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Structural, Spectroscopic (FT-IR, Raman and NMR), Non-linear Optical (NLO), HOMO-LUMO and Theoretical (DFT/CAM-B3LYP) Analyses of N-Benzyloxycarbonyloxy-5-Norbornene-2,3-Dicarboximide Molecule

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N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide,
Vibrational spectroscopy,
^{1}H and ^{13}C NMR chemical shifts,
Non-linear optical properties,
DFT/CAM-B3LYP

Abstract: The experimental spectroscopic investigation of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide ($C_{17}H_{15}NO_5$) molecule has been done using ^{1}H and ^{13}C NMR chemical shifts, FT-IR and Raman spectroscopies. Conformational forms have been determined depending on orientation of N-benzyloxycarbonyloxy and 5-norbornene-2,3-dicarboximide (NDI) groups of the title compound. The structural geometric optimizations, vibrational wavenumbers, NMR chemical shifts (in vacuum and chloroform) and HOMO-LUMO analyses for all conformers of the title molecule have been done with DFT/CAM-B3LYP method at the 6-311++G(d,p) basis set. Additionally, based on the calculated HOMO and LUMO energy values, some molecular properties such as ionization potential (I), electron affinity (A), electronegativity (χ), chemical hardness (η), chemical softness (ζ), chemical potential (μ) and electrophilicity index (ω) parameters are determined for all conformers. The non-linear optical (NLO) properties have been studied for the title molecule. We can say that the experimental spectral data are in accordance with calculated values.

N-Benziloksikarboniloksi-5-Norbornen-2,3-Dikarboksimid Molekülünün Yapısal, Spektroskopik (FT-IR, Raman ve NMR), Doğrusal Olmayan Optik (NLO), HOMO-LUMO ve Teorik (DFT/CAM-B3LYP) Analizleri

Anahtar Kelimeler
N-Benziloksikarboniloksi-5-norbornen-2,3-dikarboksimid,
Titreşim spektroskopisi,
^{1}H ve ^{13}C NMR kimyasal kaymaları,
Doğrusal olmayan optik özellikler,
DFT/CAM-B3LYP

Özet: N-Benziloksikarboniloksi-5-Norbornen-2,3-Dikarboksimid molekülünün deneysel spektroskopik incelenmesi, ^{1}H ve ^{13}C NMR kimyasal kayma, FT-IR ve Raman spektroskopileri kullanılarak yapılmıştır. Konformasyonel formlar molekülün N-Benziloksikarboniloksi ve 5-Norbornen-2,3-Dikarboksimid (NDI) gruplarının yönelimine bağlı olarak belirlenmiştir. Molekülün bütün konformerleri için yapısal geometrik optimizasyonlar, titreşimsel dalgasayıları, NMR kimyasal kaymaları (vakum ve kloroform içinde) ve HOMO-LUMO analizleri 6-311++G(d,p) temel setinde DFT/CAM-B3LYP metodu ile yapılmıştır. Ayrıca, hesaplanan HOMO ve LUMO enerji değerlerine bağlı olarak, iyonlaşma potansiyeli (I), elektron çekiciliği (A), elektronegatiflik (χ), kimyasal sertlik (η), kimyasal yumuşaklık (ζ), kimyasal potansiyel (μ) ve elektrofilik indeksi (ω) parametreleri gibi kuantum moleküler tanımlayıcılar molekülün bütün konformerleri için belirlenmiştir. Molekülün doğrusal olmayan optik (NLO) özellikleri çalışılmıştır. Deneysel spektroskopik veriler hesaplanan değerler ile iyi bir uyum içerisinde olduğunu söyleyebiliriz.

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1. Introduction

Recently, norbornene-dicarboximides based groups have attracted much research interest. Especially, polynorbornene structures have perfect dielectric features, mechanical strength and exhibit membrane properties and can be used to generate composite materials [1-6]. Therefore, norbornenes are very attractive momomers for macromolecular design of poymers with desired properties [7]. Besides, some norbornene-dicarboximides show binding affinity and selectivity towards serotonin receptors [8,9]. The synthesis and some chemical properties of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide can be found in literature [10].

In this work, we aimed to exhibit the molecular properties such as vibrational frequencies (FT-IR and Raman), ^{1}H and ^{13}C NMR chemical shifts, molecular geometric structural parameters, HOMO-LUMO analyses and quantum molecular descriptors that are depended on HOMO and LUMO energy values of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide molecule. Detailed structural, spectroscopic, electronic and non-linear optical analyses for the title molecule are not available in the literature. It is well-known that the quantum chemical computations provide a powerful support for experimental studies. Many researchers apply quantum mechanical computational methods to investigate structural, spectroscopic, electronic, magnetic, thermodynamic and optical properties of the molecular systems [11-16]. Recently, these methods have been widely used in order to determine the structural parameters such as vibrational frequencies, magnetic properties (NMR chemical shifts and NMR spin-spin couplings), electronic parameters (UV-Vis. spectral parameters, HOMO, LUMO, NBO, MEP, ...), thermodynamic properties (enthalpy, entropy, heat capacity, thermal energy, zero-point energy, Gibbs free energy, Helmholtz free energy, ...) and non-linear optical properties of the molecular systems theoretically. Our study differs from the literature in terms of computational methods. The quantum chemical investigations of the compound have been performed by DFT/CAM-B3LYP method with the 6-311++G(d,p) basis set, for the first time.

2. Computational Methods

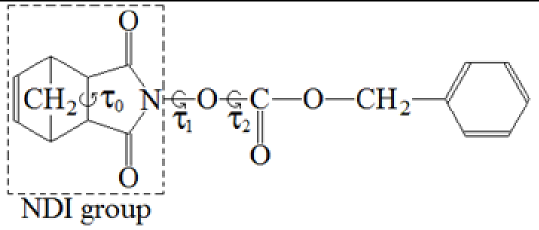
The molecular geometric optimizations, molecular conformational analysis, vibrational frequencies, ^{1}H and ^{13}C NMR chemical shifts (in vacuum and chloroform), HOMO and LUMO analyses (in vacuum and ethanol) and NLO properties of the title compound have been performed using the Gaussian 09W program package [17]. The calculated results have been visualized using GaussView5 program [18]. All of the computations have been fulfilled using CAM-B3LYP range-separated hybrid functional (long range corrected version of B3LYP using the Coulomb-attenuating method) in DFT (Density Functional Theory) method with the 6-311++G(d,p) basis set [19-21]. The calculated vibrational wavenumbers were scaled with 0.960 for 1700-4000 cm^{-1} region and 0.980 for 0-1700 cm^{-1} one.

For proton and carbon-13 NMR isotropic chemical shift computations, the optimized molecular structures of the compound were first obtained at the CAM-B3LYP/6-311++G(d,p) computational level in vacuum and chloroform using integral equation formalism polarizable continuum model (IEFPCM). Then, proton and carbon-13 NMR chemical shifts were computed with gauge invariant atomic orbital (GIAO) approach [22-24]. The HOMO and LUMO energy values and surface were simulated using the CAM-B3LYP/6-311++G(d,p) level. Considering the calculated HOMO and LUMO energy values, the some molecular properties such as ionization potential (I), electron affinity (A), electronegativity (χ), chemical hardness (η), chemical softness (ζ),chemical potential (μ) and electrophilicity index (ω) parameters were calculated. The non-linear optical (NLO) properties (the mean polarizability (α_{total}), the anisotropy of the polarizability ($\Delta\alpha$) and the first hyperpolarizability (β_0)) were performed with the CAM-B3LYP/6-311++G(d,p) computational level.

3. Results and Discussion

3.1. Molecular structure analysis

The optimized molecular conformational forms, computed total molecular energies and τ_0 (C3-C2-C1-C14), τ_1 (C14-N16-O17-C18) and τ_2 (N16-O17-C18-O20) torsion angle values (the computed with the CAM-B3LYP/6-311++G(d,p) level) of the title compound is given in Figure 1. Conformational analysis has been performed depending on both C3-C2-C1-C14 torsion angle in N-benzyloxycarbonyloxy group and C14-N16-O17-C18, N16-O17-C18-O20 torsion angles in 5-norbornene-2,3-dicarboximide (NDI) group. According to performed computations, the eight conformational forms have been found for the title molecule. The conformer 1 is most stable structure with energy value of -1087.45869209 a.u.. The most unstable form is conformer 8 with energy value of -1087.45293017 a.u.. The τ_0, τ_1 and τ_2 torsion angle values for conformer 1 are computed as 118.8°, 86.2° and 180.0°, respectively. The form of NDI group in this conformer of the title molecule is found as chair (zig-zag). The experimental molecular geometric parameters (bond lengths and angles) of the title molecule are not available in the literature. Therefore, the calculated bond lengths and angles for all conformers of the title compound are presented in Table 1.



τ_0=C3-C2-C1-C14
τ_1=C14-N16-O17-C18
τ_2=N16-O17-C18-O20

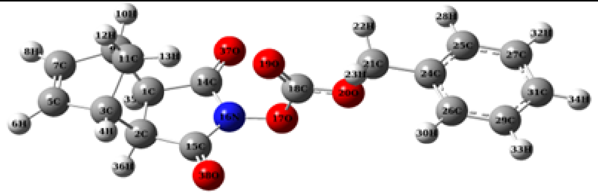
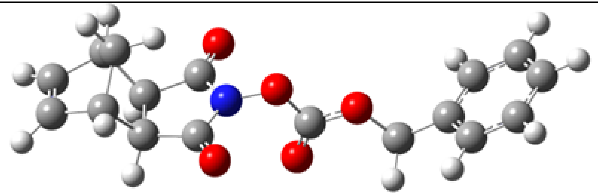
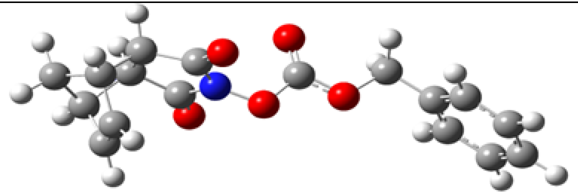
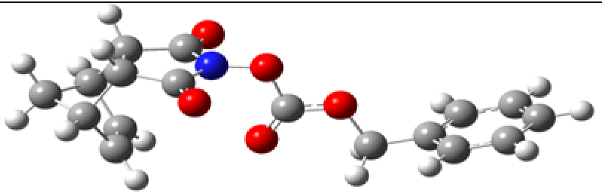
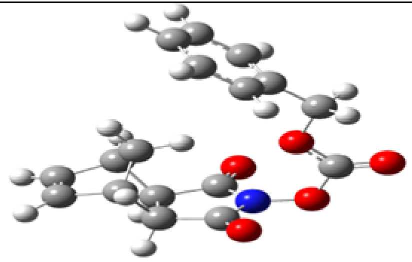
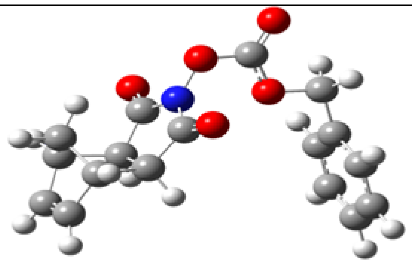
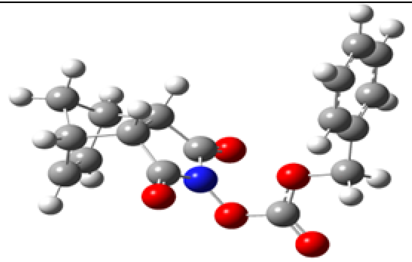
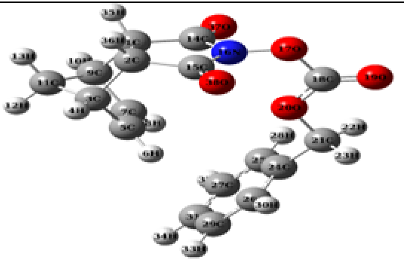
Conformer 1	**Conformer 2**
	
E(RCAM-B3LYP)=-1087.45869209 Hartree τ_0=118.8°, τ_1=86.2°, τ_2=180.0° Form of NDI group= Chair (zig-zag)	E(RCAM-B3LYP)=-1087.45755796 Hartree τ_0=119.2°, τ_1=-91.7°, τ_2=180.0° Form of NDI group= Chair (zig-zag)
Conformer 3	**Conformer 4**
	
E(RCAM-B3LYP)=-1087.45662749 Hartree τ_0=-121.7.8°, τ_1=92.7°, τ_2=-180.0° Form of NDI group=Boat	E(RCAM-B3LYP)=-1087.45605792 Hartree τ_0=-121.9°, τ_1=-88.4°, τ_2=180.0° Form of NDI group=Boat
Conformer 5	**Conformer 6**
	
E(RCAM-B3LYP)=-1087.45523243 Hartree τ_0=119.2°, τ_1=89.5°, τ_2=0.0° Form of NDI group= Chair (zig-zag)	E(RCAM-B3LYP)=-1087.45460090 Hartree τ_0=119.1°, τ_1=-92.9°, τ_2=0.0° Form of NDI group= Chair (zig-zag)
Conformer 7	**Conformer 8**
	
E(RCAM-B3LYP)=-1087.45368629 Hartree τ_0=-121.2°, τ_1=93.6°, τ_2=0.0° Form of NDI group=Boat	E(RCAM-B3LYP)=-1087.45293017 Hartree τ_0=-123.5°, τ_1=-87.1°, τ_2=0.2° Form of NDI group=Boat

Figure 1. The conformational forms of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide.

The C5=C7, C14=O37 and C15=O38 double bond lengths in NDI groups of all conformers are calculated as 1.331 Å, 1.197-1.199 Å and 1.197-1.198 Å, respectively. The C-N bond lengths in NDI group of the compound are computed as 1.394-1.396 Å (for all conformers). Similarly, the C-C single bond lengths (C1-C2, C1-C9, C1-C14, C2-C3, C2-C15, C3-C5, C-C11, C7-C9 and C9-C11) in this group are obtained at the interval 1.511-1.566 Å for all conformers.

Table 1. The optimized molecular geometric parameters for all conformers of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide.

Parameters (Å, °)	Conf. 1	Conf. 2	Conf. 3	Conf. 4	Conf. 5	Conf. 6	Conf. 7	Conf. 8
C1-C2	1.552	1.551	1.550	1.550	1.552	1.551	1.549	1.550
C1-C9	1.563	1.564	1.566	1.565	1.563	1.564	1.566	1.564
C1-C14	1.514	1.514	1.511	1.512	1.514	1.514	1.511	1.512
C2-C3	1.563	1.564	1.566	1.565	1.563	1.564	1.566	1.564
C2-C15	1.514	1.514	1.511	1.512	1.514	1.514	1.511	1.512
C3-C5	1.519	1.519	1.518	1.517	1.520	1.519	1.518	1.517
C3-C11	1.541	1.541	1.542	1.541	1.540	1.541	1.542	1.542
C5-C7	1.331	1.331	1.331	1.331	1.331	1.331	1.331	1.331
C7-C9	1.519	1.519	1.518	1.517	1.520	1.519	1.518	1.518
C9-C11	1.541	1.541	1.542	1.541	1.540	1.541	1.542	1.543
C14-N16	1.396	1.394	1.394	1.396	1.395	1.394	1.394	1.395
C14-O37	1.197	1.197	1.199	1.197	1.197	1.198	1.198	1.198
C15-N16	1.396	1.394	1.394	1.396	1.395	1.394	1.394	1.396
C15-O38	1.197	1.197	1.198	1.197	1.197	1.198	1.198	1.197
N16-O17	1.363	1.362	1.362	1.362	1.366	1.366	1.366	1.366
O17-C18	1.376	1.378	1.376	1.376	1.375	1.376	1.375	1.374
C18-O19	1.193	1.191	1.192	1.191	1.188	1.188	1.188	1.188
C18-O20	1.312	1.313	1.313	1.314	1.322	1.320	1.321	1.320
O20-C21	1.455	1.454	1.454	1.453	1.455	1.454	1.454	1.454
C21-C24	1.496	1.496	1.496	1.496	1.496	1.496	1.496	1.496
C24-C25	1.391	1.391	1.391	1.391	1.392	1.392	1.392	1.392
C24-C26	1.391	1.391	1.391	1.391	1.392	1.392	1.392	1.391
C25-C27	1.387	1.387	1.387	1.387	1.387	1.387	1.387	1.388
C26-C29	1.387	1.387	1.387	1.387	1.387	1.387	1.387	1.388
C27-C31	1.388	1.388	1.388	1.388	1.389	1.389	1.389	1.389
C29-C31	1.388	1.388	1.388	1.388	1.389	1.389	1.389	1.389
C2-C1-C9	102.9	102.9	103.0	103.0	102.9	103.0	103.0	103.0
C2-C1-C14	105.7	105.7	105.9	105.9	105.7	105.7	105.9	105.9
C9-C1-C14	113.0	113.3	115.5	115.7	113.4	113.3	115.4	116.5
C1-C2-C3	102.9	102.9	103.0	103.0	102.9	103.0	103.0	103.1
C1-C2-C15	105.7	105.7	105.9	105.9	105.7	105.7	105.9	105.8
C3-C2-C15	113.0	113.3	115.5	115.7	113.4	113.3	115.4	116.0
C2-C3-C5	104.9	104.9	107.1	106.9	104.9	104.9	107.1	106.9
C2-C3-C11	100.8	100.9	99.1	99.2	100.8	100.9	99.1	99.2
C5-C3-C11	100.2	100.0	100.2	100.2	100.2	100.0	100.2	100.1
C3-C5-C7	107.6	107.6	107.7	107.7	107.6	107.6	107.7	107.8
C5-C7-C9	107.6	107.6	107.7	107.7	107.6	107.6	107.7	107.7
C1-C9-C7	104.9	104.9	107.1	106.9	104.9	104.9	107.1	107.2
C1-C9-C11	100.8	100.9	99.1	99.2	100.8	100.9	99.1	99.0
C7-C9-C11	100.2	100.0	100.2	100.2	100.2	100.0	100.2	100.2
C3-C11-C9	93.8	93.9	94.0	94.0	93.9	93.9	94.0	94.0
C1-C14-N16	105.9	106.0	105.6	105.6	106.0	106.0	105.7	105.7
C1-C14-O37	129.3	129.2	129.5	129.6	129.3	129.2	129.5	129.6
N16-C14-O37	124.7	124.8	124.8	124.8	124.8	124.8	124.8	124.7
C2-C15-N16	105.9	106.0	105.6	105.6	106.0	106.0	105.7	105.7
C2-C15-O38	129.3	129.2	129.5	129.6	129.3	129.2	129.5	129.5
N16-C15-O38	124.7	124.8	124.8	124.8	124.8	124.8	124.8	124.8
C14-N16-C15	116.3	116.6	116.9	116.7	116.4	116.5	116.9	116.7
C14-N16-O17	121.6	121.7	121.4	121.6	121.8	121.6	121.4	121.8
C15-N16-O17	121.6	121.7	121.4	121.6	121.8	121.6	121.4	121.4
N16-O17-C18	112.2	112.0	112.1	112.8	116.6	116.0	116.0	117.3
O17-C18-O19	124.8	124.9	125.0	125.1	119.7	119.6	119.7	119.4
O17-C18-O20	106.5	106.3	106.3	106.2	112.3	112.1	112.2	112.5
O19-C18-O20	128.7	128.9	128.8	128.7	128.0	128.3	128.2	128.1
C18-O20-C21	115.1	115.0	115.0	115.0	114.9	115.2	115.2	114.7
O20-C21-C24	107.9	107.9	107.9	107.9	107.7	107.7	107.7	108.0
C21-C24-C25	120.4	120.4	120.4	120.4	120.4	120.4	120.4	120.3
C21-C24-C26	120.4	120.4	120.4	120.4	120.4	120.4	120.4	120.5
C25-C24-C26	119.3	119.2	119.2	119.2	119.3	119.3	119.3	119.2
C24-C25-C27	120.4	120.4	120.4	120.4	120.4	120.4	120.4	120.4
C24-C26-C29	120.4	120.4	120.4	120.4	120.4	120.4	120.4	120.5
C25-C27-C31	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
C26-C29-C31	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
C27-C31-C29	119.9	119.9	119.9	119.9	119.9	119.9	119.9	119.9

In the literature, there are the experimental single crystal X-Ray analysis for compounds including 5-norbornene-2,3-dicarboximide group [9,25-29]. For N-pheny-5-norbornene-2,3-dicarboximide molecule, the C=C, C=O and C-N bond lengths were reported as 1.315(9) Å, 1.199(6)-1.213(6) Å and 1.376(7)-1.377(7) Å by Liang et al. [28], respectively. Similarly, Dvorkin et al. [26] recorded 1.311(3)-1.291(4) Å for C=C bond lengths, 1.198(2)-1.210(3) Å for C=O ones and 1.361(2)-1.362(2) for C-N ones for two compounds containing 5-norbornene-2,3-dicarboximide group. The C18-O17, C18=O19, C18-O20, C21-O20 and C21-C24 bond lengths in N-benzyloxycarbonyloxy group of all conformers are found as 1.374-1.378 Å, 1.188-1.193 Å, 1.312-1.322 Å, 1.453-1.455 Å and 1.496 Å, respectively. The N16-O17 bond length between N-benzyloxycarbonyloxy group and 5-norbornene-2,3-dicarboximide one is computed at the interval 1.362-1.366 Å for all conformers. In the literature, the experimental X-Ray single crystal analysis of N-(benzyloxycarbonyloxy) succinimide (or benzyl 2,5-dioxopyrrolidin-1-yl carbonate) molecule reported by Hu et al. [29]. They were recorded 1.379(4) Å, 1.179(4) Å, 1.312(4) Å, 1.464(4) Å and 1.484(5) Å values for the C18-O17, C18=O19, C18-O20, C21-O20 and C21-C24 bond lengths, respectively [29]. Similarly, they were reported as 1.391(3) Å the N16-O17 bond length between succinimide group and N-(benzyloxycarbonyloxy) one, while the C14=O37, C15=O38, C14-N16 and C15-N16 bond lengths in succinimide group were found as 1.193(4) Å, 1.202(4) Å, 1.376(4) Å and 1.383(4) Å, respectively [29].

The C14-N16-C15, N16-C14-O37, N16-C15-O38, N16-O17-C18, O17-C18-O19, O17-C18-O20, C18-O20-C21, O19-C18-O20 and O20-C21-C24 bond angles for conformer 1 form of the title molecule have been computed as 116.3°, 124.7°, 124.7°, 112.2°, 124.8°, 106.5°, 115.1°, 128.7° and 107.9°, while they were measured as 117.2(3)°, 124.4(3)°, 124.6(3)°, 112.0(2)°, 124.9(3)°, 104.8(3)°, 113.6(2)°, 130.4(3)° and 108.8(3)°, respectively [29].

3.2. Vibrational frequencies

There are 38 atoms and 108 normal vibrational modes (3N-6) of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide molecule. The measured [30] and calculated vibrational wavenumbers, IR intensities, Raman scattering activities and vibrational band assignments for the most stable molecular conformation of the studied molecule can be found in Table 2. The experimental [30] and simulated (for conformer 1) IR spectra of the title compound are given in Figure 2. Similarly, the experimental [30] and simulated (for conformer 1) Raman spectra of the title molecule are given in Figure 3. The linear correlation coefficients (R^2) between the experimental and calculated wavenumbers have been found as 0.99975 ($\nu_{cal.} = 0.99955\nu_{exp.} + 2.21849$) (for IR wavenumbers) and 0.99961 ($\nu_{cal.} = 0.99745\nu_{exp.} + 2.05360$) (for Raman wavenumbers).

The CH stretching vibrations in aromatic compounds and CH bonds with sp^2 hybrid occur absorption bands in the region 3000-3100 cm^{-1}, whereas the CH bonds with sp^3 hybrid (such as methyl, methylene,…) cause to stretching modes at the interval 2800-3000 cm^{-1} [31-33]. The observed band at 3132 (IR)-3138 (R) cm^{-1} is corresponded to =CH stretching mode in NDI group of the compound. The calculated wavenumbers for this band have been found at 3107 and 3084 cm^{-1}. Similarly, the CH stretching bands of phenyl ring are emerged at 3061 (IR), 3068 (R) and 3089 (IR) cm^{-1}, while the computed wavenumber values for the aromatic CH stretching vibrations are found at 3057, 3060, 3068, 3078 and 3087 cm^{-1}. The stretching band for the CH groups in the NDI group is recorded at 3030 cm^{-1} and they are computed at 3029, 3026, 3002 and 2995 cm^{-1}. Similarly, the symmetric stretching vibrations of methylene groups in the title molecule are found at 2965 (IR)-2969 (R) (exp.)/2965 (cal.) cm^{-1} and 2982 (IR)-2985 (R) (exp.)/2971 (cal.) cm^{-1}, while the asymmetric stretching modes are found at 3023 (R) (exp.)/3020 (cal.) cm^{-1} and 3023 (cal.) cm^{-1}. Additionally, the C-H in-plane and out-of-plane bending vibrations cause to absorption bands in the region 1000-1600 cm^{-1} and 650-1000 cm^{-1}, respectively [31-33]. The experimental and computed CH in-plane and out-of-plane bending modes in the phenyl and NDI groups of the title molecule are summarized in Table 2.

The O=C stretching vibration, which is highly characteristic, gives rise to strong absorption bands in the region 1540-1870 cm^{-1}. Also, position of this band depends on the physical state, electronic and mass effects of neighboring substituents, intra- and inter-molecular hydrogen bond interactions, conjugations and size of ring [31-33]. In our study, the position of stretching modes of the O=C groups in five member ring are shifted towards the high frequency region due to decrease in size of ring. The O=C stretching vibrations in the carbonate ester (R_1-O(C=O)O-R_2) and NDI groups of the title molecule are observed at 1738 (IR), 1780 (IR)-1783 (R) and 1807 (IR/R) and 1738 (IR) cm^{-1} and the computed wavenumbers corresponding to them are obtained at 1769, 1791 and 1827 cm^{-1}, respectively. Generally, the O-C stretching mode gives rise to strong absorption bands in the region 1000-1300 cm^{-1} in acids, alcohols, ether and esters groups [31-34]. In this connection, the O-C stretching vibrations is found at 1265 (IR)-1268 (R) (exp.)/1274 (cal.), 1118 (cal.), 1019 (cal.) and 987 (cal.) cm^{-1} as mixed with other vibrational bands. The NO stretching mode between O17 atom in carbonate ester group and N16 atom in NDI one is observed at 1376 (IR)-1377 (R) cm^{-1}, while this band is computed at 1391 cm^{-1}. The out-of-plane bending ($\gamma O_{17}O_{19}O_{20}C_{18}$ and $\gamma O_{17}C_{14}C_{15}N_{16}$) vibrations in the carbonate ester group and *N*-

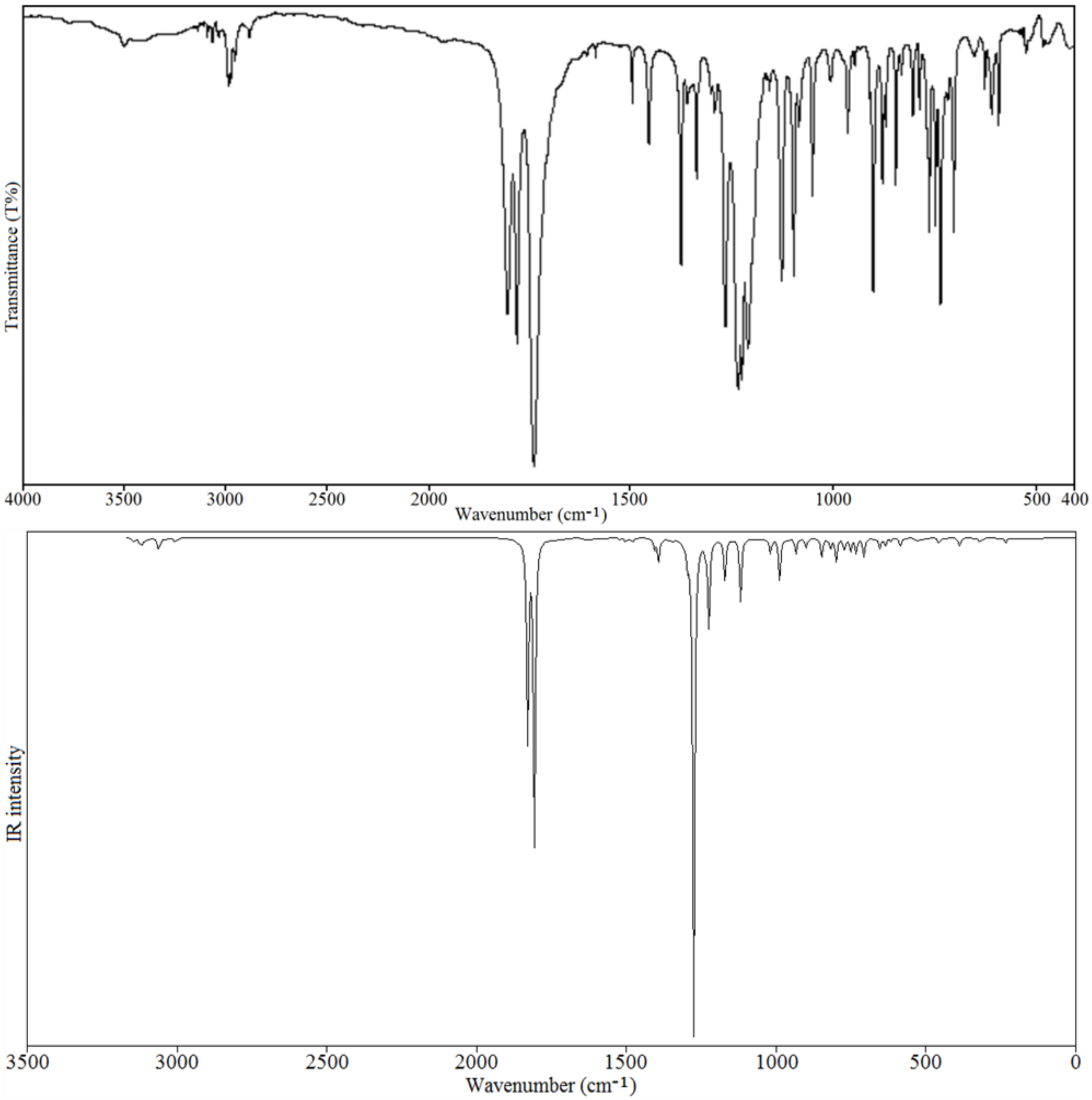


Figure 2. The measured (top) [30] and computed (bottom) (for conformer 1) IR spectra of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide.

hydroxysuccinimide one of the title compound are observed at 786 (IR)-789 (R) cm^{-1} and 368 (R) cm^{-1} and the computed values for these modes are found at 776 cm^{-1} and 386 cm^{-1}, respectively.

The aromatic CC skeletal stretching vibrations usually occur in the region 1400-1625 cm^{-1} and below 1400 cm^{-1} as mixed with other bands [35,36]. The observed bands at 1594 (IR)-1590 (R) and 1572 (R) cm^{-1} and the computed bands at 1655, 1633 and 1522 cm^{-1} can be assigned to the CC stretching modes in phenyl ring. Additionally, as seen in Table 2, the calculated wavenumber at 1343 cm^{-1} and the observed and computed wavenumbers below 1400 cm^{-1} as mixed with other vibrations are assigned to CC stretching modes of phenyl ring. The stretching vibrational bands ($\nu C_{21}C_{24}$) for bond between methylene group and phenyl ring are observed at 1225 (IR) and 847 (IR)-848 (R) (exp.) cm^{-1} and they have been computed at 1235 and 846 cm^{-1}. The in-plane (δphenyl) and out-of-plane (τphenyl) bending vibrational modes are found at 590 (IR)-576 (R) (exp.)/584(cal.), 625 (IR)-627 (R) (exp.)/629 (cal.), 847 (IR)-848 (R) (exp.)/846 (cal.) and 1012 (cal.) cm^{-1} and 416 (IR)-421 (R) (exp.)/411 (cal.) cm^{-1}, respectively. The vibrational bands (stretching, in-plane bending and out-of-plane bending modes) and their assignments of NDI group have been listed in Table 2.

3.3. NMR chemical shift analyses

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique that can be used to determine the isotropic chemical shifts of atom nucleus in different

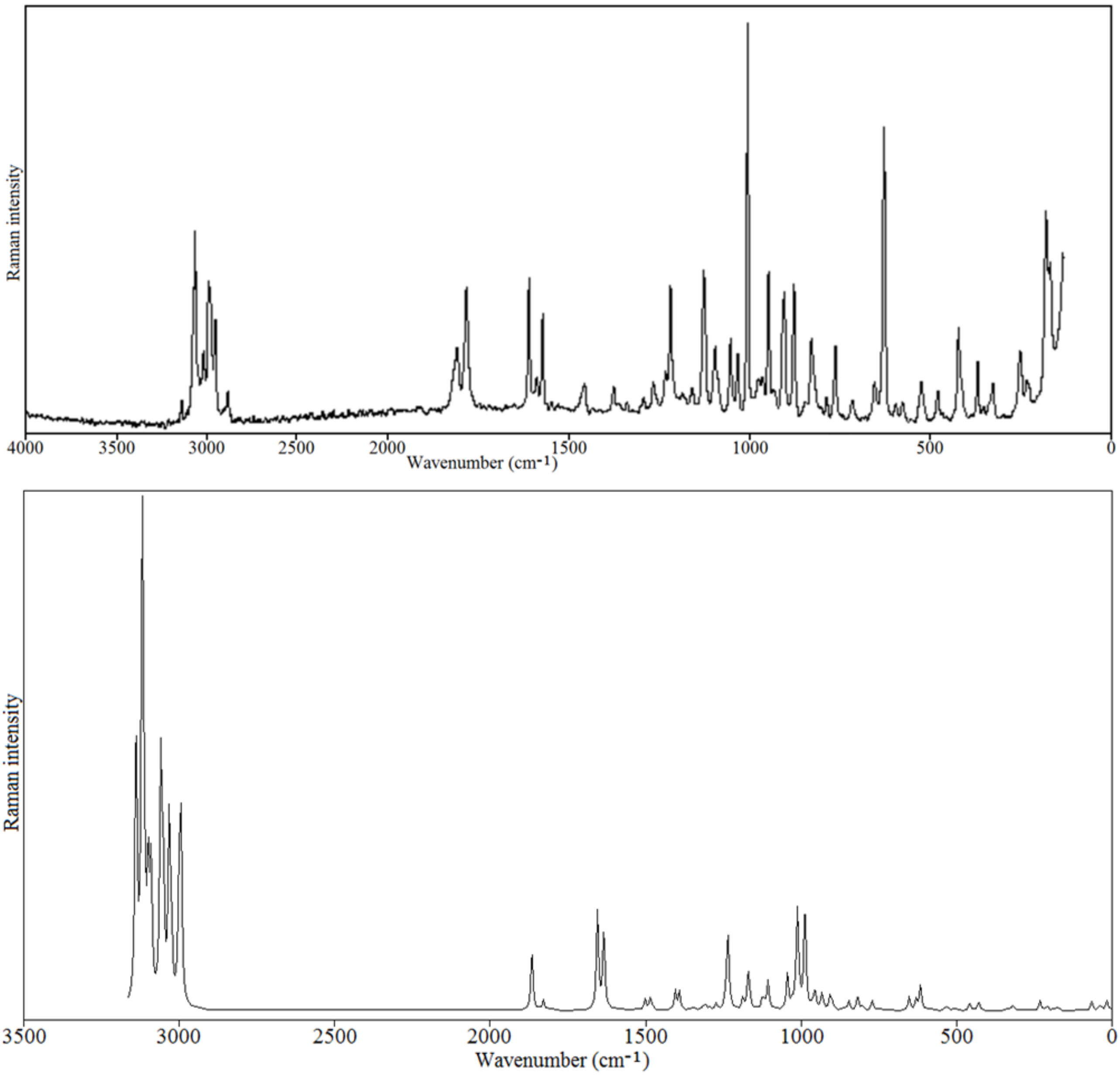


Figure 3. The measured (top) [30] and computed (bottom) (for conformer 1) Raman spectra of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide.

chemical environment, the content and purity of a compound, stable conformational form of molecule and functional groups in molecules [37-40]. The experimental ^{1}H and ^{13}C NMR isotropic chemical shift values recorded in chloroform-d of the title compound are listed in Table 3 [30]. Additionally, the computed ^{1}H and ^{13}C NMR isotropic chemical shifts for the title molecule have been obtained by GIAO method with the CAM-B3LYP/6-311++G(d,p) level in vacuum and chloroform solvent using IEFPCM solvent model. The calculated NMR isotropic chemical shifts are listed in Table 3.

The carbon-13 NMR chemical shifts are observed at values varying from 169.51 ppm to 44.70 ppm, while they are computed in the region 42.67-174.18 ppm in vacuum and 42.67-177.01 ppm in chloroform for the title molecule. The electronegativity, conjugation and inductive effects can cause an increase in carbon-13 NMR chemical shifts due to polarization of the electron distribution of the molecule. In this connection, the C14 and C15 carbon atoms that are bonded electronegative N and O atoms are given rise to resonance signal at 169.51 ppm, while they computed at 174.18/177.01 and 174.78/177.01 ppm (in vacuum/chloroform), respectively. Similarly, the C18 atom bonded electronegative oxygen atom is recorded at 151.36 ppm and computed at 156.92 ppm in vacuum and 156.99 ppm in chloroform. The obtained chemical shifts for these carbon atoms are higher than those of other carbon in the title molecule. It is well-known that the carbons with sp^2 hybrid and aromatic carbon atoms occur signals in the region 100-150 ppm [37-40]. As expected, the C5, C7, C24, C25, C26, C27, C29 and C31 carbon atoms are given signals in the region 128.46-134.67 ppm, the computed values for these carbon atoms are between 132.34 - 144.51 ppm in vacuum and 132.62 - 144.70

Table 2. The experimental [30] and computed vibrational wavenumbers for conformer 1 form of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide.

Assingments	Exp. freq. (cm^{-1}) [30]		The computed vibrational parameters		
	IR	Raman	Freq.	I_{IR}	S_{Raman}
Lattice mode	-	-	13	0.294	0.412
Lattice mode	-	-	16	0.001	3.193
Lattice mode	-	-	35	1.084	0.263
Lattice mode	-	-	38	1.703	1.686
Lattice mode	-	-	65	0.071	3.132
Lattice mode	-	-	78	0.883	0.079
Lattice mode	-	-	92	3.523	0.295
Lattice mode	-	-	100	0.018	0.761
τ$C_{18}O_{20}C_{21}C_{24}$	-	-	136	0.424	0.103
δNDI+δ$C_{18}O_{20}C_{21}$+δ$O_{20}C_{21}C_{24}$	-	169	175	3.940	1.242
δNDI+τphenyl	-	180	206	2.402	1.206
δNDI	-	233	212	0.459	0.861
δ$C_{18}O_{20}C_{21}$+δ$O_{20}C_{21}C_{24}$	-	252	231	11.046	3.852
δNDI+δOCN	-	298	319	9.858	1.708
δ$O_{17}C_{18}O_{20}$+δOCN	-	327	329	0.016	0.709
δ$C_{21}C_{24}C_{26}$+ρCH_2	-	-	332	0.854	0.020
δNDI+δOCN+δ$O_{20}C_{21}C_{24}$+τphenyl	-	353	339	2.432	0.810
γ$O_{17}C_{14}C_{15}N_{16}$+δ$O_{17}C_{18}O_{19}$	-	368	386	20.611	0.784
τphenyl	416	421	411	0.000	0.007
τNDI	470	477	428	2.008	3.284
τphenyl+ δ$O_{17}C_{18}O_{20}$+δNDI+δOCN	480	-	456	12.430	2.746
ρCH_2 in NDI	508	-	508	3.533	0.741
τphenyl+δ$O_{17}C_{18}O_{20}$+δNDI+δOCN	523	524	528	7.748	0.995
τNDI	538	-	535	0.348	1.367
δphenyl+δ$C_{18}O_{20}C_{21}$	590	576	584	20.018	0.365
(δCNC+δNCC) in NDI	607	599	616	7.156	10.677
δphenyl	625	627	629	0.012	4.543
τNDI	-	-	634	18.291	0.104
(νCC+τHCCC+δNDI) in NDI+δ$O_{17}C_{18}O_{20}$	650	653	652	26.565	5.528
δNDI+δOCN	701	-	703	4.063	0.215
τHCCC in phenyl+γOCCN+δOCO	715	715	706	40.446	0.030
τHCCC in NDI	734	-	732	36.116	0.386
τHCCC in NDI+	746	742	750	30.218	1.115
τHCCC in phenyl	762	764	771	28.082	4.161
γ$O_{17}O_{19}O_{20}C_{18}$	786	789	776	1.849	0.185
δNDI+γ$O_{17}O_{19}O_{20}C_{18}$	-	804	798	57.790	0.091
δNDI	802	-	803	0.246	1.530
δNDI+νNO	-	-	817	25.019	5.011
δNDI	830	831	819	0.672	1.613
δphenyl+ν$C_{21}C_{24}$	847	848	846	45.419	4.261
τHCCC in phenyl	869	-	855	0.001	0.128
(νCC+δHCC) in NDI	877	880	899	23.052	3.074
(δHCC+νCC) in NDI	900	906	906	1.624	6.422
(δHCC+νCC) in NDI	908	-	914	0.739	0.089
(δHCC+νCC) in NDI	-	-	928	0.443	1.256
τHCCC in phenyl	-	937	933	37.563	6.866
(ρCH_2+νCC+δCCC+δHCC) in NDI	948	949	955	4.087	8.310
τHCCC in NDI	963	967	963	3.726	2.027
ρCH_2	-	977	964	3.069	0.299
ν$O_{20}C_{21}$+γ$C_{21}C_{25}C_{26}C_{24}$+τHCCC in phenyl	-	-	987	105.581	47.755
τHCCC in phenyl	-	-	990	0.015	0.008
(τHCCC+wCH_2) in NDI	1006	1007	1004	0.014	2.757
τHCCC in phenyl	-	-	1010	0.279	5.261
(ρCH_2+τHCCC) in NDI	-	-	1011	3.840	20.191
δphenyl	-	-	1012	0.484	19.677
ν$O_{17}C_{18}$+ν$O_{20}C_{21}$+νCC in NDI	-	-	1019	33.523	3.926
(ρCH_2+δHCC) in NDI	-	1034	1029	3.931	2.764
(δHCC+νCC+δCCC) in phenyl	1050	1054	1044	1.289	16.700
(δHCC+νCC+δOCN) in NDI	1084	-	1085	0.510	0.212
δHCC in phenyl	1096	1097	1100	4.535	0.325
δHCC in NDI	-	-	1106	0.187	12.760
νCC in NDI+νNO+ν$O_{17}C_{18}$+ν$O_{20}C_{21}$	-	-	1118	147.214	3.610
(tCH_2+δHCC) in NDI	1126	1129	1125	0.653	5.025
δHCC in phenyl	1156	1161	1164	0.091	3.556
(δHCC+νCC) in NDI	1167	-	1170	104.541	17.635
(δHCC+νCC) in NDI	-	1189	1187	0.004	2.078
δHCC in phenyl	-	-	1187	2.981	3.702
νNC+(νCC+δHCC) in NDI	1210	1220	1224	210.748	1.239
ν$C_{21}C_{24}$+(δHCC+νCC) in phenyl+wCH_2	1226	-	1235	14.380	33.230
δHCC in NDI	1233	1235	1236	2.639	2.735
(δHCC+tCH_2) in NDI	-	-	1241	1.192	4.530
tCH_2	-	-	1245	0.033	2.101

Table 2. (Continue)

(δHCC+νCC) in NDI	-	-	1272	0.634	0.867
$\nu O_{20}C_{18}+wCH_2+\delta HCC$ in NDI	1265	1268	1274	1160.487	2.383
($\delta HCC+wCH_2$) in NDI	-	-	1279	0.558	0.057
(δHCC+νCC) in NDI	1292	1294	1295	45.211	1.377
(δHCC+νCC) in NDI	1305	-	1307	3.361	2.009
($\delta HCC+\nu CC+wCH_2$) in NDI	-	-	1309	5.014	0.337
tCH_2+(νCC+δHCC) in phenyl	-	-	1315	1.697	1.580
δHCC in phenyl+tCH_2	1337	1335	1343	0.162	0.340
($\delta HCC+\nu CC+wCH_2$) in NDI	1360	1362	1348	7.956	1.164
$\nu NO+\delta CNC+wCH_2+\delta HCC$ in NDI	1376	1377	1391	57.412	9.390
wCH_2	-	-	1404	24.385	9.972
(δHCC+νCC) in phenyl+tCH_2	1455	1468	1476	7.290	0.886
$\delta_s CH_2$	-	-	1484	8.520	6.543
$\delta_s CH_2$ in NDI	1496	-	1501	9.362	5.638
(δHCC+νCC) in phenyl+$\nu C_{21}C_{24}$	-	1572	1522	3.578	1.249
(νCC+δHCC) in phenyl	1594	1590	1633	0.491	8.840
$\nu C_5=C_7$	1616	1610	1635	4.073	33.731
(νCC+δHCC) in phenyl	-	-	1655	0.236	51.369
νO=C in NDI	1738	-	1769	720.166	0.468
$\nu O_{19}=C_{20}$+νO=C in NDI	1780	1783	1791	468.083	5.891
νO=C in NDI+$\nu O_{19}=C_{20}$	1804	1807	1827	6.435	33.409
$\nu_s CH_2$ in NDI	2965	2959	2965	7.076	128.066
$\nu_s CH_2$	2982	2985	2971	8.957	79.179
νCH in NDI	-	-	2995	2.805	44.141
νCH in NDI	-	-	3002	5.893	135.245
$\nu_{as} CH_2$ in NDI	-	3023	3020	9.940	71.760
$\nu_{as} CH_2$	-	-	3023	5.228	24.024
νCH in NDI	-	-	3026	17.564	20.001
νCH in NDI	3030	-	3029	3.112	160.435
νCH in phenyl	-	-	3057	2.991	15.180
νCH in phenyl	3061	-	3060	1.366	84.345
νCH in phenyl	-	3068	3068	6.313	93.668
νCH in phenyl	-	-	3078	16.283	35.640
$\nu C_{5,7}H_{6,8}$	-	-	3084	2.506	93.867
νCH in phenyl	3089	-	3087	8.926	314.392
$\nu C_{5,7}H_{6,8}$	3132	3138	3107	9.135	215.560

Note. ν, stretching; δ, in-plane bending; δ_s, scissoring; τ, torsion; γ, out-of-plane bending; δ_s, scissoring; w, wagging; t, twisting; I_{IR}, IR intensity (km/mol); S_{Raman}, Raman scattering activity; NDI, 5-norbornene-2,3-dicarboximide.

Table 3. The experimental (chloroform-d) [30] and calculated (vacuum/chloroform) ^{13}C and ^1H NMR isotropic chemical shifts (with recpect to TMS, all values in ppm) for conformer 1 form of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide.

Atoms	$\delta_{exp.}$ [30]	$\delta_{cal.}$	Atoms	$\delta_{exp.}$ [30]	$\delta_{cal.}$
C1	44.70	44.46 / 44.93	H4	3.42	3.06 / 3.10
C2	44.70	44.46 / 44.93	H6	6.16	6.59 / 6.70
C3	43.00	44.83 / 44.84	H8	6.16	6.59 / 6.70
C5	134.67	144.51 / 144.70	H10	3.43	3.06 / 3.10
C7	134.67	144.51 / 144.70	H12	1.75	1.39 / 1.47
C9	43.00	44.83 / 44.84	H13	1.51	2.12 / 1.98
C11	51.12	42.67 / 42.67	H22	5.27	4.89 / 5.02
C14	169.51	174.18 / 177.01	H23	5.27	4.89 / 5.02
C15	169.51	174.78 / 177.01	H28	7.37	7.72 / 7.84
C18	151.36	156.92 / 156.99	H30	7.37	7.72 / 7.84
C21	72.36	71.98 / 71.66	H32	7.37	7.63 / 7.76
C24	133.48	137.94 / 137.71	H33	7.37	7.63 / 7.76
C25	128.73	135.00 / 135.23	H34	7.37	7.57 / 7.70
C26	128.73	134.99 / 135.23	H35	3.30	2.22 / 2.45
C27	128.46	132.34 / 132.62	H36	3.30	2.22 / 2.45
C29	128.46	132.34 / 132.62			
C31	129.10	132.97 / 133.48			

ppm in chloroform. The sp^3 carbons or alkyl carbons (methyl, methylene,…), amine ones, thiol ones, alcohol ones and halogenated aliphatic ones (-C-X (X=F, Cl, Br, I)) give NMR signals in the regions 15-35, 30-70, 18-55, 55-85 and 0-80 ppm, respectively [38]. The NMR chemical shift signal for C21 atom is recorded at 72.36 ppm and it is computed at 71.98/71.66 ppm (in vacuum/chloroform). Besides, the NMR isotropic chemical shifts for the C1, C2, C3, C9 and C11 atoms in the NDI group of the title compound are observed in the region 43.00-51.12 ppm, while they have been calculated at the interval 42.67-44-83 ppm in vacuum and 42.67-44.93 ppm in chloroform.

The aromatic rings produce large deshielding effects and their π-bonding electrons act as a conductor and the protons attached to carbon atoms in aromatic rings give resonance signals in the region 6-8 ppm [37-40]. The H28, H30, H32, H33 and H33 hydrogen atoms in phenyl ring are given signal at 7.37 ppm, while they have been computed at the interval 7.57 – 7.72 ppm in vacuum and 7.70-7.84 ppm in chloroform. Likewise, the recorded and computed values for H6 and H8 hydrogen atoms are at 6.16 ppm (exp.)/6.56 (cal. in vacuum)/6.70 (cal. in chloroform). The NMR isotropic chemical shift values for other hydrogen atoms in the title molecule are summarized in Table 3.

3.4. HOMO and LUMO analyses

The main orbitals taking part in chemical reaction is frontier molecule orbitals (FMOs) called as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [41]. The HOMO is directly correlated with the ionization potential of the compound. Behaving as an electron donor, it can be considered as valance band of the system. The LUMO is directly correlated with the electron affinity. It can be thought as conductivity band of the system due to behaving as an electron acceptor. The HOMO-LUMO energy band gap that is an important parameter for investigation of molecular electrical transport properties can use to determine molecular chemical stability. The molecules can be defined as “soft molecules” or “hard molecules” based on the HOMO-LUMO energy band gap that is the small or large, respectively. Therefore, the molecules that are belonged to the low HOMO-LUMO energy gap are more reactive [42]. Additionally, the molecular quantum mechanical parameters such as ionization potential, electron affinity, chemical reactivity, kinetic stability, polarizability, chemical hardness and softness, chemical potential, aromaticity, electronegativity and electrophilicity index can be found using HOMO-LUMO energy band gap [43]. The computed HOMO and LUMO energies and computed molecular quantum mechanical descriptors with the CAM-B3LYP/6-311++G(d,p) level are listed in Table 4 for the title molecule.

Table 4. The calculated quantum molecular descriptors for conformer 1 form of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide (vacuum/ethanol).

Parameters (eV)	Values
E_{LUMO} (eV)	0.224 / 0.041
E_{HOMO} (eV)	-8.790 / -8.692
Energy bandgap $/E_{\text{HOMO}}- E_{\text{LUMO}}/$	9.014 / 8.732
Ionization potential ($I = -E_{\text{HOMO}}$)	8.790 / 8.692
Electron affinity ($A = -E_{\text{LUMO}}$)	-0.224 / -0.041
Chemical hardness ($\eta = (I-A)/2$)	4.507 / 4.366
Chemical softness ($\zeta = 1/2\eta$)	0.111 / 0.115
Electronegativity ($\chi = (I+A)/2$)	4.283 / 4.326
Chemical potential ($\mu = -(I+A)/2$)	-4.283 / -4.326
Electrophilicity index ($\omega = \mu^2/2\eta$)	2.035 / 2.143

The HOMO-1, HOMO, LUMO and LUMO+1 simulations and their energy values for the title molecule are depicted in Figure 4. The energy gaps between HOMO and LUMO and HOMO-1 and LUMO+1 are 9.014/8.732 eV and 9.105/9.040 eV, respectively. The HOMO is mainly localized over whole molecule, whereas the LUMO is mostly placed on N-benzyloxycarbonyloxy group. Likewise, the HOMO-1 and LUMO+1 are centered on phenyl and 5-norbornene-2,3-dicarboximide, respectively.

3.5. NLO properties

The organic, inorganic and organometallic non-linear optical (NLO) materials have been effectively used due to their future potential applications in the fields of physics, chemistry and engineering. Especially, the effective NLO materials with high performance have been very interesting in the optoelectronic and microelectronics fields such as optical telecommunications, signal processing, optical interconnections, optical computing, optical information processing, sensor protection, optical switching, dynamic image processing and various other photonic technologies [44]. The mean polarizability (α_{total}), the anisotropy of polarizability ($\Delta\alpha$) and first hyperpolarizability (β_0) values are important key factors to determine NLO properties of molecular systems. The polarizabilities, static first hyperpolarizabilities and dipole moments of the title molecule are computed with the CAM-B3LYP/6-311++G(d,p) level using the finite-field approach.

The polarizabilities and first hyperpolarizabilities have been computed in terms of atomic units (a.u) by Gaussian 09W program. They have been converted into electrostatic unit (esu) (1 a.u = 0.1482×10^{-24} electrostatic unit (esu) for α values and 1 a.u = 8.6393×10^{-33} esu for β values). The mean polarizability (α_{total}), the anisotropy of the polarizability ($\Delta\alpha$), the mean first hyperpolarizability (β_0) and the total static dipole moment (μ_{total}), values have been computed using the following equations [36,44].

$$\alpha_{total} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (1)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\begin{bmatrix}(\alpha_{xx}-\alpha_{yy})^2 + (\alpha_{yy}-\alpha_{zz})^2 \\ +(\alpha_{zz}-\alpha_{xx})^2 + 6\alpha_{xz}{}^2 + 6\alpha_{xy}{}^2 + 6\alpha_{yz}{}^2\end{bmatrix}^{\frac{1}{2}} \quad (2)$$

$$\beta_0 = \begin{bmatrix}(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^2 + (\beta_{yyy}+\beta_{yzz}+\beta_{yxx})^2 \\ +(\beta_{zzz}+\beta_{zxx}+\beta_{zyy})^2\end{bmatrix}^{\frac{1}{2}} \quad (3)$$

$$\mu_{total} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}} \quad (4)$$

The calculated dipole moment values for the title molecule have been found as -0.5912 Debye for μ_x, 0.5116 Debye for μ_y, 1.3407 Debye for μ_z and 1.5520 Debye for μ_{total}.

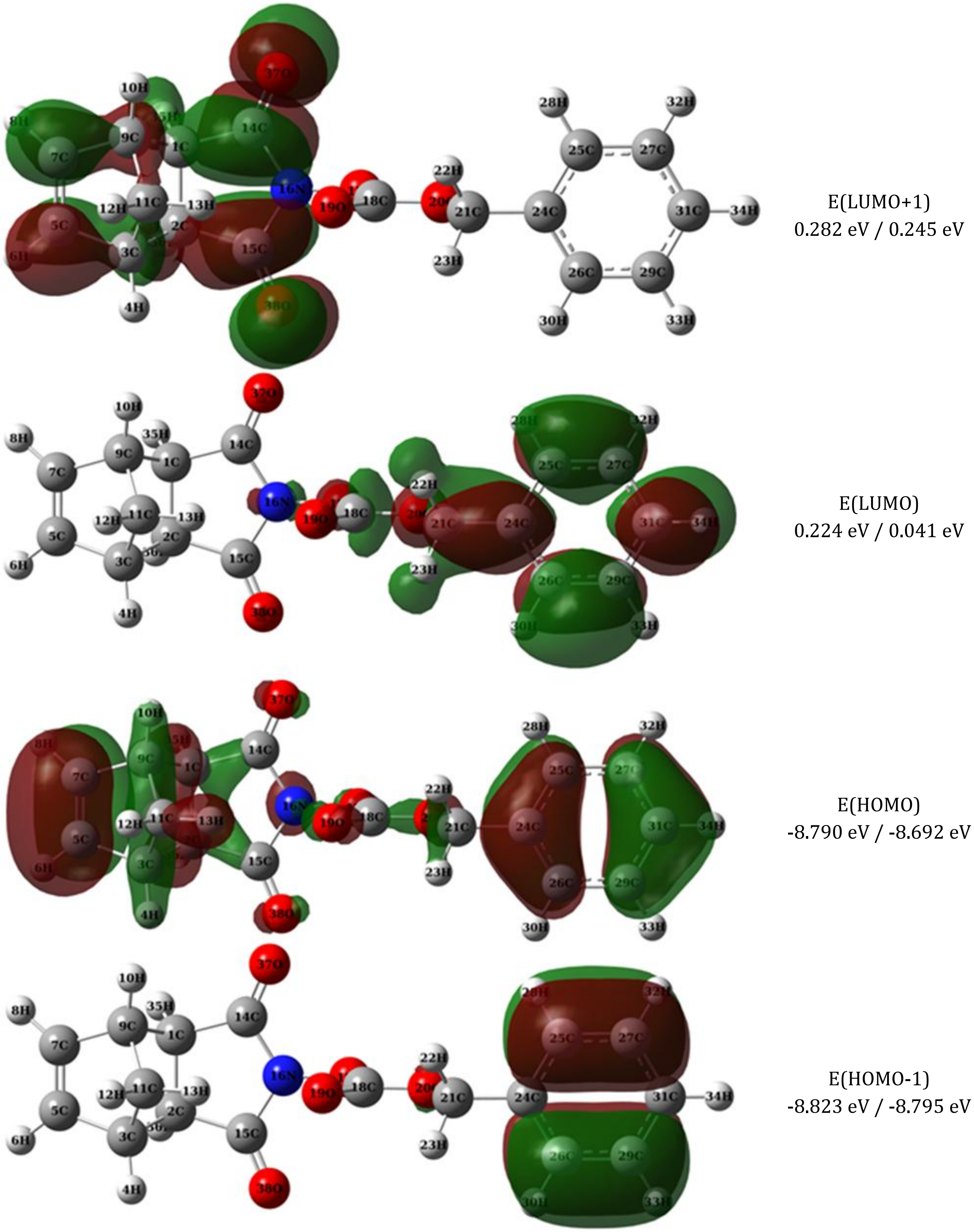


Figure 4. The LUMO+1, LUMO, HOMO and HOMO-1 shapes and their energy values for conformer 1 form of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide (vacuum/ethanol).

The mean polarizability and the anisotropy of polarizability have been obtained as 30.2533×10^{-24} esu and 15.7314×10^{-24} esu, respectively. The first hyperpolarizability value is computed as 328.7998×10^{-32} esu. The urea is one of the reference materials in NLO studies. Therefore, the NLO properties for the molecular systems can be usually compared with those urea. The calculated α_{total}, $\Delta\alpha$ and β_0 values for urea with the CAM-B3LYP/6-311++G(d,p) level are 4.8934×10^{-24} esu, 2.0109×10^{-24} esu and 47.5031×10^{-32} esu, respectively. The mean polarizability, anisotropy of polarizability and first hyperpolarizability values for the title compound are approximately 6.183, 7.823 and 6.922 times greater than those of urea, respectively.

4. Conclusions

The molecular structure, vibrational wavenumbers (FT-IR and Raman), proton and carbon-13 NMR isotropic chemical shifts, HOMO-LUMO analyses and NLO properties of N-benzyloxycarbonyloxy-5-norbornene-2,3-dicarboximide have been studied using experimental and computational (DFT/CAM-B3LYP/6-311++G(d,p) level) methods, for the first time. According to conformational analysis results, the most stable structural form is conformer 1 with 118.8°, 86.2° and 180.0° values of τ_0 (C_3-C_2-C_1-C_{14}), τ_1 (C_{14}-N_{16}-O_{17}-C_{18}) and τ_2 (N_{16}-O_{17}-C_{18}-O_{20}) torsional angles and with energy values of -1087.45869209 Hartrees, respectively. The HOMO and LUMO energy analyses of the title molecule have been theoretically studied. The quantum molecular descriptors have been determined depending on HOMO and LUMO energy values. We can declare that the molecule may be a good non-linear optical material with regard to the NLO results of the title compound.

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