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Experimental and Theoretical Investigation of Molecular Structure and Vibrational Frequencies of 3-Cyano-7-hydroxycoumarin by Density Functional Theory

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Abstract: In this research, geometrical structure and vibrational spectra of 3-cyano-7-hydroxycoumarin (3C7HC) were studied experimentally and theoretically. Experimentally, FT-IR (infrared) and FT-R (Raman) spectra of 3C7HC molecule were respectively obtained in the range of 4000-400 cm^{-1} and 3500-100 cm^{-1}. Theoretically, the optimized geometric structures, vibrational spectra and corresponding assignments according to two possible configurations of the 3C7HC molecule were investigated using the density functional method (B3LYP) with 6-311++G (d,p) basis set. When analyzes were performed, C_S symmetry property of 3C7HC molecule was used. It was seen that the experimental and calculated data of the 3C7HC molecule were highly compatible with each other.

Yoğunluk Fonksiyonel Teorisi (DFT) ile 3-Cyano-7-hydroxycoumarin molekülünün Titreşim Frekansı ve Moleküler Yapısı Üzerine Teorik ve Deneysel Bir Çalışma

Anahtar Kelimeler
3C7HC,
Titreşim frekansı,
IR,
Raman spektrumu,
DFT

Özet: Bu çalışmada 3-siyano-7-hidroksikumarin (3C7HC) molekülünün geometrik yapısı ve titreşim spektrumu deneysel ve teorik olarak incelendi. Deneysel olarak 3C7HC molekülünün FT-IR (infrared) ve FT-R (Raman) spektrumu, sırasıyla 4000-400 cm^{-1} ve 3500-100 cm^{-1} aralığında elde edildi. Teorik olarak, 3C7HC molekülünün iki muhtemel konfigürasyonuna göre optimize geometrik yapıları, titreşim spektrumları ve bunlara karşılık gelen atamalar, yoğunluk fonksiyon teori (DFT) ile B3LYP 6-311++G(d,p) temel parametreleri kullanılarak yapıldı. Analizlerde, 3C7HC molekülünün C_S simetri özelliği kullanıldı. 3C7HC molekülünün deneysel ve hesaplanan verilerinin birbirleri ile oldukça uyumlu olduğu görüldü.

1. Introduction

3-Cyano-7-hydroxycoumarine is known as 3-Cyanoumbelliferone, 7-hydroxy-2-oxo-1-benzopyran-3-carbonitrile and 7-hydroxy-2-oxochromene-3-carbonitrile, respectively. It is the derivative molecule of Coumarine, having a chemical formula of $C_{10}H_5NO_3$. Coumarine derivatives exhibit various biological activities and therapeutic properties. As a result of their presence in the chemical structures, they have been extensively studied in biomedical and industrial areas [1-14]. In recent years, the vibrational spectra and geometrical structures of Coumarine molecules have been experimentally and theoretically studied by many researchers. DFT method has been widely used in investigation of electronic molecular system. Density functional theory is based on the assumption that the electron density of an electronic system's energy can be defined using probability terms [15-14]. In the literature, no study was found on experimental and theoretical investigation of 3C7HC molecule.

In this study, experimental and theoretical conformations of 3C7HC molecule were carried out. The vibrational frequencies and geometrical structure of 3C7HC molecule were calculated with DFT/B3LYP method using 6-311++G(d,p) basis set. The calculated geometrical parameters and vibrational frequencies were compared with experimental results and previous studies.

2. Material and Method

2.1. Experimental details

3-cyano-7-hydroxycoumarin with 97% purity was purchased commercially from Sigma-Aldrich

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Company USA and used in pure form without further purification. The 3C7HC sample is found as powder at room temperature. 3C7HC was pelleted with KBr at room temperature using approximately 10 MPa pressure. The FT-IR spectrum of the 3C7HC was obtained within 4000-100 cm^{-1} range with the Perkin Elmer Spectrometer. FTR spectrum of 3C7HC was obtained within the range of 3200-100 cm^{-1} with Jasco NRS-3100 Raman Spectrometer.

2.2. Computational method

Optimized geometric structures, vibrational frequencies, zero-point energies and dipole moments according to two different conformation of 3C7HC were calculated with B3LYP 6-311++G(d,p) basis parameters of DFT method. The computations were made with Gaussian 09 [25] and Gauss-View software [26]. While the vibrational frequencies of 3C7HC were calculated theoretically, the 0.9614 scale was used [27].

3. Results and Discussion

3.1. Molecular geometry

3C7HC molecule has a planar geometric structure represented by the Cs symmetry which consists of identity E and a mirror plane σ elements. In this study, two probable conformers of optimized geometrical structures of the 3C7HC molecule with hydroxyl group (O-H) oriented in line with C-O bonding were investigated. When O-H is farther away from the oxygen atom of the pyrone ring of 3C7HC, the conformer is called as rotamer (Rot1). When O-H is closer to the oxygen atom, the conformer is called as rotamer2 (Rot2). The optimized geometrical structures of the Rot1 and Rot2 conformers of 3C7HC molecule are shown in Fig. 1. Orientation angles of O-H for conformers of 3C7HC are 110.6^0 for Rot1 and 249.6^0 for Rot2.

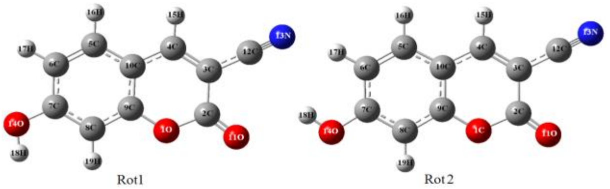

Figure1. Rot1 and Rot2 orientations of the 3C7HC molecule.

In the case of Rot1 and Rot2 of the 3C7HC molecule the zero-point, relative energy and dipole moments are given in Table 1.

The relative energy between two conformers is considerably low and it has a value of ~0.32 kcal/mol. As indicated by zero-point energies and dipole moments of the molecule, Rot1 conformer is more stable. Experimental [28, 29] and computed geometric parameters of conformers of 3C7HC molecule were compared in Table 2. The largest differences in computed and experimental parameters were obtained as Rot1 (0.04 Å), Rot2 (0.042 Å) for the bond lengths, and Rot1 (1.7^0), Rot2 (1.8^0) for the bond angles.

Table 1. Zero-point, relative energy and dipole moment of 3C7HC

Conformers	Zero-point energy [Hartree/particle]	Relative energy [kcal/mole]	Dipole moment [Debye]
Rot1	-664.537840	0.314799	8.0795
Rot2	-664.537338		9.7508

Table 2. Rot1 and Rot2 conformers of 3C7HC

Parameters	Exp.^{a}	Calculated		Parameters	Exp.^{a}	Calculated	
		Rot1	Rot2			Rot1	Rot2
Bond lengths (Å)				Bond angles (°)			
O1-C2	1.367	1.399	1.397	O1-C2-C3	118.2	118	118.1
C1-C9	1.382	1.359	1.36	O1-C2-O11	115.9	115.2	115.3
C2-C3	1.433	1.47	1.471	C2-C3-C4	120.6	121.1	121.1
C2-O11	1.224	1.197	1.197	C2-C3-C12	-	117.5	117.5
C3-C4	1.341	1.365	1.364	C3-C12-N13	178.5^b	178.3	178.2
C3-C12	1.430^b	1.425	1.425	C3-C4-C10	121	121.2	121.1
C12-N13	1.145^b	1.155	1.155	C3-C4-H15	-	119.6	119.6
C4-C10	1.424	1.424	1.425	C4-C10-C9	118.2	117.7	117.8
C4-H15	-	1.085	1.085	C10-C5-C6	120.7	121.1	120.9
C10-C5	1.411	1.411	1.408	C10-C5-H16	-	119	119.1
C10-C9	1.368	1.408	1.41	C5-C6-C7	120.7	119.5	119.6
C5-C6	1.393	1.377	1.38	C5-C6-H17	-	121.7	120.4
C5-H16	-	1.084	1.084	C6-C7-C8	120.6	120.9	120.9
C6- C7	1.396	1.408	1.408	C6-C7-O14	-	116.6	122.2
C6-H17	-	1.082	1.085	C7-O14-H18	-	110.6	110.5
C7-C8	1.398	1.393	1.393	C7-C8-C9	118	118.7	118.7
C7-O14	1.351	1.356	1.357	C7-C8-H19	-	122	120.8
O14-H18	-	0.964	0.964	C8-C9-C10	123	121.7	121.8
C8-C9	1.376	1.39	1.387	C8-C9-O1	117	117.2	117.3
C8-H19	-	1.084	1.082	C2-O1-C9	121.9	123.6	123.7
Rot1 angle = 110.6^0				Rot2 angle = 249.6^0			

^{a}Taken from Ref.[28] ^{b}Ref.[29]

3.2. Vibrational analysis

3C7HC molecule has 19 atoms and is in the CS symmetry. 19 atoms' three cartesian displacements were provided with 57 internal modes that is;

$$\Gamma_{\mathrm{inter.}} = 38\,\mathrm{A}' + 19\,\mathrm{A}'' \qquad (1)$$

In the event of translation ($\Gamma_{\mathrm{trans.}} = \mathrm{A}' + 2\mathrm{A}''$) and rotation ($\Gamma_{\mathrm{rot.}} = 2\mathrm{A}' + \mathrm{A}''$) from Cs point group table, vibrational modes are expressed as;

$$\Gamma_{\mathrm{vib.}} = \Gamma_{57} - \Gamma_{\mathrm{trans.}} - \Gamma_{\mathrm{rot.}} = 35\mathrm{A}' + 16\mathrm{A}'' \qquad (2)$$

In infrared (FT-R) and Raman (FT-R) all vibrational values are active. In the Cs symmetry, the 2N-3 of the vibrations is in plane and the N-3 of the vibrations is out of plane [30]. As a result, 35 out of 51 vibrations frequencies of the 3C7HC molecule are in plane and 16 of them are out of plane. Out of plane vibrations of the molecule are represented with A'' symmetries, while planar vibrations are represented with A' symmetries. This is clearly indicated in visual examination of vibrations performed with Gauss-View visualization program.

FT-IR and FT-R spectra of 3C7HC molecule are given in Fig.2 and Fig. 3. Observed and computed vibrational frequencies, Raman activities, infrared intensities, in plane -out of plane assignments are given in Table 3. Correlation values of vibrational frequencies for both conformers are given in the Table. The obtained results, normal coordinate analysis and the vibrational frequencies are significantly consistent with the results of previous studies.

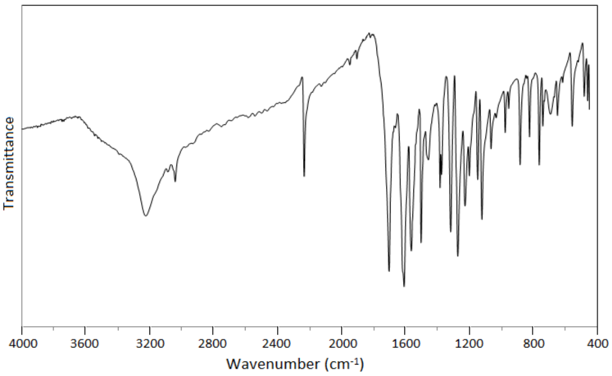

Figure 2. FT-IR spectrum of 3C7HC molecule.

3.2.1. C-H vibrations

CH stretching vibrations in the aromatic molecular structures widely occur in the form of weak multiple bands within 3100-3000 cm^{-1}interval. This region generally represents C-H stretching vibrations [31]. In this region the characteristics of substituent have no significant effect on the bands and four C-H stretching vibrations occur in 3C7HC molecule. In this study, aromatic C-H stretching vibrations of 3C7HC were obtained as 3090, 3043 cm^{-1} in FT-IR and 3089cm^{-1} in FT-R. In plane C-H bending vibrations are related with C-C stretching vibrations and the vibrations of aromatic molecular structures demonstrated in 1500-1100 cm^{-1} region [32]. C-H in plane bending vibrations of 3C7HC were obtained as 1611, 1566, 1505, 1460, 1385, 1374, 1318, 1272, 1230, 1203, 1150, 1123, 1066, 976, 953 cm^{-1} at FT-IR and 1608, 1596, 1557, 1459, 1374, 1314, 1273, 1233, 1160, 1127, 1068, 980 cm^{-1} at FT-R. The absorption bands stemming from C–H out of plane bending vibrations generally occurred within 1000–750 cm^{-1} region [33, 34]. The observed bands 885, 825, 765 cm^{-1} in FT-IR and 741cm^{-1} in FT-R were assigned to C-H out of plane bending vibrations of 3C7HC.

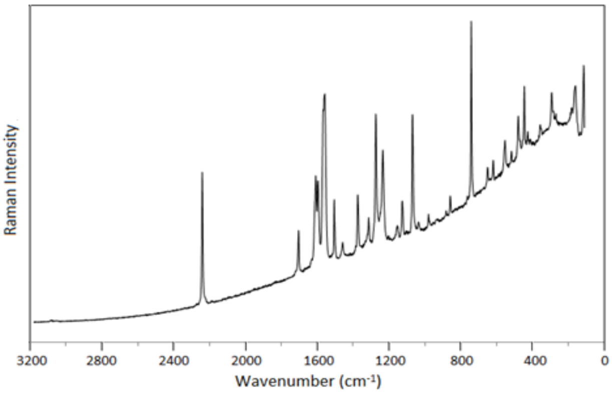

Figure 3. FT-R spectrum of 3C7HC molecule.

3.2.2. O-H vibrations

O-H bending and stretching vibrations can be identified with stretching vibration of the frequency band that is related to the hydrogen bonding extent. Because the oxygen atom is lighter than the hydrogen atom, the stagnation of the molecular structure had no effect on the O-H stretching vibration. O-H stretching vibrations are demonstrated by strong absorption bands in 3700-3584 cm^{-1} region [16]. In this study, the O-H stretching vibration was obtained as 3690 cm^{-1} in FT-IR. Generally, O-H in plane bending stretching vibrations are found with C-H in plane and CC stretching vibrations. O-H in plane bending stretching vibrations demonstrated in 1617-1114 cm^{-1} region [16, 37]. In plane bending stretching vibrations were obtained as 1566, 1505, 1460, 1385, 1374, 1318, 1274, 1230, 1150, 1123, 1066, 976 cm^{-1} at FT-IR and 1596, 1557, 1459, 1374, 1314, 1273, 1233, 1160, 1127, 1068, 980 cm^{-1} at FT-R. O-H out of plane bending vibrations demonstrated as in 450-350 cm^{-1} region [35-38]. Out of plane bending vibration was obtained as 359 cm^{-1} at FT-R. It has been verified that the experimental and calculated O-H vibrations are in accordance with the previous studies.

3.2.3. CO vibrations

CO stretching vibrations are called carbonyl groups and have a decisive feature. C=O stretching vibrations are widely studied with FT-IR and FT-R. The C=O stretching vibrations are demonstrated in 1780-1700 cm^{-1} region [38-40]. In this research, C=O stretching vibration of 3C7HC molecule was obtained as 1705 cm^{-1} at FT-IR and 1704 cm^{-1} at FT-R. C-O stretching vibrations of pyrone rings of coumarins demonstrated in 1250-850 cm^{-1} region [38-40]. C-O stretching vibrations were obtained as 1272,1150, 1123, 976, 953 cm^{-1} at FT-IR and 1273, 1160, 1127, 980 cm^{-1} at FT-R. C-O in plane bending vibrations was obtained as 652 cm^{-1} at FT-IR and 650 cm^{-1} at FT-R. C-OH stretching vibrations were obtained as 1460, 1272, 1203 cm^{-1} at FT-IR and 1459, 1273, 1215 cm^{-1} at FT-R. All C-OH vibrations are significantly consistent with the previous studies [16,38-40].

3.2.4. CN vibrations

There is a limited number of absorbing groups in the area where C≡N stretching is, so C≡N stretching restraint is quite easy. The bands showing the absorption vibration of cyano groups are quite dense within the range 2240-2220 cm^{-1} and the stretching vibrations in this region show a characteristic feature of C≡N. The amplitude of C≡N stretching vibration is demonstrated as a significantly strong band 2223 cm^{-1} in FT-IR and 2224 cm^{-1} in FT-R for 4-methy-2-cyanobiphneyl [15,39] and 2229 cm^{-1} at FT-IR and 2221 cm^{-1} at FT-R for 3-cyano-4-methylcoumarin [15].

Table 3. Experimental and computed vibrational frequencies of Rot1 and Rot2 conformers of 3C7HC

Symmetry	**Assignments**	**Exp. freq.(cm^{-1})**		**Calculated frequencies (cm^{-1})**					
				Rot1			**Rot2**		
		IR	**R**	**DFT**	**IR int. (km/mole)**	**R act. (Å^4/amu)**	**DFT**	**IR int. (km/mole)**	**R act. (Å^4/amu)**
A^{I}	ν(OH)	3700	-	3676	121	122	3680	141	249
A^{I}	ν(CH)	3090	3089	3085	1	1	3093	2	104
A^{I}	ν(CH)	-	-	3063	3	2	3063	5	159
A^{I}	ν(CH)	-	-	3059	4	114	3057	2	51
A^{I}	ν(CH)	3043	-	3056	1	4	3045	7	110
A^{I}	ν(CN)	2235	2339	2245	45	1072	2245	44	1078
A^{I}	ν(C=O)	1705	1704	1752	569	95	1752	560	96
A^{I}	ν(C=C)+ν(CC)	1611	1608	1591	405	152	1596	480	332
A^{I}	ν(C=C)+ν(CC)+δ(CH)+δ(OH)	1566	1596	1580	281	530	1580	68	339
A^{I}	ν(C=C)-ν(CC)+δ(CH)+δ(OH)	1505	557	1534	96	420	1532	261	533
A^{I}	ν(CC)+ν(C-OH)+δ(CH)+δ(OH)	1460	1459	1478	37	21	1475	66	1
A^{I}	ν(C=C)+ν(CC)+δ(CH)+δ(OH)	1385	-	1416	64	57	1421	21	58
A^{I}	ν(C=C)+ν(CC)+δ(OH)+δ(CH)	1374	1374	1338	68	147	1337	10	97
A^{I}	ν(CC)+δ(CH)+δ(OH)	1318	1314	1332	5	102	1332	23	48
A^{I}	ν(CO)+ν(C-OH)+δ(CH)+δ(OH)	1272	1273	1288	16	13	1282	158	18
A^{I}	ν(CC)+δ(CH)+δ(OH)	1230	1233	1237	58	63	1235	191	108
A^{I}	ν(CC)+ν(C-OH)+δ(CH)	1203	1215	1225	157	58	1222	21	20
A^{I}	ν(CC)+ν(CO)+δ(CH)+δ(OH)	-	1160	1164	69	20	1176	40	82
A^{I}	δ(CH)+δ(OH)	1150	-	1143	307	15	1149	4	6
A^{I}	ν(CC)+ν(CO)+δ(CH)+δ(OH)	1123	1127	1125	28	4	1113	103	2
A^{I}	δ(CH)	1066	1068	1095	23	4	1105	144	9
A^{I}	ν(CO)+δ(CH)+δ(OH)	976	980	973	53	89	973	116	83
A^{I}	ν(CO)+δ(CH)	953	-	941	21	14	943	12	10
A^{II}	γ(CH)	-	-	936	9	1	927	19	2
A^{II}	γ(CH)	885	-	916	9	2	899	0	1
A^{I}	δ(ring)	-	859	834	1	7	833	1	7
A^{II}	γ(CH)	825	-	813	46	0	827	26	0
A^{I}	δ(ring)+ν(C-OH)	-	-	802	3	0	803	5	0
A^{II}	γ(ring)+γ(CH)	765	-	793	10	0	768	29	0
A^{II}	γ(ring)	740	741	729	17	3	727	17	3
A^{I}	δ(ring)+δ(CN)	-	-	722	4	49	719	1	52
A^{II}	γ(ring)	697	-	694	1	0	684	3	0
A^{I}	δ(ring)+δ(CN)+δ(CO)	652	650	630	5	5	631	5	4
A^{II}	γ(ring)	618	620	613	5	1	609	11	1
A^{I}	δ(ring)	-	-	598	1	2	597	1	1
A^{I}	δ(ring)+δ(CN)	554	553	548	22	1	549	17	2
A^{II}	γ(ring))+γ(CN)	526	516	514	0	3	514	0	3
A^{I}	δ(ring)+δ(C-OH)	482	479	445	16	10	446	1	10
A^{II}	γ(ring)	460	446	440	10	0	443	2	0
A^{I}	δ(ring)+δ(CN)	-	427	432	3	6	431	6	6
A^{I}	δ(ring)+δ(C-OH)	-	-	408	7	7	408	3	8
A^{II}	γ(CH)+γ(ring)	-	-	400	3	1	397	1	2
A^{II}	γ(OH)	-	359	362	115	2	343	112	2
A^{I}	δ(ring)	-	-	336	2	9	336	10	8
A^{II}	γ(ring)	-	294	267	0	1	268	3	1
A^{I}	ρ(ring)	-	-	248	4	2	249	0	2
A^{II}	γ(ring)	-	-	238	0	1	237	1	1
A^{II}	γ(ring)	-	163	166	7	0	165	5	0
A^{I}	ρ(CN)	-	115	126	3	3	126	3	3
A^{II}	*w*(ring)	-	-	87	2	0	87	0	0
A^{II}	*w*(ring)	-	-	58	0	1	58	1	1
R ot1 R^2 = 0,9991						Rot2 R^2 = 0,9991			

ν:stretching,δ:bending,γ:out of plane bending, ρ: rocking,*w*:wagging.

In this research, the stretching vibration was observed as 2235 cm^{-1} at FT-IR and 2239 cm^{-1} at FT-R. C≡N in plane bending vibrations are demonstrated in 617-437 cm^{-1}region [15]. In plane C≡N bending vibrations were obtained as 652, 554 cm^{-1} at FT-IR and 650, 553, 427 cm^{-1} at FT-R, whereas out of plane C≡N bending vibration was obtained as 526 cm^{-1} at FT-IR and 516 cm^{-1} at FT-R. C≡N rocking vibration was obtained as 115 cm^{-1} at FT-R.

3.2.5. CC Ring vibrations

CC stretching vibrations are significantly dominant in spectra of coumarin derivate molecules and it has the characteristic of the aromatic ring. CC stretching vibrations of aromatic structures are demonstrated strongly within 1624-726 cm^{-1} range [16]. In this study, stretching vibrations for 3C7HC molecule were obtained as 1611, 1566, 1505, 1460, 1385, 1374, 1318, 1227, 1203, 1123 cm^{-1} at FT-IR and 1608, 1596, 1557, 1459 cm^{-1}, 1374, 1314, 1233, 1150, 1127 cm^{-1} at FT-R. In plane -out of plane bending ring vibrations of 3C7HC molecule are shown in Table 3. It has been verified that these values obtained are consistent with the previous studies [16, 40].

4. Discussion and Conclusion

In this research, FT-IR and FT-R spectra were obtained and vibrational assignments are shown in detail for the first time for 3C7HC. The differences in observed and scaled vibrational frequencies were found to be significantly low. FT-IR and FT-R spectra of 3C7HC were studied by using B3LYP 6-311++G(d,p) parameter of density functional theory. Vibrational frequencies of optimized molecular structures, geometry parameters, relative energy and dipole moment, corresponding vibrational assignments, FT-IR intensities and FT-R activities of the two different conformers of 3C7HC were obtained using DFT method. The calculated geometrical parameters and vibrational frequencies of these conformers were found to be consistent with the experimental data.

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