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Molecular Structure and Vibrational Spectra of 5,7-Dichloro-8-hydroxyquinaldine by Density Functional Theory and *ab initio* Hartree-Fock Calculations

K. ARICI* and H. KOKSAL†
Kilis 7 Aralik Universitesi Fen-Edebiyat Fakultesi Fizik Bolumu, Kilis, Turkey
E-mail: arici@kilis.edu.tr

The fourier transform infrared spectra and fourier transform Raman spectra of 5,7-dichloro-8-hydroxyquinaldine (5,7-DCIHQM) are recorded in solid phase. The molecular geometry, vibrational frequencies, infrared and Raman intensities of 5,7-DCIHQM in ground state have been calculated by using *ab initio* Hartree-Fock (HF) and density functional theory DFT(B3LYP and B3PW91) methods with 6-31G (d) basis set level. On the basis of the comparison between calculated and experimental results and the comparison with related molecule, assignments of fundamental vibrational modes are examined. The optimized geometric parameters (bond lengths and bond angles) obtained by using HF show the best agreement with the experimental values of 5,7-DCIHQM. Comparison of observed fundamental vibrational frequencies of 5,7-DCIHQM and calculated results by DFT (B3LYP and B3PW91) and HF approach for molecular vibrational problems.

Key Words: 5,7-Dichloro-8-hydroxyquinaldine, Molecular structure, Density functional theory.

INTRODUCTION

8-Hydroxyquinoline and its derivatives are well known for their antifungal, antibacterial and antiamoebic activities[1]. These molecules are widely employed as a good organic ligand binding with many metal cations due to its low quantum yield in aqueous and some organic solutions[2]. Quinoline family compound are widely used as a parent compound to make drug cancer[3] and an anaesthetic in the transportation of fish[4]. It also takes part in manufacturing oil soluble dyes.

The IR spectra of 8-hydroxyquinoline was predicted by Srivastava *et al.*[5]. The infrared spectra of some bivalent and tervalent metal chelate compounds of 8-hydroxyquinoline were reported by Magee and Gordon[6-8]. Chatum *et al.*[9] have investigated excited state dynamics of 8-hydroxyquinoline dimers. Li and Fang[10] have carried out a combined CASSCF, density functional theory (DFT) and MP study on the ground and excited state proton transfer of 8-hydroxyquinoline. Krisnakumar and Ramasamy have investigated DFT and vibrational spectra of 8-hydroxyquinoline and isoquinoline[11]. IR and raman spectra of 4-aminoquinaldine and 5-aminoquinoline

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†Kahramanmaras Sutcu Imam Universitesi Fen-Edebiyat Fakultesi Kimya Bolumu Kahramanmaras, Turkey.

was predicted by Puviarasan *et al.*[12]. Bahgat *et al.*[13] have carried out DFT calculations of 8-hydroxyquinoline and its derivative 5,7-dichloro-8-hydroxyquinoline. Aysen *et al.*[14] have calculated theoretical HF and DFT of 2-,4-,6-methylquinoline. Recently, vibrational and quantum mechanical calculations of 6- and 8-methylquinoline were reported by Kurt and Yurdakul[15].

Inspite of its above mentioned importance, no theoretical calculation and experimental studies of free 5,7-dichloro-8-hydroxyquinaldine (5,7-DCIHQM) have been published yet. Therefore, an investigation is made on the structure and vibrational frequencies of free 5,7-dichloro-8-hydroxyquinaldine. The aim of this study is to predict the structure and vibrational spectra of 5,7-dichloro-8-hydroxyquinaldine by means of the Hartree-Fock (HF) and density functional theory (DFT) (B3LYP and B3PW91) levels of theory.

EXPERIMENTAL

5,7-Dichloro-8-hydroxyquinaldine (5,7-DCIHQM) sample were purchased from Sigma-Aldrich Chemical Company with a stated purity of 99 % and it was used as such without further purification. The sample was prepared using a KBr disc technique. The infrared spectrum of compound was recorded between 4000-400 cm^{-1} on a Shimadzu 8300 FT-IR spectrometer which was calibrated using polystyrene bands. The FT-Raman spectrum of the sample was recorded between 3500-5 cm^{-1} regions on FRA-106/s spectrometer at METU, Ankara, Turkey.

Computational details: The molecular structure of 5,7-DCIHQM in the ground state (*in vacuo*) are optimized by HF, B3LYP and B3PW91 with the 6-31G (d) basis set. The optimized structural parameters were used in the vibrational frequency calculations at HF and DFT levels.

Density functional theory for all studies reported in this paper has the following from

$$E_{xc} = (1-a_0)E_{xLSDA} + a_0^{ExHF} + a_x^{\Delta ExB88} + a_c^{EcLYP} + (1- a_c)\, E_c^{VWN}$$

where, the energy terms are the Slater exchange, the Hartree-Fock exchange, Becke's exchange functional correlation, the gradient correlated correlation functional of Lee, Yang and Parr and the local correlation functional of Vosko, Wilk and Nusair[16]. HF/6-31G (d), B3LYP/6-31G (d) and B3PW91/6-31G (d) level of theory with the optimized geometries have been used to calculate all parameters of the 5,7-DCIHQM.

All the calculated vibrational frequencies are scaled by 0.8928[17] for HF/6-31G (d), 0.963 for B3LYP/6-31G (d) and 0.9567 for B3PW91/6-31G (d) basis set[18]. Molecular geometry is not restricted and all the calculations are performed by using GaussView molecular visualization program[19] and GAUSSIAN03 program package on the personal computer[20].

RESULTS AND DISCUSSION

The molecule of 5,7-DCIHQM consist of 21 atoms. The 57 normal modes of 5,7-DCIHQM, which span in the irreducible representation as 57 vibrational modes under the C_1 point group have been assigned according to the detailed motion of the individual atoms. All the 57 fundamental vibrations are active both IR and Raman.

The molecular structure and numbering of the atoms of 5,7-DCIHQM is shown in Fig. 1. We reported some geometric parameters and vibrational frequencies of 5,7-DCIHQM getting by *ab initio* HF and DFT (B3LYP and B3PW91) methods and compared with observed bond lengths and bond angles[12,21-24].

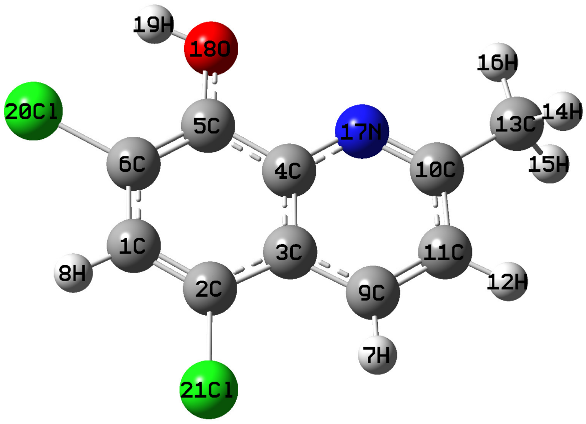

Fig. 1. Structure and atoms numbering of 5,7-dichloro-8-hydroxyquinaldine

Geometric structure: The optimized structure parameter of 5,7-DCIHQM calculated by *ab initio* HF and DFT (B3LYP and B3PW91) levels with the 6-31G (d) basis set are listed in the Table-1, in accordance with the atoms numbering scheme given in Fig. 1. Our calculated results indicate that the aromatic rings of the studied molecules are distorted from regular hexagonal due to the steric and electronic effects of electron donating substituent of the quinoline.

As discussed in earlier report[25], it is well known that HF methods underestimate bond length and BLYP methods predicts bond length which are systematically too long, particularly C-H bond lengths[26]. Since, large deviation from experimental C-H bond length may arise from the low scattering factors of hydrogen atoms in the X-ray diffractions experiment.

To the best of our knowledge, experimental X-ray data of 5,7-DCIHQM are not available in the literature. Therefore, we could not compare the calculation results given in Table-1, with the experimental data as the studied by Kurt *et al.*[27]. Only optimized geometric parameters of 5,7-DCIHQM are compared to those of previous reports[12,21-24].

The optimized geometric parameters (bond length and bond angles) by HF, B3LYP and B3PW91 with 6-31G (d) as the basis set is listed in Table-1 and compared with the combined experimental crystal geometry[12,21-24]. The optimized parameters obtained by the various methods are approximately similar. But some bond lengths of HF method are underestimate.

TABLE 1
GEOMETRIC PARAMETERS. BOND LENGTHS (Å) AND BOND ANGLES (°) OPTIMIZED FOR 5,7-DCIHQM

Bond lengths (Å)	HF 6-31G (d)	B3LYP 6-31G (d)	B3PW91 6-31G (d)	Ref. 12	Ref.[a] 21	Ref.[b] 21	Ref. 23	Ref. 24
C1-C2	1.351	1.373	1.373	1.361	1.365	1.381	1.363	1.360
C1-C6	1.412	1.409	1.407	1.393	1.427	1.403	1.405	1.409
C1-H8	1.072	1.083	1.083	0.930	–	–	–	0.95
C2-C3	1.423	1.422	1.420	1.412	1.410	1.405	1.411	1.414
C2-C*l*21	1.744	1.761	1.747	–	–	1.721	1.726	–
C3-C4	1.403	1.431	1.428	1.409	1.428	1.425	1.409	1.420
C3-C9	1.420	1.419	1.416	1.413	1.402	1.399	1.404	1.428
C4-C5	1.433	1.434	1.432	1.417	1.393	1.425	1.414	1.412
C4-N17	1.351	1.359	1.355	1.376	1.374	1.385	1.360	1.375
C5-C6	1.362	1.386	1.385	1.364	1.371	1.367	1.405	1.364
C5-O18	1.333	1.348	1.342	1.355	1.367	1.346	1.323	–
C6-C*l*20	1.746	1.763	1.749	–	–	–	1.721	–
C9-H7	1.072	1.085	1.085	0.93	–	–	–	–
C9-C11	1.352	1.371	1.370	1.352	1.357	1.359	1.350	1.364
C10-C11	1.423	1.424	1.421	1.415	1.389	1.395	1.400	1.410
C10-C13	1.506	1.508	1.503	1.494	–	–	–	–
C10-N17	1.293	1.320	1.318	1.319	1.331	1.324	1.312	1.293
C11-H12	1.075	1.086	1.087	0.93	–	–	–	–
C13-H14	1.086	1.097	1.097	0.96	–	–	–	–
C13-C15	1.081	1.091	1.092	0.96	–	–	–	–
C13-H16	1.086	1.097	1.097	0.96	–	–	–	–
O18-H18	0.948	0.974	0.972	0.86	–	–	–	–
Bond angle (°)								
C2-C1-C6	119.7	119.4	119.5	121.4	121.4	120.3	120.1	120.3
C2-C1-H8	121.0	120.9	120.7	119.3	–	–	–	119.9
C6-C1-H8	119.3	119.7	119.6	119.3	–	–	–	119.9
C1-C2-C3	120.8	121.2	121.0	119.4	120.0	121.1	–	121.3
C1-C2-C*l*21	118.9	118.6	118.7	–	–	118.2	118.8	–
C3-C2-C*l*21	120.3	120.2	120.2	–	–	120.6	–	–
C2-C3-C4	118.9	118.8	118.9	119.8	118.8	118.1	116.9	117.7
C2-C3-C9	124.4	124.6	124.5	123.9	123.4	125.2	127.0	123.9
C4-C3-C9	116.6	116.5	116.5	116.3	117.7	116.7	–	118.2
C3-C4-C5	119.9	119.7	119.7	118.8	119.6	120.0	–	119.9
C3-C4-N17	122.8	122.9	122.9	123.5	121.6	122.6	123.4	122.7
C5-C4-N17	117.2	117.4	117.3	117.7	118.7	117.4	–	117.4
C4-C5-C6	118.4	118.3	118.3	120.0	121.4	119.6	116.8	120.1
C4-C5-O18	117.2	117.7	117.8	121.0	120.3	121.2	118.8	–
C6-C5-O18	124.4	123.9	123.9	118.9	118.4	119.2	124.4	–
C1-C6-C5	122.2	122.5	122.5	120.5	118.7	120.8	121.8	120.5
C1-C6-C*l*20	118.0	118.7	118.8	–	–	–	–	–
C5-C6-C*l*20	119.8	118.7	118.7	–	–	–	119.7	
C3-C9-H7	119.7	119.3	119.3	120.0	–	–	–	–
C3-C9-C11	119.5	119.6	119.6	119.9	119.6	120.3	119.6	117.7
H7-C9-C11	120.8	121.0	121.0	120.0	–	–	–	–
C11-C10-C13	119.9	120.3	120.3	120.5	–	–	–	–
C11-C10-N17	121.9	122.1	122.1	121.9	123.4	123.3	122.9	126.2

C13-C10-N17	118.2	117.6	117.5	117.5	–	–	–	–
C9-C11-C10	119.5	119.7	119.6	120.0	119.7	119.2	119.6	119.0
C9-C11-H12	120.8	120.6	120.6	120.0	–	–	–	120.5
C10-C11-H12	119.7	119.7	119.7	120.0	–	–	–	120.5
C10-C13-H14	110.7	111.0	111.0	109.5	–	–	–	–
C10-C13-H15	109.8	109.7	109.7	109.5	–	–	–	–
C10-C13-H16	110.7	111.1	111.0	109.5	–	–	–	–
H14-C13-H15	109.0	108.9	108.9	109.5	–	–	–	–
H14-C13-H16	107.4	107.0	107.1	109.5	–	–	–	–
H15-C13-H16	109.0	108.9	108.9	109.5	–	–	–	–
C4-N17-C10	119.6	119.1	119.0	118.1	117.5	117.9	118.4	116.4
C5-O18-H19	110.8	108.4	108.3	113.0	–	–	–	–

As seen from Table-1, for C-N distances, the HF/6-31G (d) bond lengths are shorter than experimental data of B3LYP and B3PW91 values. For example, while C4-N17 experimental bond lengths are 1.374, 1.358, 1.367, 1.360 and 1.375 Å in the literature[12,21-24], the calculated HF, B3LYP and B3PW91 values of these bond lengths are in the present study are 1.351, 1.359 and 1.355 Å, respectively. This bond length was calculated by Kurt and Yurdakul[15] at the 1.354 (HF), 1.365 (B3LYP) and 1.377 (BLYP) for 6-methylquinoline. Aysen *et al.*[14] calculated this bond length 1.602 (HF) and 1.368 (DFT)/6-31** level, Krisman *et al.*[11], 1.339 (B3LYP)/6-31G (d) level for 8-hydroxyquinoline.

The experimental bond length C10-C13 is 1.49 Å comparable to previous report[22]. This bond are calculated 1.506 (HF), 1.508 (B3LYP) and 1.503 (B3PW91) and the experimental C10-C13 bond is smaller than the calculated data. Kurt *et al.* calculated this bond length values at the 1.5092 (HF), 1.5076 (B3LYP) and 1.5167 (BLYP) for 3-chloro-4- methyl aniline[27] and at the 1.509 (HF), 1.509 (B3LYP) and 1.519 (BLYP) for 6-methylquinoline[15]. Aysen *et al.*[14] calculated this bond length values at the 1.5063 (HF)/6-31** and 1.5098 (B3LYP)/6-31** level for 2-methylquinoline.

The C2-CI21 bond length are calculated at the 1.744 (HF), 1,761 (B3LYP) and 1.747 (B3PW91). The C-CI bond length in the 3-chloro-4-methyl aniline molecule were calculated Kurt *et al.*[27] at the 1.75 (HF), 1.767 (B3LYP) and 1.789 (BLYP). Karabacak *et al.*[20] calculated at the 1.730 (HF), 1.750 (B3LYP) and 1.737 (BLYP) for 2-chloronicotinic acid molecule. Sundaraganesan *et al.*[28] found at the 1.730 (HF) and 1,742 (B3LYP) for 2,4-dichloro-6-nitrophenol molecule.

The optimized bond angles C4-N17-C10 and C9-C11-C10 are smaller than typical hexagonal angle of 120°. But C1-C2-C3, C3-C4-N17, C1-C6-C5 and C11-C10-N17 bond angles are more than approximately 2.8° hexagonal angles. These C11-C10-N17 and C4-N17-C10 angles were calculated as 122.36 (HF)/6-31** 122.38 (B3LYP)/6-31** and 119.37(HF)/6-31** and 118.93 (B3LYP)/6-31** level, respectively, for 2-methylquinoline[14]. Krishnakumar and Ramasamy calculated those angles at the (B3LYP) 121.4 and 120.7 °, respectively for 8-hydroxyquinoline[11]. Arici *et al.*[25] calculated these C11-C10-N17 bond angle 123.336(HF), 123.256 (B3LYP) and 123.282 (BLYP) and C4-N17-C10 bond angle 118.482 (HF), 117.891 (B3LYP) and 117.621 (BLYP) in the 8-hydroxyquinoline molecule.

The C1-C6-C5 bond angle was calculated as 121.585 (HF)/6-31G (dp) and 121.564 (B3LYP)/6-31G (dp) level for 2,3-dichloro-6-nitrophenol by Sundaraganesan *et al.*[28]. Our calculated for C1-C6-C5 bond angle 122.2 (HF), 122.5 (B3LYP) and 122.5 (B3PW91). For C1-C2-C3 bond angle, 120.8 (HF), 121.2 (B3LYP) and 121.0 (B3PW91). As seen Table-1, these data clearly show that the substituted CI and methyl groups in the place of ring hydrogen appreciably affected the C1-C2-C3, C3-C4-N17, C1-C6-C5 and C11-C10-N17 bond angles.

Assignment of fundamentals: On the basis IR and Raman spectra of 5,7-dichloro-8-hydroxyquinaldine on experimental data and our calculations and the reported infrared spectra with references[11,13-15], we made a reliable one-to-one correspondence between our fundamentals and any of our frequencies calculated by the HF, DFT (B3LYP and B3PW91) methods. The calculated and experimental frequencies results are given in Table-2. Infrared and Raman spectra of 5,7-DCIHQM is shown in Fig. 2.

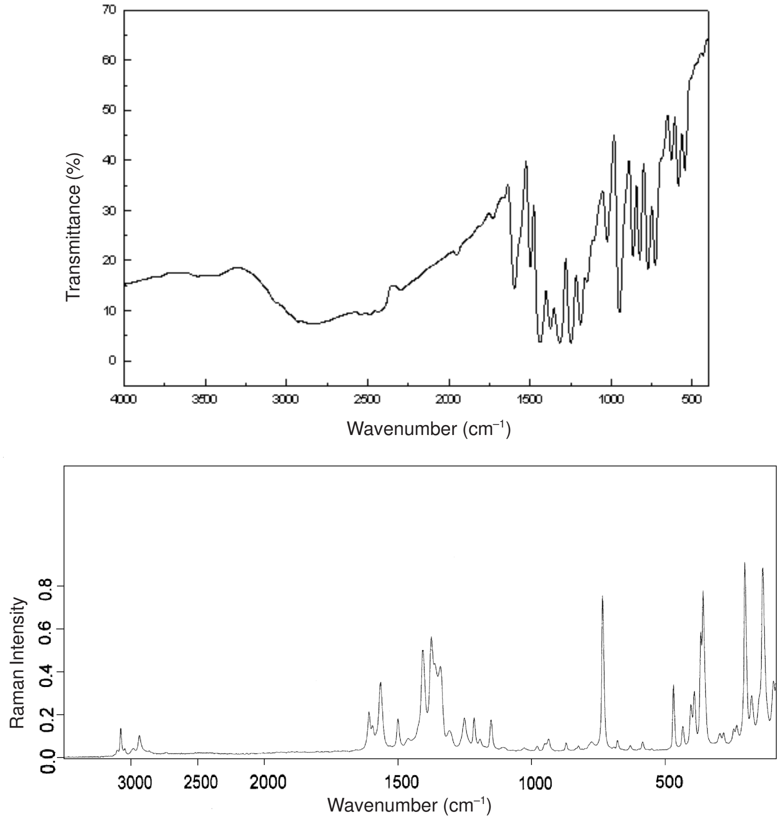

Fig. 2. Infrared and Raman spectra of 5,7-DCIHQM molecule

The O-H stretching vibrations are sensitive to hydrogen bonding. In some samples, intermolecular hydrogen bonding may occur, the resulting hydroxyl group bond which appears at 3590-3400 cm^{-1} being sharp unaffected by concentration

TABLE-2
COMPARISON OF THE CALCULATED AND EXPERIMENTAL (FT-IR AND RAMAN) VIBRATIONAL SPECTRA OF FREE 5,7-DCIHQM

M	HF/6-31G (d)			B3LYP/6-31G (d)			B3PW91/6-31G (d)			*Exp. in this study		Exp. 11	Exp. 13	Exp. 14	Exp. 15	Approx. mode description in this study
	Freq^{a}	I (IR)	I (Ra)	Freq^{b}	I (IR)	I (Ra)	Freq^{c}	I (IR)	I (Ra)	Freq^{c} (IR)	Freq^{c} (Ra)	IR	IR	IR	IR	
ν_{1}	72	0.66	0.08	69	0.68	0.20	69	0.82	0.19							CH$_3$ torsion
ν_{2}	84	0.03	0.54	81	0.13	0.78	81	0.12	0.86							γ ring + γ(C-OH) + γ(C-CI) + C(H$_3$) torsion
ν_{3}	89	0.32	0.64	88	0.27	0.80	86	0.23	0.75			98				γ(C-CH) + γ(C-CI) + CH$_3$torsion
ν_{4}	138	0.25	1.49	136	0.18	1.43	135	0.32	1.42		132 s	137				γ(C-CH) + γ (C-CI) + γ(C-OH)
ν_{5}	175	1.41	1.77	176	1.25	2.67	175	1.31	2.62		177 w					δ ring + δ(C-CH$_3$) + δ(C-CI)
ν_{6}	189	0.58	2.38	189	0.55	3.06	189	0.52	2.99			194				δ(C-CI)
ν_{7}	210	9.69	0.42	210	6.30	0.42	209	6.62	4.23		200 s					γ(C-N + C-CH) + γ (C-OH) + γ(C-CH$_3$)
ν_{8}	270	0.55	1.04	270	0.07	0.46	268	0.06	0.47			266				γ(C-CH) + γ(C-CH$_3$)
ν_{9}	278	3.24	0.80	277	3.39	0.77	275	3.86	0.74							Ring def. + δ(C-CI) + δ(C-OH) + δ(C-CH$_3$)
ν_{10}	335	6.74	8.01	336	6.29	9.44	337	6.13	7.82							Ring def. + ν(C-CI) + ν(C-OH) + δ(C-CH$_3$)
ν_{11}	345	3.86	2.93	344	4.50	3.09	343	4.12	2.73							Ring def. + ν(C-CI) + rock (OH) + δ(C-CH$_3$)
ν_{12}	356	109.0	1.88	364	0.60	0.08	364	0.57	0.07		356 s	355				γ(C-C+C-N + C-O) + rock (CH$_3$)
ν_{13}	373	0.19	8.96	373	0.20	9.96	373	0.21	10.55							ν ring + δ(OH) + δ(C-CH$_3$)
ν_{14}	387	22.02	0.26	418	22.46	2.38	414	14.85	2.33		390 m	422	413 γCCCC			γ(C-CH + C-N) + γ(OH)
ν_{15}	431	1.67	3.86	440	79.44	2.73	442	87.37	2.50	432 w		440	431 δCCC			γ(C-CH) + γ(OH)
ν_{16}	447	1.59	5.34	449	1.47	5.71	446	1.34	5.70	465 w	468 m	465	461 δCCC	472	477 m (oop CH bend + CCC, CCN bend)	Ring def. + ν(C-CH$_3$)
ν_{17}	550	11.27	0.19	533	10.71	0.16	530	13.28	0.14	545 w		545	524 γCCCC	530	508 w (oop CH bend + ring CCN, CCC def. + CH$_3$ def.)	γ(C-C + C-H + O-H) + rock (CH$_3$)
ν_{18}	561	0.15	0.55	563	1.19	1.21	561	0.13	1.23							Ring def. + δ(C-CH$_3$) + δ(C-OH)
ν_{19}	606	0.18	2.28	585	0.04	1.86	583	0.03	1.83	584 w		575	567 δCCC	597		γ(C-C + C-H + C-N) + rock (CH$_3$)
ν_{20}	609	6.46	0.66	612	5.67	0.11	607	5.47	0.13	628 w		636	619 δCCC	628	615 w (ip ring CH bend + CH$_3$ bend.)	ν ring + δ(C-OH)
ν_{21}	667	5.52	0.73	658	1.84	0.52	656	2.09	0.51					656		γ(C-C + C-H + C-N) + rock (CH$_3$)
ν_{22}	679	10.23	1.40	672	15.05	0.23	674	8.86	0.31	682 sh			688 γCCCC			Ring def. + ν(C-CH$_3$)
ν_{23}	701	3.83	19.39	703	2.79	28.76	705	3.31	29.00			710	701 νCC			Ring breath. + ν(C-OH)
ν_{24}	738	99.89	1.07	735	90.45	0.18	741	93.13	0.04	729 m	731 s	741	746 Ring brat.		765 m (oop. ring CH, CCC bend.)	Ring def. + ν(C-CI) + ν(C-CH$_3$)
ν_{25}	780	1.93	1.51	761	3.41	1.02	755	30.37	0.97	771 m		781	783 γCCCC	787	797 m (oop CH + CC + CN bend)	γ(C-C + C-H + C-N) + rock (CH$_3$)
ν_{26}	833	26.43	1.08	814	12.10	1.85	806	14.70	1.57	824 m		818	819 γHCCC	812	831 vs (asym CH str (in CH$_3$))	γ(C-H) + rock (CH$_3$)
ν_{27}	899	28.72	6.13	839	21.33	1.20	833	23.48	1.07	866 m		867	869 γHCCC	861		γ(C-H)
ν_{28}	901	17.32	2.04	912	22.14	2.60	910	22.11	2.55			896	883 νCC	883	881 m (ring CC str + ip C-CH$_3$ bend, ip ring CCC bend.)	Ring def. + δ(C-H) + δ(O-H) + rock (CH$_3$)
ν_{29}	934	40.31	1.77	919	44.40	1.09	921	43.56	1.24				926 νCC			Ring def. + rock (CH$_3$) + δ(C-H) + δ(O-H)

ν_{30}	998	3.50	6.95	959	0.58	0.03	953	0.61	0.04	948 s		958	948 γHCCH	950		γ(C-H)
ν_{31}	1006	0.38	0.53	998	1.31	1.86	992	1.87	1.98							δ(C-H) + rock (CH_3)
ν_{32}	1044	3.60	1.29	1031	40.24	0.72	1019	5.30	0.65	1024 m		1034	1031 δHCC		1035 m (C-C-H bend (in CH_3) + CH str. + CCC bend.)	rock (CH_3)
ν_{33}	1067	3.50	4.21	1067	31.79	3.50	1065	2.,28	3.66			1059	1098 CH_3 rock	1050		Ring def. + δ(C-OH) + rock (CH_3) + δ(C-H)
ν_{34}	1072	33.45	50.27	1136	22.92	5.51	1129	20.95	5.09	1111 sh			1116 δHCC		1118 m (ip. CH bend + CC str.)	δ(C-H)
ν_{35}	1159	45.29	10.51	1183	8.10	2.98	1180	60.76	2.17	1149 m	1151 w	1147	1140 δHCC	1143	1140 w (CCH bend (in CH_3) 4 ip ring CH bend + CC str.)	δ(C-H) + δ(O-H)
ν_{36}	1193	21.09	2.67	1201	62.26	0.99	1203	99.66	1.12	1188 s		1206	1173 δHCC	1205		δ(C-H) + δ(O-H) + ring breat + ν(C-CH_3)
ν_{37}	1217	143.5	5.03	1216	90.68	1.26	1216	61.71	3.09		1214 w	1221	1220 δHCC	1229		δ(C-H) + δ(O-H) + ν(C-C)
ν_{38}	1225	0.81	5.90	1238	6.21	14.01	1237	60.63	12.53	1244 s	1251 w	1273	1253 δHCC			δ(C-H) + δ(O-H) + ν(C-C) + rock (CH_3)
ν_{39}	1310	14.00	108.58	1317	20.80	15.60	1317	13.30	14.71	1314 s		1286	1319 νCC			δ(C-H) + δ(O-H) + ν(C-N) + rock (CH_3)
ν_{40}	1317	62.55	1.79	1325	30.04	67.22	1330	47.15	24.09				1336 νCC	1335	1323 w (ip. CH bend + CC, CN str. +C- CH_3 str.)	δ(C-H) + δ(O-H) + ν(C-C) + ν(C-N)
ν_{41}	1348	63.76	223.69	1358	95.83	162.49	1361	43.60	127.71					1364		δ(C-H) + δ(O-H) + ν(C-C) + (CH_3) asym bend.
ν_{42}	1386	36.82	30.10	1380	0.96	15.10	1369	27.72	39.05	1372 s	1372 m	1381	1388 sym. βCH_3	1370	1374 m (ip. CH bend + CC, CN str. + C- CH_3 str)	(CH_3) sym. Bend
ν_{43}	1395	24.14	26.95	1386	77.01	79.61	1384	94.42	129.68		1404 m	1410		1404		δ(C-H) + ν(C-C)
ν_{44}	1442	48.20	34.26	1439	54.11	58.49	1429	33.95	56.06	1437 s		1434				δ(O-H) + (CH_3) asym. bend.
ν_{45}	1454	6.47	20.01	1458	7.12	21.70	1443	8.41	21.12			1454	1453 δHCC		1444 m (ring CC str + CN str + CCH bend (ring +CH_3))	(CH_3) asym. Bend
ν_{46}	1467	72.13	3.81	1464	34.13	6.52	1462	64.13	15.87			1472	1472 asym. βCH_3	1479		δ(C-H) + δ(O-H) + CH_3 asym. bend.
ν_{47}	1492	58.26	10.92	1491	32.98	11.89	1491	37.84	9.02	1497 m	1499 w	1508	1481 asym. βCH_3		1501 s (ring CC str + CN str + CCH bend (ring + CH_3))	δ(C-H) + δ(O-H) + ν(C-C) + (CH_3) asym bend.
ν_{48}	1587	12.64	55.48	1548	7.13	21.70	1554	17.52	45.63	1572 sh	1563 m		1574 νCC	1581	1569 m (ring CC str + CN str + CCH bend (ring + CH_3))	ν(C-C) + δ(O-H) + ν(C-N) + (CH_3) asym bend.
ν_{49}	1615	123.6	4.17	1581	95.55	7.18	1582	94.82	9.13	1596 m	1607w	1577	1618 νCC	1614	1594 m (ring CC str +CN str + CCH bend (ring + CH_3))	δ(C-H) + δ(O-H) + δ(C-C)
ν_{50}	1641	81.19	7.89	1603	56.65	17.23	1605	59.41	16.58	1659 w					1626 w (ring CC str + CN str + CCH bend (ring + CH_3))	ν(C-C) + ν(C-N) + (CH_3) asym bend
ν_{51}	2863	26.98	201.98	2934	19.69	286.02	2925	17.28	291.73	2836 br			2950 νCH		2860 w (ring C-C str. + ip CCH bend.)	ν(CH_3) sym.
ν_{52}	2908	24.97	114.37	2983	15.83	126,89	2984	12.69	127.07	2924 w			3010 νCH	3013	2918 w (symC-H str (in CH3))	ν(CH_3) asym.
ν_{53}	2969	8.68	60.58	3047	5.63	60.48	3042	4.43	61.91			3048			2946 w (C-H str (in CH3))	ν(CH_3) asym.
ν_{54}	3018	9.86	106.42	3080	9.60	119.64	3070	7.71	111.27	3063 w	3072 w	3084		3075	2979 w (C-H str (in CH3))	ν(C-H)
ν_{55}	3052	3.94	77.37	3110	4.43	92.69	3095	4.43	99.66			3097		3094	3014 m (C-H str.)	ν(C-H)
ν_{56}	3054	1.18	77.45	3121	1.03	80.18	3143	1.16	80.17				3142 νCH			ν(C-H)
ν_{57}	3655	130.1	64.94	3555	83.25	84.14	3555	92.41	81.55			3418		3379		ν(O-H)

[Frequency (cm^{-1}), IR intensities (km mol^{-1}), Raman scattering actives (A amu^{-1})]. [a] Scaling factor (s.f.): 0.8929. [b]s.f.: 0.963. [c]s.f.: 0.9567. *Exp.: experimental, M: mode. * ν: stretching, δ: in plane bending, γ: out-of-plane bending, rock.: rocking, Wagg.: wagging, sym.: symmetry, asym.: asymmetry, def.: deformation.

change[29]. This O-H stretching band was observed by Srivastava *et al.*[5], at 3400 cm^{-1} (in nujol) and 3667 cm^{-1} (liquid phase). The O-H in plane bending vibration occurs in the general of 1430-1330 cm^{-1}. The O-H out-of plane bending vibration occurs[28] in 960-875 cm^{-1}. In the present study the O-H stretching vibration at 3590-3400 cm^{-1} region was not observed. But, the O-H out-of plane bending vibrations are assigned at 545 and 432 (390 Raman) cm^{-1}. And O-H in plane bending bands was observed from 1596-1149 cm^{-1} total seven bands. Out-of plane bending bands are smaller than range 960-875 cm^{-1} region. The O-H out-of plane and in plane bending bands[28,29] observed at 685 and 1240 (Raman) cm^{-1}, respectively. In previous paper[25], in plane and out-of plane bending bands we observed at 1580 and 574 cm^{-1}, respectively.

The identification of C-N vibrations is difficult task, since the mixing of several bonds is possible in this region. C-N stretching vibration bands was observed 1659, 1562 (1563 Ra.) and 1314 cm^{-1}. These bands were calculated at HF (1615, 1586 and 1310 cm^{-1}), at B3LYP (1603, 1548 and 1317 cm^{-1}) and at B3PW91 (1582, 1554 and 1317 cm^{-1}). Puviarasan *et al.*[12] observed C=N and C-N bands in IR at 1518 and 1280, respectively. This C-N stretching band[25] observed at 1281 and 1276 cm^{-1} to be strong in IR spectra.

The C-CH$_3$ stretching band was observed by Shukla *et al.*[30] at 1208 and 1223 cm^{-1} in toluene and *o*-xylene, respectively. In this study, the C-CH$_3$ stretching band was observed at 1188 cm^{-1} and calculated at HF (1193), B3LYP (1202) and B3PW91(1203 cm^{-1}). Yurdakul *et al.*[24] observed this band at 1210 cm^{-1} (IR, Raman) and assigned it only to be ν(C-CH$_3$) stretching band. We observed band at 2836 (br) cm^{-1} assigned the symmetric C-H stretching band in CH$_3$ group. The asymmetric C-H stretching band of the same group also observed at 2924 cm^{-1}. These symmetric and asymmetric stretching C-H bands was observed at 2858 (s), 2926 (vs) cm^{-1}, respectively by Yurdakul *at al.*[31]. The band at 3063 (w, IR) and 3072 (w, Raman) in our spectra is assigned to be ring ν(C-H) stretching and calculated at HF (3108), B3LYP (3080) and B3PW91 (3070 cm^{-1}) level of theory. This band was observed at 3029 cm^{-1} (m, IR) and 3030 cm^{-1} (vs, Raman)[27,31].

The C-C*l* stretching vibrations give generally strong absorption in the region 821-550 cm^{-1} for IR and Raman[28,31-33]. This strong characteristic absorptions due to C-CI stretching vibrations are also observed in present study. The ring halogen stretching mode (C-CI) were observed as medium IR and strong Raman band at 729 and 731 cm^{-1}, respectively. The calculated C-CI stretching mode are 738, 735 and 741 cm^{-1} for HF, B3LYP and B3PW91, respectively. The bending modes were located at 292-143 cm^{-1} for ring-chloro vibrations[32,34]. We observed the C-CI in plane bending at 177 cm^{-1} (w, Raman). The calculated C-CI bending modes are 175, 176 and 175 cm^{-1} for HF, B3LYP and B3PW91, respectively.

As seen from Table-2 and Fig. 2, although the Raman intensities are very low at calculations with experimentally strong vibrations, the IR intensities are very high at calculations with experimentally weak vibrations in the lower frequencies region.

Among the calculated fundamentals, the best agreements between experimental and calculated intensities are in high frequency region (*ca.* 2800-3050 cm^{-1}). Theoretical and experimental low intensities may lead to the wrong identification in the assignment of fundamentals[35], especially in the lowest frequencies region.

As known previously, because of seasons, such as anharmonic effect, vibrational intensity could not be estimate very accurately using quantum chemistry software till now.

To make comparison with experimental data, we determined correlation values based on the calculations. The correlations of computed frequencies from experiment (IR) are found to be 0.9991, 0.9989, 0.9990 for HF/6-31G (d), B3LYP/6-31G (d) and B3PW91/6-31G (d), respectively. It is noticed that this means the HF/6-31G (d) calculation is better than B3LYP/6-31G (d) and B3PW91/6-31G (d). The experimental fundamentals are in getter agreement with the scaled fundamentals and are found to have a good correlation for HF than B3LYP and B3PW91.

Conclusion

First time, the experimental and theoretical infrared and Raman spectra of the compound 5,7-dichloro-8-hydroxyquinaldine (5,7-DCIHQM) are studied. The geometric and vibrational frequencies of the 5,7-DCIHQM molecule were calculated by using HF, B3LYP and B3PW91methods with 6-31G (d) level. The optimized geometric parameters (bond lengths and bond angles) obtained by using HF show the best agreement with the experimental values of 5,7-DCIHQM. Comparison of the observed fundamental vibrational frequencies and calculated results for this molecule indicate that HF is superior to scaled B3LYP and B3PW91 approach for molecular vibrational problems.

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