4	1	ν_{CC} , R3, 30 + δ_{CH_2} , rocking, C18, C24, 28
51	1089	1247	1119	1116	1243	1122	1118	1075	1063	1069	1068	1058	1076	1140	1093	1096	1132	1088	1088	34	5	ν_{CC} , R3, 16 + δ_{CH_2} , rocking, C18, C22, 14
52	1061	1219	1094	1091	1216	1097	1093	1050	1039	1044	1044	1034	1052	1096	1051	1054	1092	1050	1050	16	2	δ_{CH_2} , rocking, C18, C22, C24, 50
53	1045	1212	1088	1085	1210	1092	1088	1040	1029	1034	1034	1024	1041	1080	1035	1038	1080	1038	1038	22	3	ν_{CC} , R1, R2, R3, 47
54	1033	1177	1056	1054	1174	1059	1056	1030	1019	1024	1026	1016	1033	1069	1025	1028	1063	1022	1022	1	0	δ_{CH_3} , rocking, 39
55	1005	1174	1054	1051	1171	1057	1053	1024	1013	1018	1024	1014	1031	1062	1018	1021	1057	1016	1016	0	0	δ_{CH_3} , rocking, 29
56	1005	1160	1041	1039	1153	1040	1037	1016	1005	1010	1007	998	1014	1061	1017	1020	1054	1013	1013	18	3	δ_{CH_2} , rocking, C22, C24, 17 + δ_{CCH} , 21
57	993	1157	1038	1036	1150	1038	1034	986	975	981	984	975	991	1038	995	998	1038	998	998	34	5	ν_{CC} , R1, 17 + ν_{CO} , R2, 17 + δ_{CCH} , 15

TABLE 3: Continued.

Number	Exp.	HF						BLYP						B3LYP						Assignments, PED (%) ^b		
		6-31G(d)			6-31G(d,p)			6-31G(d)			6-31G(d,p)			6-31G(d)			6-31G(d,p)				IR intensity Abs. Rel.	
		Unscal	Sca.	Unscal	Unscal	Sca.	Unscal	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.	Unscal	Sca.					
58	960	1128	1012	1010	1126	1016	1012	964	953	959	961	952	968	1014	972	975	1012	973	973	7	1	δ_{CH_3} , deform, C26, C30, C34, 90
59	947	1109	995	993	1105	997	994	953	943	948	947	938	954	995	954	957	990	952	952	42	6	ν_{CC} , 29 + δ_{CCH} , R1, R2, 29
60	928	1067	957	955	1065	961	958	941	931	936	935	926	942	979	939	941	972	934	934	0	0	ν_{CC} , C-CH3, 41
61	928	1062	953	951	1054	951	948	910	900	905	907	898	914	961	921	924	958	921	921	11	2	δ_{CH_3} , rocking, 62
62	920	1026	921	919	1023	923	920	904	894	899	901	893	907	945	906	909	942	905	906	14	2	ν_{CCH_3} , 22 + δ_{CCH} , CH3, 19
63	910	1014	910	908	1010	911	908	902	892	897	899	891	905	936	897	900	932	896	896	2	0	ν_{CCH_3} , 38 + δ_{CCH} , CH3, 24
64	910	1012	908	906	1007	909	905	901	891	896	896	888	902	934	895	898	929	893	893	0	0	ν_{CO} , R1, 14 + ν_{CC} , R1, R2, 14 + δ_{CH_2} , rocking, C24, 13
65	883	1009	905	903	1006	908	905	870	860	865	863	855	869	910	872	875	907	872	872	16	2	δ_{CCH} , 20 + δ_{CH_2} , rocking, C19
66	873	997	895	893	993	896	893	857	848	852	855	847	861	907	870	872	902	867	867	7	1	ν_{CN} , R3, 14 + ν_{CO} , C23-O17, 13
67	862	984	883	881	981	885	882	841	832	836	839	831	845	892	855	858	891	856	857	42	6	δ_{CH_2} , rocking, C24, 21 + δ_{CCH} , 10
68	852	977	877	875	974	879	876	828	819	823	830	822	836	877	841	843	878	844	844	27	4	ν_{CC} , 14 + δ_{CCH} , 18
69	835	956	858	856	955	862	859	817	808	813	816	808	822	868	832	834	867	833	834	11	2	δ_{CCH} , 14 + δ_{CC} , 12 + δ_{COC} , 12
70	825	942	845	843	940	848	845	810	801	806	808	800	814	854	819	821	852	819	819	3	0	δ_{CC} , 13 + δ_{CCH} , 13
71	808	920	826	824	918	828	825	792	783	788	791	784	797	835	800	803	833	801	801	9	1	δ_{CCH} , 35 + δ_{CC} , 34
72	764	899	807	805	898	810	807	779	770	775	777	770	783	817	783	785	815	783	784	21	3	δ_{COC} , 11 + ν_{CO} , 10 + δ_{CC} , 10
73	750	875	785	783	875	790	787	743	735	739	743	736	748	778	746	748	777	747	747	3	0	δ_{CC} , 20 + ν_{CC} , 18
74	729	847	760	758	846	763	761	726	718	722	725	718	730	760	729	731	757	728	728	5	1	γ_{C} , C15, 40
75	729	818	734	732	817	737	735	712	704	708	707	700	712	757	726	728	755	726	726	21	3	ν_{CCH} , 20 + δ_{CC} , 18
76	685	812	729	727	811	732	729	696	688	692	692	686	697	736	706	708	732	704	704	28	4	δ_{CC} , 24
77	633	737	661	660	737	665	663	653	646	649	654	648	659	681	653	655	681	655	655	10	1	γ_{C} , 21 + ν_{CC} , 21
78	582	675	606	604	674	608	606	589	583	586	589	583	593	617	591	593	617	593	593	10	2	δ_{CC} , 26
79	546	641	575	574	640	578	575	563	557	560	560	555	564	588	564	565	586	563	563	13	2	δ_{CC} , 20 + δ_{CCN} , 20
80	524	562	504	503	562	507	505	499	494	496	501	496	505	520	499	500	520	500	500	5	1	δ_{CC} , 28 + δ_{CCN} , 24
81	0	537	482	481	537	485	483	469	464	466	469	465	472	490	470	471	490	471	471	4	1	δ_{CC} , 20 + δ_{CC} , 22 + ν_{CCH} , 20
82	0	527	473	472	527	476	474	459	454	456	461	457	464	482	462	463	482	463	463	3	0	γ_{C} , 25 + δ_{CC} , 16
83	0	495	444	443	495	447	445	445	440	443	441	437	444	461	442	443	459	441	441	3	0	γ_{C} , 17
84	0	477	428	427	477	430	429	421	416	419	425	421	428	437	419	420	440	423	423	4	1	γ_{C} , 18 + δ_{CC} , 18
85	0	443	398	397	442	399	397	385	381	383	389	385	392	403	386	387	404	388	388	4	1	δ_{CC} , 34
86	0	429	385	384	429	387	386	381	377	379	382	378	385	398	382	383	400	384	385	1	0	γ_{C} , 26
87	0	388	348	347	388	350	349	339	335	337	340	337	342	352	337	338	353	339	339	2	0	δ_{CC} , 57 + τ_{CC} , 15
88	0	376	337	337	377	340	339	337	333	335	335	332	337	350	336	336	349	335	336	1	0	δ_{CCH} , 11 + δ_{COC} , 46
89	0	358	321	321	358	323	322	320	316	318	324	321	326	332	332	319	334	321	321	16	2	τ_{CN} , 26 + τ_{CC} , 13 + γ_{C} , 13
90	0	341	306	305	341	308	307	305	302	303	305	302	307	316	303	304	315	303	303	1	0	

TABLE 3: Continued.

Number	Exp.	HF						B1LYP						B3LYP						IR intensity	Assignments, PED (%) ^b	
		6-31G(d)			6-31G(d,p)			6-31G(d)			6-31G(d,p)			6-31G(d)			6-31G(d,p)					Abs. Rel.
		Unscal	Sca.	Sca.	Unscal	Sca.	Sca.	Unscal	Sca.	Sca.	Unscal	Sca.	Sca.	Unscal	Sca.	Sca.	Unscal	Sca.	Sca.			
91	0	336	302	301	336	303	302	299	296	297	299	296	301	298	299	311	299	299	2	0	$\tau_{CC}, 20 + \gamma_C, 10$	
92	0	311	279	278	311	281	280	272	269	271	272	269	274	271	272	283	272	272	4	1	$\tau_{CC}, 21 + \gamma_C, 16$	
93	0	305	274	273	303	273	272	268	265	267	270	267	272	277	266	266	268	258	0	0	$\delta_{CCH}, 10 + \tau_{CC}, 76$	
94	0	275	247	246	274	247	246	259	256	258	250	248	252	263	252	253	246	236	237	0	0	$\tau_{CC}, 13 + \tau_{CO}, 12 + \tau_{CN}, 12$
95	0	239	214	214	239	216	215	213	211	212	216	214	218	222	213	213	224	215	215	4	1	$\tau_{CC}, 31$
96	0	233	209	209	230	208	207	204	202	203	210	208	212	212	203	204	215	207	207	2	0	$\tau_{CN}, 20 + \delta_{CON}, 18 + \delta_{CCC}, 20$
97	0	227	204	203	228	206	205	201	199	200	197	195	198	208	199	200	200	192	192	0	0	$\tau_{CCH3}, 65$
98	0	197	177	176	197	178	177	162	160	161	169	167	170	171	164	164	177	170	170	1	0	$\tau_{CC}, 33 + \tau_{CN}, 32$
99	0	186	167	167	186	168	167	157	155	156	161	159	162	170	163	163	169	162	162	0	0	$\tau_{CN}, 13 + \tau_{CC}, 16$
100	0	148	133	133	148	134	133	136	135	135	136	135	137	141	135	136	139	134	134	1	0	$\tau_{CCH3}, 47$
101	0	123	110	110	123	111	111	108	107	107	110	109	111	113	108	109	113	109	109	2	0	$\tau_{CC}, R1, R2, R3, 48$
102	0	86	77	77	86	78	77	79	78	79	80	79	81	78	78	82	79	79	79	0	0	$\delta_{NCO}, N13-C15-O17, 49$
103	0	74	66	66	74	67	67	65	64	65	65	64	65	67	64	64	65	62	62	2	0	$\tau_{CO}, C15-O17, 59$
104	0	44	39	39	44	40	40	43	43	43	46	46	46	43	41	41	46	44	44	0	0	$\tau_{CN}, C15-N13, 50$
105	0	22	20	20	21	19	19	19	19	19	14	14	14	18	17	17	11	11	11	0	0	$\tau_{CN}, C15 - N13, 45$
r		0.9997	0.9997	0.9997	0.9997	0.9997	0.9997	0.9998	0.9998	0.9998	0.9998	0.9998	0.9998	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999		
Mean deviation		190.49	14.55	11.01	181.49	15.05	9.60	12.73	-4.08	4.27	8.49	-5.89	19.52	66.71	0.96	5.32	61.31	-0.24	0.13			
Mean absolute deviation		190.49	34.33	34.02	181.49	34.93	34.37	21.23	15.75	17.1	20.24	16.22	26.00	66.81	10.99	11.56	61.41	9.69	9.67			
Average absolute error		13.61	2.69	2.57	13.08	2.77	2.59	1.48	1.39	1.36	1.41	1.42	1.61	4.47	0.96	0.99	4.07	0.86	0.86			
RMS _{mol}		201.95	37.40	37.61	191.47	37.94	38.43	26.65	18.49	20.81	25.40	19.37	34.91	76.04	13.40	14.29	71.20	12.34	12.34			
RMS _{over}		176.28	32.65	32.83	167.13	33.11	33.54	23.26	16.14	18.16	22.17	16.91	30.48	66.37	11.7	12.47	62.15	10.77	10.77			
Scaling factor		1.000	0.8974	0.8953	1.000	0.9024	0.8992	1.000	0.9891	0.9945	1.000	0.9906	1.0072	1.000	0.9587	0.9614	1.000	0.9612	0.9614			

^a Harmonic frequencies (in cm⁻¹) and IR intensities (km/mol).^b v: stretching; δ : in-plane bending; γ : out-of-plane bending; τ : torsion; sym: symmetric; asym: asymmetric; R1: C19-O12-C21-C20-C25; R2: C19-O12-C21-C16-C24; R3: C16-C21-C18-N13-C22. PED less than 10% are not shown.

close to those reported in the literature [27–33]. These results indicate that the B3LYP calculations approximate the observed fundamental frequencies much better than the HF results. The small difference between experimental and calculated vibrational modes is observed. It must be due to the fact that hydrogen bond vibrations present in crystal lead to strong perturbation of the infrared frequencies (and intensities) of many other modes. Also, we state that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase [17, 19, 20, 23–25, 30–34].

Finally, we calculated the optimal scaling factors, which are crucial for IR spectral predictions, using the PAVF 1.0 program [26]. Without accounting for different vibrations, only single-uniform scaling factors were calculated. The values obtained are 0.8974/0.9024, 0.9587/0.9612, and 0.9891/0.9906 for the HF, B3LYP, and BLYP (6-31G(d)/6-31G(d,p)) methods, respectively. They are very close to those recommended by Scott and Radom [21] for the same levels of theory and increase in the same order of the HF, B3LYP and BLYP methods. Thus, for future IR spectral predictions for unknown derivatives of the title compound, one can recommend scaling factors of 0.897/0.902, 0.959/0.961, and 0.989/0.991 for the HF, B3LYP, and BLYP (6-31G(d)/6-31G(d,p)) methods, respectively.

The IR bands at 3082, 3067, and 3010 cm^{-1} in FT-IR spectrum of the title compound have been designated to νCH stretching fundamentals of C20, C25, and C19 atoms, respectively [23, 35, 36]. The wavenumbers corresponding to the aliphatic νCH stretching are listed in Table 3. All the calculated values in each method are overestimated, as well known in theoretical quantum mechanic assignment concerning hydrocarbons. After we applied the scale factor both calculated in this research and given by Scott and Radom [21] for all the methods, we observed a good concordance between the experimental and the calculated values. The vibrational spectra show six bands in the aliphatic νCH stretching region and evident overlap between the different C–H stretching modes. The asymmetric and the symmetric $\nu\text{C–H}$ stretching bands for $-\text{CH}_2-$ group are listed in Table 3. These assignments were also supported by the literature [20, 23, 35, 37]. The in-plane and out-of-plane bending vibrations of C–H group have also been identified for the title compound and they are presented in Table 3.

The carbonyl stretching vibrations are found in the region 1780–1700 cm^{-1} [38, 39]. The sharp intense band in IR spectrum at 1686 cm^{-1} can be assigned to the carbonyl group $\nu\text{C=O}$ stretching vibration.

The vibrational modes concerning the bond angle bending ($-\text{CH}_2-$), scissoring, wagging, twisting, and rocking are well defined in all the calculations. As seen from Table 3, the bands observed at 1460, 1451, and 1431 cm^{-1} in FT-IR spectrum correspond to scissoring deformation of $-\text{C}(18)\text{H}_2-$, $-\text{C}(22)\text{H}_2-$ and $-\text{C}(24)\text{H}_2-$ group in the title compound, respectively [37, 40]. 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 [36, 37, 40, 41]. Twisting and wagging vibrational

modes of the $-\text{CH}_2-$ groups were assigned in the range of 1350–1163 cm^{-1} . The above result is in close agreement with the literature values [36, 37, 40–42]. These vibrational modes are described in the tables by mean of the general symbol δCH_2 . The rocking $-\text{CH}_2-$ is assigned in the wavenumber range of 1109–852 cm^{-1} , and the wavenumber shift of these bands is due to the atom nature in which the $-\text{CH}_2-$ group is bonded. The $-\text{CH}_2-$ rocking vibrational modes are generally intensive bands which can be appreciating the vibrational coupling with other vibrational modes [36, 37]. These bands are assigned using calculated potential energy distribution.

For the assignments of CH_3 group frequencies, 15 fundamental vibrations can be associated to CH_3 groups. Nine stretching, three umbrella, and three rocking vibration modes are designated the motion of the methyl group. The CH_3 asymmetric and symmetric stretching frequencies are established at 3067, 3010, 3003, and 2923 cm^{-1} in infrared spectrum. The three methyl hydrogen deformation modes are also well established in the spectrum. We have observed the methyl deformation mode at 1474, 1451, 1431, and 1409 cm^{-1} in the infrared spectrum.

The C–C stretching vibrations in cyclic alkanes appeared as weak bands, so these vibrations are of little importance for structural study [43]. The IR bands appearing at 1360, 1247, 1222, 1211, 1180, 1163, 1128, 1109, 1089, 1045, 993, 947, and 928 cm^{-1} were assigned to νCC vibrations coupled with the δCCCH for the title compound. So, in our study, the C–C stretching vibrations are observed as medium-intensity bands. These results were confirmed by Gunasekaran et al. [44].

The identification of CN vibrations is a difficult task, since the mixing of vibrations is possible in CN stretching vibration frequencies region. However, with the help of both the animation option of Gaussian programs and theoretical calculations (VEDA 4), the CN vibrations are identified and assigned in this study. The IR bands appearing at 1409, 1282 and 1211 cm^{-1} are assigned to νCN vibrations. These results agree with Sundaraganesan et al. [45].

Epoxide group could be identified via its characteristic C–O stretching bands which gives two different absorption bands in the fingerprint region around ~ 800 –950 and ~ 1250 cm^{-1} , respectively [46, 47]. There is also a third band in the range 750–850 cm^{-1} . The IR bands appearing at 1180, 993, and 883 cm^{-1} are assigned to C–O stretching vibrations. These results agree with Evtushenko et al. [47]. The difference between observed and literature values is coming from the effects of the aromatic rings.

The $\nu\text{C–Cl}$ stretching vibrations give generally strong bands in the region of 710–505 cm^{-1} . The band observed at 685 cm^{-1} in FT-IR spectrum has been assigned to $\nu\text{C–Cl}$ stretching vibration in the present investigation [37].

2.4. Other Molecular Properties. Several calculated thermodynamic parameters are presented in Table 4. The total energies and the changes in the total entropy of the title compound at room temperature at different methods also presented.

TABLE 4: Theoretically computed energies, zero-point vibrational energies, entropies and dipole moment for the title compound.

Thermodynamic parameter	HF		BLYP		B3LYP	
	6-31G(d)	6-31G(d,p)	6-31G(d)	6-31G(d,p)	6-31G(d)	6-31G(d,p)
Total energy (a.u.)	-1316.1201	-1316.1634	-1321.6722	-1321.6975	-1322.0277	-1322.0532
Zero-point vibrational energy (kcal/mol)	206.307	205.270	184.792	184.321	191.332	190.656
Entropy (cal/mol K)						
Total	130.140	130.324	138.036	130.906	135.418	128.758
Translational	42.862	42.862	42.862	42.862	42.862	42.862
Rotational	33.707	33.705	33.821	33.775	33.757	33.725
Vibrational	53.571	53.758	61.353	54.269	58.799	52.170
Dipole moment (D)	4.4	4.4	3.8	3.7	4.0	3.9

3. Experimental

Dichloromethane (DCM) was distilled from calcium hydride. Reactions were monitored by thin layer chromatography (TLC) using precoated silica plates (Macherey Nagel sil G UV254). Compounds were visualized using ultraviolet fluorescence, alkaline potassium permanganate solution, or acidic cerium (IV) sulphate solution. Column chromatography was carried out using Macherey Nagel Kieselgel 60 (230–240 mesh).

3.1. Instrumentation. Melting points were determined using an Electrothermal-9300 Digital Melting Points Apparatus (Electrothermal Inc., Essex, UK). The ^1H and ^{13}C NMR spectra were recorded on a BrukerAvance DPX-400 spectrometer at the TÜBİTAK Analytical Laboratory (Ankara, Turkey). The chemical shifts are quoted in ppm, as δ values downfield of tetramethylsilane (TMS) or relative to the residual solvent resonance. Electron ionisation mass spectra (EI, 70 eV) were obtained on a Perkin Elmer Clarus 500 mass spectrometer. Elemental analysis was carried on LECO CHNS 932, TÜBİTAK Analytical Laboratory (Ankara, Turkey). The room-temperature-attenuated total reflection Fourier transform infrared (FT-IR ATR) spectrum of the *tert*-butyl 3a-chloroperhydro-2,6a-epoxyxireno[e]isoindole-5-carboxylate was recorded using Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism (4000–525 cm^{-1} ; number of scans: 250; resolution: 1 cm^{-1}) in the solid (Figure 3).

3.2. Synthesis of *tert*-butyl 3a-chloroperhydro-2,6a-epoxyxireno[e]isoindole-5-carboxylate. To a solution of meta-chloroperbenzoic acid (*m*-CPBA) (120 mg, 0.66 mmol), which had previously been purified and re-crystallized from dry diethyl ether, in dichloromethane (10 mL), cooled to 0 °C, was added dropwise a solution of *tert*-butyl 7a-chloro-1,6,7,7a-tetrahydro-3a,6-epoxyisoindole-2-carboxylate (0.66 mmol) in dichloromethane (10 mL) over a period of 3 min (Scheme 1). The reaction mixture was stirred at room temperature for 4 h and then diluted with cold 4% sodium bicarbonate solution (4 mL). The organic layer was separated, washed with water (3 $\times$ 20 mL), and concentrated in vacuum.

FIGURE 3: FT-IR spectrum of *tert*-butyl 3a-chloroperhydro-2,6a-epoxyxireno[e]isoindole-5-carboxylate.

The residue was subjected to flash column chromatography. As white crystal (110 mg, 56%). M.p.: 137–139 °C, TLC, (hexane: ethyl acetate (7 : 3)): R_f: 0.26. ^1H NMR (400 MHz CDCl_3) δ : 4.63 (d, 1H, H4, J = 5.1 Hz), 4.01–3.73 (m, 4H, H7, H8), 3.75 (d, 1H, H3, J = 3.3 Hz, AB), 3.52 (d, 1H, H2, J = 3.3 Hz, AB), 2.52 (dd, 1H, H5, J_1 = 5.1 Hz, J_2 = 12.5 Hz, AB), 1.90 (d, 1H, H5, J = 12.5 Hz, AB), 1.45 (s, 9H, H11, H12, H13). ^{13}C NMR (75 MHz CDCl_3) δ : 154.0 (C9, q), 91.1 (C1, q), 80.2 (C10, q), 77.2 (C4), 75.3 (C6, q), 60.5 (C2), 49.1 (C7), 48.3 (C8), 45.3 (C5), 42.1 (C3), 28.4 (C11, C12, C13). GC-MS (m/z): 288 [M^+ , %100], 252 [M^+ -(Cl), %55], 213 [M^+ -(OtBu), % 45], 167 [M^+ -(C8H9N), %85]. Elemental analysis (%) for $\text{C}_{13}\text{H}_{18}\text{ClNO}_4$: theoretical (experimental) C, 54.26 (54.03); H, 6.31 (6.15); N, 4.87 (4.71).

3.3. Calculations Details. The conformation analysis study was performed by Spartan 06 program package [15, 16]. All the other calculations were performed with the Gaussian 03W program package on a double xeon/3.2 GHz processor with 8 GB Ram [48]. The molecular structure of the title compound, in the ground state, is optimized by using HF, BLYP and B3LYP methods with the standard 6-31G(d) and 6-31G(d,p) basis sets. The vibrational frequencies were

also calculated with these methods. The frequency values computed at these levels contain known systematic errors [27–29, 49–53]. Therefore, we have used the scaling factor for HF, B3LYP, and BLYP methods [17, 21–25]. We have also calculated optimal scaling factors for all investigated methods. We have also calculated optimal scaling factors for all investigated methods. 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 [52]. Furthermore, theoretical vibrational spectra of the title compound were interpreted by means of potential energy distributions (PEDs) using VEDA 4 program [54].

4. Conclusions

The frequency assignment for the *tert*-butyl 3a-chloroperhydro-2,6a-epoxyoxireno[e]isoindole-5-carboxylate has been done for the first time from the FT-IR spectrum recorded. The conformation stability, equilibrium geometries, and harmonic frequencies of the title compound were determined and analyzed both at HF and DFT level of theories utilizing 6-31G(d) and 6-31G(d,p) basis sets. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. The IR spectrum of the title compound was interpreted in terms of the potential energy distribution (PED) analysis. Optimal uniform scaling factors were calculated for the title compound. 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 0.897/0.902, 0.959/0.961, and 0.989/0.991 for HF, B3LYP, and BLYP (6-31G(d)/6-31G(d,p)), respectively.

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