

# Analysis of vibrational spectra of 8-hydroxyquinoline and its 5,7-dichloro, 5,7-dibromo, 5,7-diiodo and 5,7-dinitro derivatives based on density functional theory calculations

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**Abstract:** The geometry, frequency and intensity of the vibrational bands of 8-hydroxyquinoline and its 5,7-dichloro, 5,7-dibromo, 5,7-diiodo and 5,7-dinitro derivatives were obtained by the density functional theory (DFT) calculations with Becke3-Lee-Parr (B3LYP) functional and 6-31G\* basis set. The effects of chloride, bromide, iodide and nitro substituent on the vibrational frequencies of 8-hydroxyquinoline have been investigated. The assignments have been proposed with aid of the results of normal coordinate analysis. The observed and calculated spectra are found to be in good agreement.

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*Keywords:* DFT calculations; vibrational spectra; 8-hydroxyquinoline, 5,7-dichloro, 5,7-dibromo, 5,7-diiodo, 5,7-dinitro-hydroxyquinoline

## 1 Introduction

8-hydroxyquinoline (HQ) and its derivatives are well known for their antifungal, antibacterial and antiamebic activities [1]. 8-hydroxyquinoline (HQ) have been extensively used for the extraction and analytical determination of metal ions [2, 3]. The vibrational spectrum of 8-hydroxyquinoline was also predicted theoretically at different levels of approximation [4, 5]. Recently, Cheatum et al. [6] have investigated excited state dynamics of 8-hydroxyquinoline dimmers, and Li and Fang [7] have carried out a combined CASSCF, density functional theory (DFT) and MP2 study on the ground- and

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excited-state proton transfer processes of HQ. The inclusion of halogen atoms at the 5th and 7th positions of HQ molecule lead to variation of charge distribution in the molecule and consequently this greatly affects the structure, electronic and vibrational parameters. Hence, in this study, an attempt has been made to interpret the vibrational spectra of 5,7-dichlorohydroxyquinoline (DCIHQ), 5,7-dibromohydroxyquinoline (DBrHQ), 5,7-diiodohydroxyquinoline (DIHQ) and 5,7-dinitrohydroxyquinoline (DNHQ) by applying the density functional theory calculations based on Beck3-lee-Yang-Parr (B3LYP) and 6-31G\* basis sets. The experimental observed spectral data of the title compounds are found to be well comparable to that of the spectral data obtained by quantum chemical methods. Theoretical spectra were drawn on MS Excel sheet by using the wave numbers and vibrational IR activates to interpret experimental vibrational spectra.

## 2 Experimental

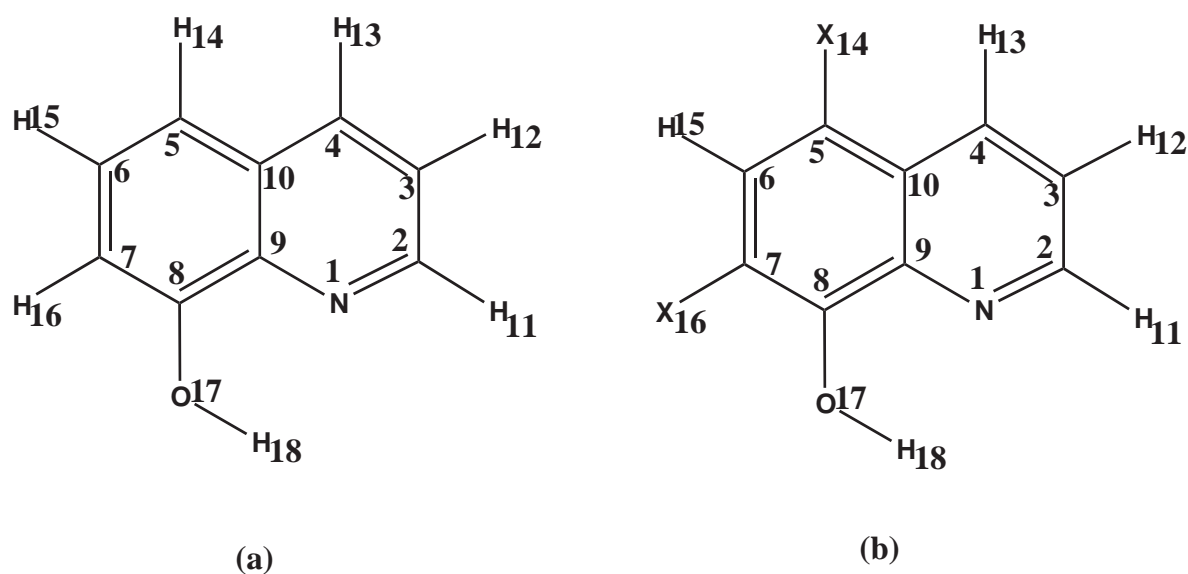
8-hydroxyquinoline and its derivatives were obtained as previously described in the literature [8].

### 2.1 Infrared spectra

The infrared spectra were recorded with a Nicolet Magna 750 FT-IR spectrometer equipped with a room temperature DTGS detector. The spectra of the solid (in the 4000 - 400  $\text{cm}^{-1}$  spectral region) recorded in the form of KBr pellets at 2  $\text{cm}^{-1}$  spectral resolution accumulating 128 scans.

## 3 Computational details

The molecular geometry optimization, energy and vibrational frequency calculations were carried out with GAUSSIAN 94W software package [9] using the B3LYP functionals [10, 11] combined with standard 6-31G\* basis set. The cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming Cs point group symmetry. Scaling of the force field was performed according to the SQM procedure [12, 13] using selective scaling in the natural internal coordinate representation [14, 15]. Transformations of the force field and subsequent normal coordinate analysis including the least square refinement of the scaling factors, calculation of potential energy distribution (PED) and the prediction of IR intensity were done on a PC with the MOLVIB program (version 7.0 - G77) written by Sundius [16, 17]. For the plots of simulated IR, pure Lorentzian band shapes were used with a bandwidth (FWHM) of 6  $\text{cm}^{-1}$ . The symmetry of the molecules was also helpful in making vibrational assignments. The symmetries of the vibrational modes were done by using the standard procedure [18] of decomposing the traces of the symmetry operation into the irreducible representation. The symmetry analysis for the vibrational modes of the title molecules were presented in some details in order to describe the basis for the assignments.



**Fig. 1** (a) Molecular model of HQ along with numbering of atoms; (b) molecular model of 5,7-DXHQ along with numbering of atoms (where X = Cl, Br, I, NO<sub>2</sub>).

## 4 Results and discussion

### 4.1 Molecular geometry

The labeling of atoms in HQ, DClHQ, DBrHQ, DIHQ and DNHQ (where N = NO<sub>2</sub>) is given in Fig. 1. The calculated structural parameters are given in Table 1. The DFT level of theory is in good agreement with the X-Ray data [19]. The C8-O17 bond length is shorter than those observed in the crystal. The elongation of the hydrogen bond is partly related with the large calculated C7-C8-O17 angle.

### 4.2 Analysis of vibrational spectra

The 48 normal modes of HQ, DClHQ, DBrHQ, DIHQ and 60 normal modes of DNHQ are distributed amongst the symmetry species as

$$3N - 6 = 33A(\text{in - plane}) + 15A'(\text{out - of - plane})$$

$$3N - 6 = 41A(\text{in - plane}) + 19A'(\text{out - of - plane})$$

Respectively, in agreement with C<sub>s</sub> symmetry. Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose the full set of 67 standard internal coordinates (containing 17 redundancies) for DClHQ, DBrHQ and DIHQ, respectively were defined as given in Table 2. For these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi and co-workers [14, 15] are summarized in Table 3. The theoretically calculated DFT force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations. The detailed vibrational assignment of fundamental modes of HQ, DClHQ,

DBrHQ, DIHQ and DNHQ along with calculated IR intensity and normal mode descriptions (characterized by PED) were reported in Tables 4 and 5. For visual comparison, the observed and simulated FTIR spectra of the title compounds were presented in Figs. 2-6, respectively. Root mean square (RMS) values were obtained in this study using the following expression,

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

The RMS error of frequencies (unscaled/B3LYP/6-31G\*) observed were found to be 73.48, 98.81, 93.70, 90.98  $\text{cm}^{-1}$  for HQ, DCIHQ, DBrHQ, DIHQ frequently and 80.94  $\text{cm}^{-1}$  for DNHQ. In order to reproduce the observed frequencies, refinement of scaling factors were applied and optimized via least square refinement algorithm which resulted a weighted RMS deviation of 14.76, 15.37, 16.94, 15.41  $\text{cm}^{-1}$  for HQ, DCIHQ, DBrHQ, DIHQ, respectively and 12.35  $\text{cm}^{-1}$  for DNHQ, between the experimental and SQM frequencies.

### 4.3 Simulation of the calculated vibrational bands

Several functions can be used to define each of the bands in the vibrational spectra. The Lorentzian function is one such function, which describes better peak shape on vibrational spectra. The intensity (I) of the Lorentzian curve as a function of wave number can be given as:

$$I(\nu) = \frac{h}{4 \left( \frac{\nu - \langle \nu \rangle}{\omega} \right)^2 + 1} \quad (2)$$

Where  $\nu$ : wave number,  $\langle \nu \rangle$ : average wave number,  $\omega$ : peak width at half height,  $h$ : peak height. Since the intensity of each peak will equal the peak area under the curve, the total peak intensity ( $I_{Tot}$ ) would be given as:

$$I_{Tot} = \int_{-\infty}^{\infty} \frac{h}{4 \left( \frac{\nu - \langle \nu \rangle}{\omega} \right)^2 + 1} d\nu = \frac{\pi h \omega}{2} \quad (3)$$

The height of each peak from Eq. (2) above can be found as:

$$h = \frac{2I_{Tot}}{\pi\omega} \quad (4)$$

Finally, the calculated spectral curve can be obtaining the IR activity values as the sum of N lorentzian function obtained from N peak:

$$I(\nu) = \sum_{i=1}^N \frac{h}{4 \left( \frac{\nu - \langle \nu \rangle}{\omega} \right)^2 + 1} \quad (5)$$

A proper macro on an Excel work sheet has been prepared based on the above function to draw both experimental and theoretical spectra on the same plot. An easy comparison can be made when both experimental and calculated results can be seen simultaneously on the same graphical representation. Peak width of half height ( $\omega$ ) were taken as 6  $\text{cm}^{-1}$  and the Lorentzian function given above was used to plot the calculated vibrational bands graphically (Figs. 2-6).

#### 4.4 Vibrational force constant

The output files of the quantum mechanical calculations contain the force constant matrix in cartesian coordinates and in Hartree/Bohr<sup>2</sup> units. These force constants were transformed to the force fields in the internal local-symmetry coordinates. The force field determined were used to calculate the vibrational potential energy distribution among the normal coordinates. The most important diagonal force constants (stretching only) of HQ and its derivatives are listed in Table 4. The bonding properties of HQ are influenced by the rearrangements of electrons during substitutions. The values of the stretching force constants between carbon-carbon atoms and between carbon- nitrogen atoms in substituted HQ are found to be less than their characteristic values, since chlorine, bromine and iodine are more electronegative and hence the bonded electrons between carbon-carbon atoms and carbon nitrogen atoms are slightly shifted towards the halogen atoms of the title compounds. The values of the stretching force constants between carbon and chlorine atoms of DCIHQ are found to be ( $3.287 \times 10^2$  and  $3.516 \times 10^2$  N m<sup>-1</sup>) higher than the values of stretching force constant between carbon and bromine atoms in DBrHQ, which are similar to the values of the force constant between carbon and iodine atoms in DIHQ. Since the bromine and iodine atoms are less electronegative than chlorine atoms.

#### 4.5 Vibrational spectra

In crystalline state, HQ and its derivatives are planar molecules and exhibits intermolecular OH...N hydrogen bond. Further, the bonding properties of HQ and its derivatives are also influenced by the arrangements of electrons during substitution. The halogen atoms (Cl, Br and I) and NO<sub>2</sub> group substituted at the 5th and 7th positions of HQ (see Fig. 1) are highly electronegative and hence they withdraw electrons from the neighboring carbon bonds. The properties of HQ and its derivatives discussed below will greatly influence the vibrational spectral data.

#### 4.6 OH vibrations

The O-H stretching vibrations are sensitive to hydrogen bonding. The non-hydrogen bonded or free hydroxyl group absorb strongly in 3550 – 3700 cm<sup>-1</sup> region.

Inter-molecular hydrogen bonding if present would reduce the O-H stretching band to 3200 – 3550 cm<sup>-1</sup> region [20]. In the present study, a medium broad band was observed at 3386 cm<sup>-1</sup> for HQ was assigned to O-H stretching vibrations, which shows that HQ molecule possesses an inter-molecular hydrogen bond in the solid state. This band is also observed at the same wavenumber in the IR spectra of the substituted HQ (see Tables 5, 6). According to NCA the in-plane bending vibration was observed at 1479 cm<sup>-1</sup> in agreement with the literature data [4, 5].

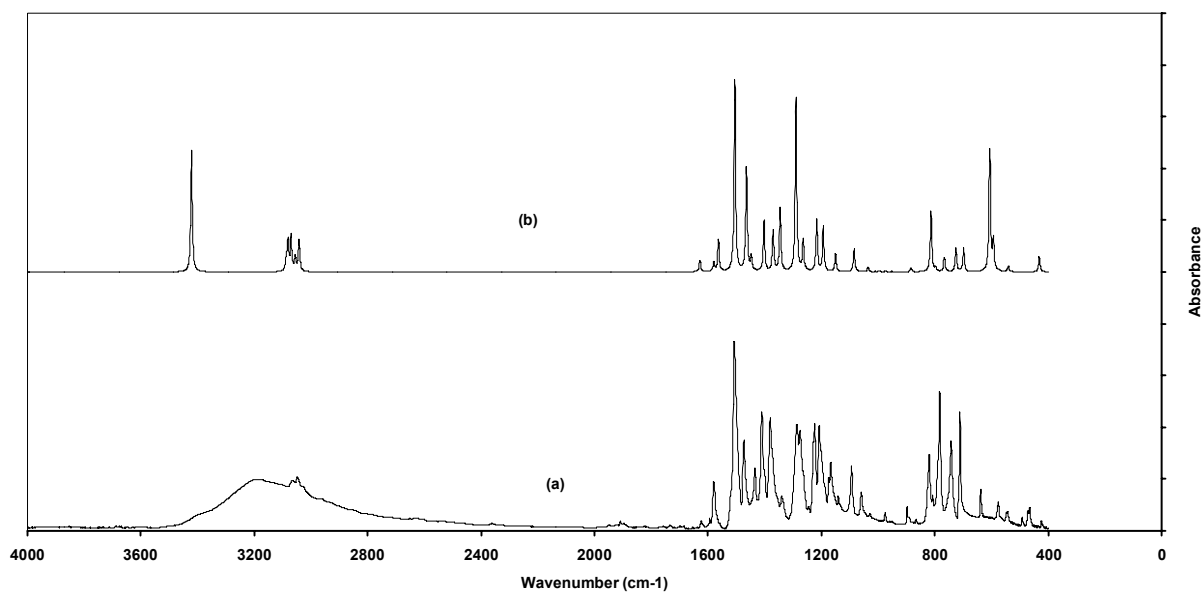


Fig. 2 FT-IR spectra of HQ : (a) observed; (b) calculated.

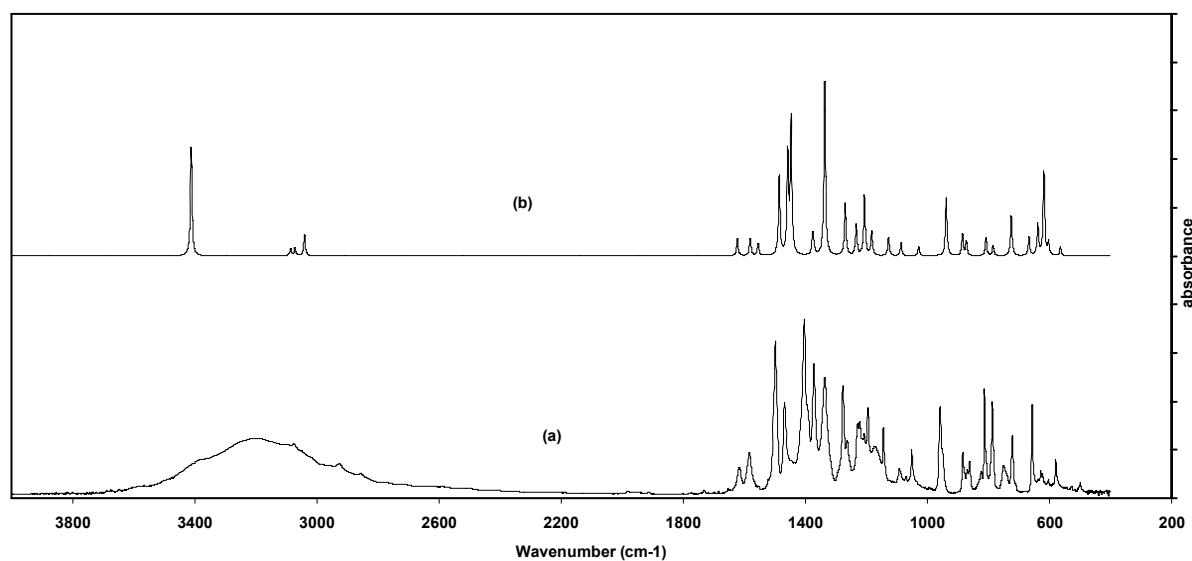


Fig. 3 FT-IR spectra of DCIHQ : (a) observed; (b) calculated.

#### 4.7 CN vibrations

In the vibrational spectra of HQ Krishnakumar et al. [4] identify the C-N stretching vibrations at 1286 and 1273 cm<sup>-1</sup>, respectively. In this study these vibrations are measured at 1286 and 1339 cm<sup>-1</sup>, respectively. According to NCA these bands are strongly mixed with CC (29%) and CO (20%). The C-N stretching are strongly affected by substitution of halogens and nitro group. These bands observed at lower wavelength in IR spectra of DCIHQ (1275, 1335 cm<sup>-1</sup>) and DBrHQ (1271, 1331 cm<sup>-1</sup>). Strong wavelength shift was observed in the IR spectra of DIHQ (1268, 1243 cm<sup>-1</sup>), since the iodine atoms are less electronegative than chlorine and bromine atoms. In the IR spectra of DNHQ these

bands observed at 1256, 1300  $\text{cm}^{-1}$ , respectively.

#### 4.8 CO vibrations

In the IR spectra of HQ the medium band observed at 1222  $\text{cm}^{-1}$  is assigned to C-O stretching. Krishnakumar et al. [4] identify the C-O stretching vibration at 1206  $\text{cm}^{-1}$ , and the in-plane and out-of-plane bending at 575  $\text{cm}^{-1}$  and 465  $\text{cm}^{-1}$ . In this study these vibrations are measured at 542  $\text{cm}^{-1}$  and 465  $\text{cm}^{-1}$ , respectively.

#### 4.9 Ring vibrations

The characteristic skeletal modes of semi-unsaturated Carbon-carbon bonds lead to appearance of a group of bands in the 1650 – 1450  $\text{cm}^{-1}$  region. In mono-substituted benzene, a change of the dipole moment during stretching modes always occurs and as a result strong to medium intensity bands are expected for aromatic C-C modes. In agreement with the literature data, the medium intensity IR bands at 1623  $\text{cm}^{-1}$  and at 1593  $\text{cm}^{-1}$  in the IR spectra of HQ has been assigned to the ring stretching modes [21] (see Table 5, 6). The rest of bands are observed at 1579, 1206, 1052, 804 and 491  $\text{cm}^{-1}$ . Due to substitution with halogens and nitro group these bands appeared in lower frequency region (see Table 5, 6). These shifts to lower frequencies are due to the changes in force constant/reduce mass ratio, and from different extents of mixing between the ring and substituent group vibrations.

#### 4.10 CX vibrations (where X = Cl, Br, I)

Strong characteristic absorptions due to the C-X stretching vibrations are observed in this study. The large frequency shift, have been observed from Cl to I. The C-Cl stretching positions of the band being influenced by the nature of the halid atoms substituted at the 5th and 7th positions of HQ derivatives. The C-Cl stretching vibrations give generally strong absorption in the region 760 - 505  $\text{cm}^{-1}$  [22]. Bromine compounds absorb strongly in the region 650 - 485  $\text{cm}^{-1}$  due to the C-Br stretching vibrations [23]. The C-I bond gives rise to bands at about 610 - 485  $\text{cm}^{-1}$  [24]. In this study, the strong IR bands obtained at 656 and 597  $\text{cm}^{-1}$  for DCIHQ have been designated to C-Cl. The C-Br vibration for DBrHQ observed at 562 and 500  $\text{cm}^{-1}$ , while the strong to medium bands observed at 578 and 497  $\text{cm}^{-1}$  in the IR spectra of DIHQ have been assigned to C-I stretching vibrations. Vibrational coupling with neighboring carbon groups may be resulted into shift in the absorption frequencies of the respective compounds.

#### 4.11 NO<sub>2</sub> group vibrations

The characteristics group frequencies of nitro group are relatively independent of the rest of the molecule, which makes this group convenient to identify. Aromatic nitro compounds

have strong absorption due to the asymmetric and symmetric stretching vibrations of the NO<sub>2</sub> group at 1582 and 1548 cm<sup>-1</sup>, respectively. Hydrogen bonding has little effect on the NO<sub>2</sub> asymmetric stretching vibrations [21]. The strong IR bands at 1326 and 1340 cm<sup>-1</sup> have designated to symmetric stretching modes of NO<sub>2</sub>. The bands at 831, 798 cm<sup>-1</sup> and at 702, 683 cm<sup>-1</sup> in DNHQ have been designated to scissoring and rocking modes of the NO<sub>2</sub> groups.

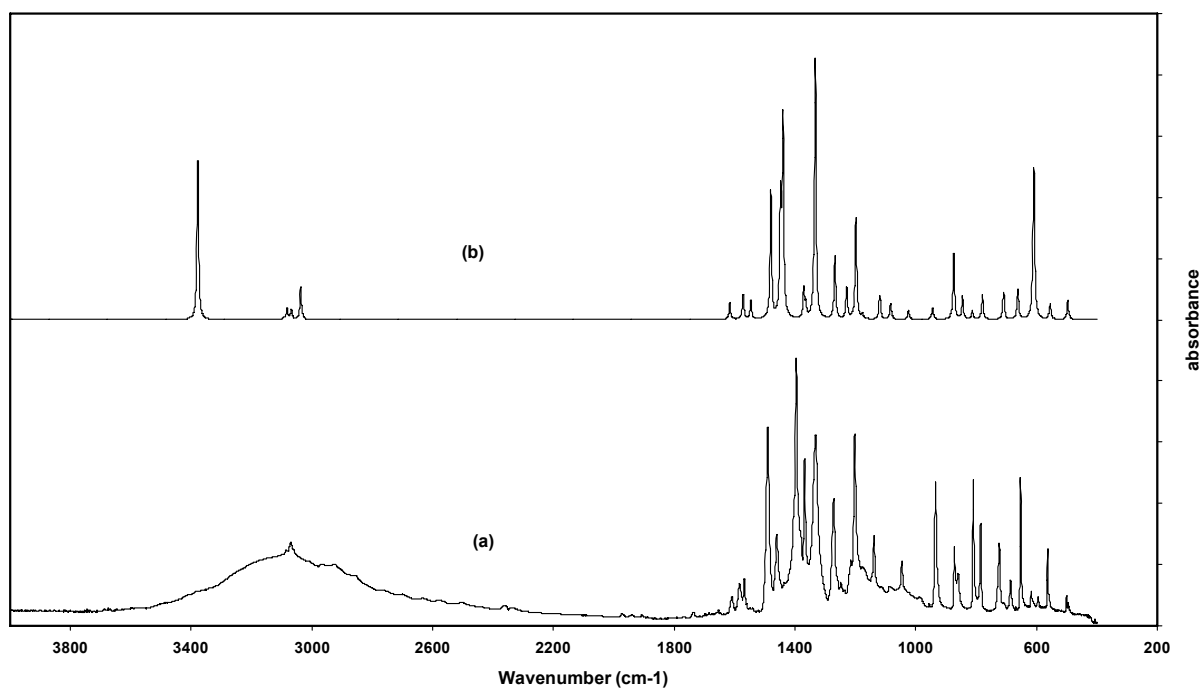


Fig. 4 FT-IR spectra of DBrHQ : (a) observed; (b) calculated.

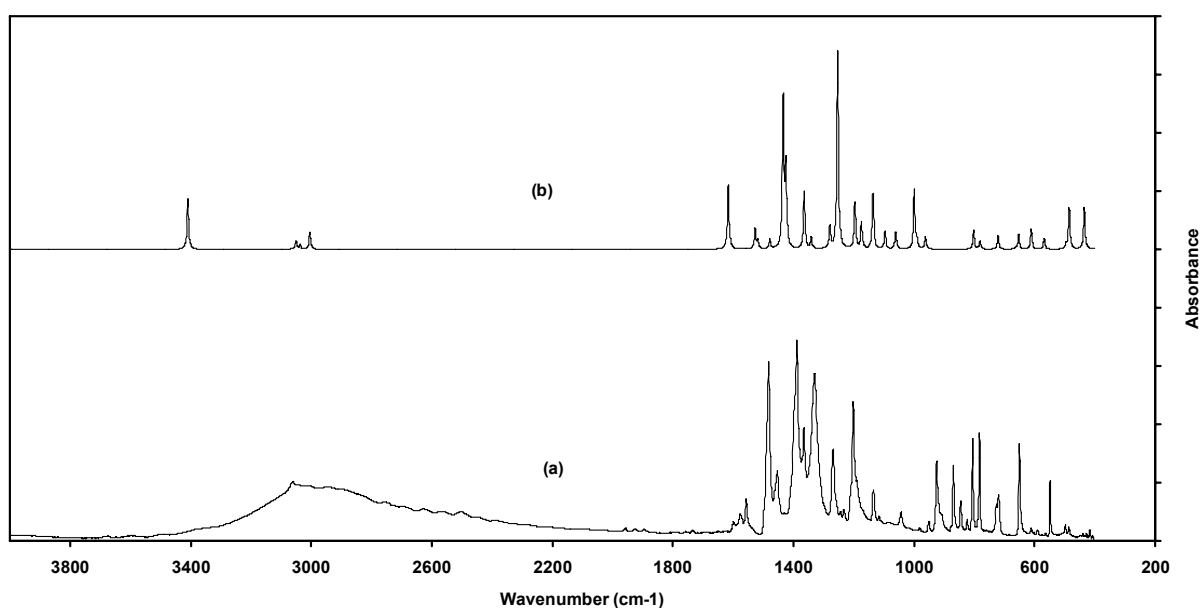
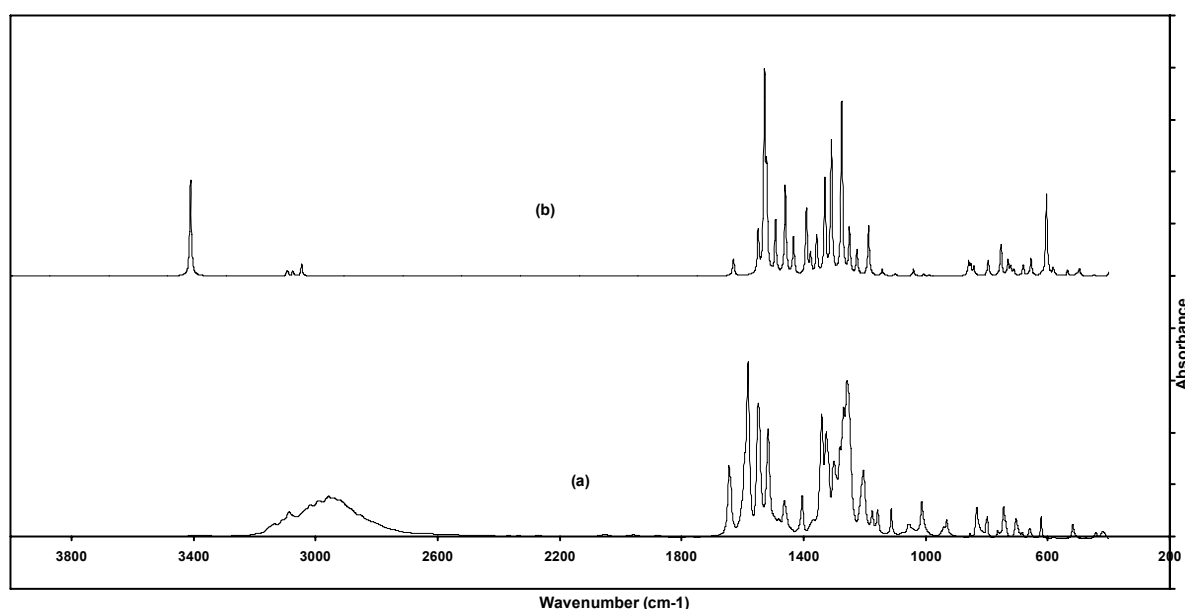


Fig. 5 FT-IR spectra of DIHQ : (a) observed; (b) calculated.



## 5 Conclusion

The structural parameters, IR frequencies and intensities of the harmonic vibrational bands of 8-HQ and its 5,7-dichloro, 5,7-dibromo, 5,7-diiodo and 5,7-dinitro analogue were calculated at the DFT level of theory using B3LYP functional and 6-31G\* basis set. The role of chloride, bromide, iodide and nitro groups in the vibrational frequencies of the title compounds were discussed. Refinement of the scaling factors applied in this study achieved a weighted RMS deviation of 14.76, 15.37, 16.94, 15.41, 12.35  $\text{cm}^{-1}$  between the experimental and SQM frequencies of HQ, DCIHQ, DBrHQ, DIHQ and DNHQ, respectively. The infrared absorption and intensities computed by B3LYP method are in reasonable agreement with the experimental data. The results confirm the ability of the methodology applied for interpretation of the vibrational spectra of the title molecules in the solid state.



**Fig. 6** FT-IR spectra of DNHQ : (a) observed; (b) calculated.

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**Table 1** Optimized geometrical parameters of HQ, DCIHQ, DBrHQ, DIHQ, DNHQ obtained by B3LYP/6-31G\* density functional calculations.

Bond length	Values in Å					Bond angle	Values in (°)					
	HQ	DCIHQ	DBrHQ	DIHQ	DNHQ		X-Ray	HQ	DCIHQ	DBrHQ	DIHQ	DNHQ
N(1)-C(2)	1.319	1.319	1.319	1.319	1.319	N(1)-C(2)-C(3)	123	123	123	123	123	121
C(2)-C(3)	1.416	1.319	1.319	1.319	1.319	C(2)-C(3)-C(4)	119	119	119	119	119	120
C(3)-C(4)	1.377	1.377	1.377	1.376	1.376	C(3)-C(4)-C(10)	119	119	119	119	119	119
C(4)-C(10)	1.418	1.417	1.417	1.417	1.419	C(4)-C(10)-C(9)	117	117	117	117	117	118
C(10)-C(5)	1.418	1.421	1.421	1.421	1.422	C(10)-C(9)-N(1)	119	119	119	119	119	119
C(5)-C(6)	1.379	1.376	1.375	1.375	1.373	C(9)-C(10)-C(5)	119	119	119	119	119	119
C(6)-C(7)	1.414	1.413	1.412	1.412	1.405	C(5)-C(10)-C(4)	122	122	122	122	122	122
C(7)-C(8)	1.382	1.382	1.381	1.381	1.382	C(10)-C(5)-C(6)	119	119	119	119	119	119
C(9)-C(10)	1.425	1.426	1.426	1.427	1.422	C(5)-C(6)-C(7)	121	120	120	121	120	121
C(9)-N(1)	1.410	1.408	1.408	1.404	1.405	C(6)-C(7)-C(8)	119	120	120	120	121	120
C(8)-O(17)	1.350	1.342	1.342	1.342	1.334	C(7)-C(8)-C(9)	118	119	119	118	119	119
O(18)-H	1.00	1.02	1.08	1.09	1.09	C(8)-C(9)-N(1)	119	119	119	119	119	120
C(5)-X	-	1.759	1.913	1.943	-	C(8)-C(9)-C(10)	120	120	120	120	120	119
C(7)-X	-	1.745	1.898	1.926	-	C(7)-C(8)-O(17)	121	122	122	122	122	119
C(5)-N	-	-	-	-	1.468	C(9)-C(8)-O(17)	119	119	119	119	119	119
C(7)-N	-	-	-	-	1.472	C(8)-O(17)-H	104	104	104	104	105	100

**Table 2** Definition of internal coordinates of DCIHQ, DBrHQ, and DIHQ.

No(i)	Symbol	Type	Definition
stretching			
1 – 2	$R_i$	C-N	C9-N1, C2-N1
3 – 11	$r_i$	C-C	C6-C5, C5-C7, C7-C8, C9-C10, C10-C6, C2-C3, C8-C9, C3-C4, C4-C5
12	$Q_i$	O-H	O17-H18
13 – 16	$T_i$	C-H	C2-H11, C3-H12, C4-H13, C6-H15
17 – 18	$S_i$	C-X	C5-X14, C7-X16
19	$q_i$	C-O	C8-O11
bending			
20 – 31	$\beta_i$	ring	N1-C2-C3, C2-C3-C4, C3-C4-C5 C4-C10-C9, C10-C9-N1, C9-N1-C2 C9-C10-C5, C10-C5-C6, C5-C6-C7 C6-C7-C8, C7-C8-C9, C8-C9-C10
32 – 39	$\theta_i$	Ring	N1-C2-C3, C2-C3-C4, C3-C4-C5 C4-C10-C9, C10-C9-N1, C9-N1-C2 C9-C10-C5, C10-C5-C6, C5-C6-C7 C6-C7-C8, C7-C8-C9, C8-C9-C10
40 – 43	$\alpha_i$	C-C-X	C10-C5-X14, C6-C5-X14, C6-C7-X14 C8-C7-X14
44 – 45	$\delta_i$	C-C-O	C7-C8-O17, C9-C8-O17
46	$\Phi_i$	C-O-H	C8-O17-H18
out-of-plane-bending			
47 – 50	$\omega_i$	C-H	N1-C3-c2-H11, C2-C4-C3-H12 C3-C4-C10-H13, C5-C7-C6-H15
51 – 52	$\omega_i$	C-X	C10-C6-C5-X14, C6-C8-C7-X16
53	$\omega_i$	C-O	C9-C7-C8-O17
torsion			
54 – 65	$t_i$	$\tau_{ring}$	N1-C2-C3-C4, C2-C3-C4-C10 C3-C4-C10-C9, C4-C10-C9-N1 C10-C9-N1-C2, C9-N1-C2-C3 C9-C10-C5-C6, C10-C5-C6-C7 C5-C6-C7-C8, C6-C7-C8-C9 C7-C8-C9-C10, C8-C9-C10-C5
66	$t_i$	$\tau_{OH}$	C9-C7-O17-H18+C7-C8-O17-H18
67	$t_i$	$\tau_B$	N1-C9-C10-C5+C8-C9-C10-C4

For numbering of atom see Fig. 1(b).

**Table 3** Definition of local symmetry coordinates and the values of corresponding scale factors used to correct the refined b3LYP/6-31G\* force fields for DCIHQ, DBrHQ and DIHQ.

No(i)	Symbol <sup>a</sup>	Definition <sup>b</sup>	Scale factors used		
			DCIHQ	DBrHQ	DIHQ
1-2	CN	R <sub>1</sub> , R <sub>2</sub>	0.922	0.899	0.822
3-11	CC	r <sub>3,r</sub> r <sub>4,r</sub> 5, r <sub>6</sub> , r <sub>7</sub> , r <sub>8</sub> , r <sub>9</sub> , r <sub>10</sub> , r <sub>11</sub>	0.897	0.899	0.885
12	OH	Q <sub>12</sub>	0.814	0.810	0.760
13-16	CH	T <sub>13</sub> , T <sub>14</sub> , T <sub>15</sub> , T <sub>16</sub>	0.912	0.912	0.895
17-18	CX	S <sub>16</sub> , S <sub>17</sub>	0.931	0.923	0.843
19	CO	q <sub>19</sub>	0.955	0.955	0.955
20	R <sub>symd</sub>	(β <sub>20</sub> + β <sub>21</sub> - 2β <sub>22</sub> + β <sub>23</sub> + β <sub>24</sub> - 2β <sub>25</sub> )/√12	0.990	0.990	0.990
21	R <sub>trigd</sub>	(β <sub>20</sub> - β <sub>21</sub> + β <sub>22</sub> - β <sub>23</sub> + β <sub>24</sub> - β <sub>25</sub> )/√6	0.990	0.990	0.990
22	R <sub>asymd</sub>	(β <sub>20</sub> - β <sub>21</sub> + β <sub>23</sub> - β <sub>24</sub> )/√2	0.990	0.990	0.990
23	R' <sub>symd</sub>	(β <sub>26</sub> + β <sub>27</sub> - 2β <sub>28</sub> + β <sub>29</sub> + β <sub>30</sub> - 2β <sub>31</sub> )/√12	0.990	0.990	0.990
24	R' <sub>trigd</sub>	(β <sub>26</sub> - β <sub>27</sub> + β <sub>28</sub> - β <sub>29</sub> + β <sub>30</sub> - β <sub>31</sub> )/√6	0.990	0.990	0.990
25	R' <sub>asymd</sub>	(β <sub>26</sub> - β <sub>27</sub> + β <sub>29</sub> - β <sub>30</sub> )/√2	0.990	0.990	0.990
26-29	bCH	(θ <sub>32</sub> - θ <sub>33</sub> )/√2, (θ <sub>34</sub> - θ <sub>35</sub> )/√2 (θ <sub>36</sub> - θ <sub>37</sub> )/√2, (θ <sub>38</sub> - θ <sub>39</sub> )/√2	0.915	0.915	0.915
30-31	bCX	(α <sub>40</sub> - α <sub>41</sub> )/√2, (α <sub>42</sub> - α <sub>43</sub> )/√2	0.922	0.922	0.900
32	bCO	δ <sub>44</sub> , δ <sub>45</sub>	0.922	0.922	0.922
33	bOH	σ <sub>46</sub>	1.092	1.094	1.164
34-37	ωCH	ω <sub>47</sub> , ω <sub>48</sub> , ω <sub>49</sub> , ω <sub>50</sub>	0.976	0.976	0.976
38-39	ωCX	ω <sub>51</sub> , ω <sub>52</sub>	0.965	0.972	0.965
40	ωCO	ω <sub>53</sub>	0.976	0.976	0.976
41	tR <sub>trigd</sub>	(τ <sub>54</sub> + τ <sub>55</sub> - 2τ <sub>56</sub> + τ <sub>57</sub> + τ <sub>58</sub> - 2τ <sub>59</sub> )/√2	0.835	0.835	0.835
42	tR <sub>symd</sub>	(τ <sub>54</sub> - τ <sub>55</sub> + τ <sub>56</sub> - τ <sub>57</sub> + τ <sub>58</sub> - τ <sub>59</sub> )/√6	0.835	0.835	0.835
43	tR <sub>asymd</sub>	(τ <sub>54</sub> - τ <sub>55</sub> + τ <sub>57</sub> - τ <sub>58</sub> )/√2	0.835	0.835	0.835
44	tR' <sub>trigd</sub>	(τ <sub>60</sub> + τ <sub>61</sub> - 2τ <sub>62</sub> + τ <sub>63</sub> + τ <sub>64</sub> - 2τ <sub>65</sub> )/√2	0.835	0.835	0.835
45	tR' <sub>symd</sub>	(τ <sub>60</sub> - τ <sub>61</sub> + τ <sub>62</sub> - τ <sub>63</sub> + τ <sub>64</sub> - τ <sub>65</sub> )/√6	0.835	0.835	0.835
46	tR' <sub>asymd</sub>	(τ <sub>60</sub> - τ <sub>61</sub> + τ <sub>63</sub> - τ <sub>64</sub> )/√2	0.835	0.835	0.835
47	tCO	τ <sub>66</sub>	0.831	0.831	0.831
48	Butterfly	T <sub>67</sub>	0.835	0.835	0.835

<sup>a</sup> These symbols are used for description of the normal modes by PED in Tables 5-6.<sup>b</sup> The internal coordinated used here are defined in Table 2.

**Table 4** Diagonal stretching force constants ( $10^2 \text{ N m}^{-1}$ ) of HQ, DCIHQ, DBrHQ, DIHQ, DNHQ.

Bond	Force constant				
	HQ	DCIHQ	DBrHQ	DIHQ	DNHQ
N(1) – C(2)	3.422	3.395	3.395	3.081	3.538
C(2) – C(3)	4.446	4.440	4.483	4.113	4.558
C(3) – C(4)	4.249	4.259	4.251	4.827	4.446
C(4) – C(10)	4.276	4.396	4.407	4.065	4.689
C(10) – C(5)	4.582	4.524	4.275	4.741	5.121
C(5) – C(6)	5.257	4.308	4.315	4.138	4.399
C(7) – C(8)	4.582	4.433	4.435	4.195	4.583
C(9) – C(10)	4.421	4.609	4.611	4.511	5.010
C(9) – N(1)	4.545	4.524	4.524	4.138	4.596
C(8) – O(17)	6.663	6.909	6.908	6.741	6.902
C(5) – X	-	3.287	2.671	2.623	-
C(7) – X	-	3.516	2.742	2.644	-
C(5) – N	-	-	-	-	3.871
C(7) – N	-	-	-	-	3.837

**Table 5** Detailed assignment of fundamental vibrations of DCIHQ, DBrHQ, DIHQ by normal modes analysis based on SQM force field calculations.

No.	symm. Spec. $C_s$	DCIHQ		DBrHQ		DIHQ		IR inte.	Characterization of normal modes with PED (%)
		observ. freq.	Calculated freq. unscaled	observ. freq.	Calculated freq. unscaled	observ. freq.	Calculated freq. unscaled		
1	A	3379	3537	3379	3530	3352	3572	65.93	OH(100)
2	A	3094	3236	3087	3238	3062	3242	0.34	CH(99)
3	A	3075	3229	3070	3227	3042	3226	10.25	CH(100)
4	A	-	3213	-	3213	3038	3211	5.62	CH(96)
5	A	3013	3181	3013	3180	3014	3176	22.68	CH(95)
6	A	1614	1670	1606	1666	1598	1705	82.89	CC(25) bOH(25) R <sub>asymd</sub> (14)
7	A	1581	1647	1582	1645	1572	1657	26.45	CC(46) bCH(21)
8	A	1552	1620	1568	1615	1572	1644	10.33	CC(44) CN(34)
9	A	1479	1540	1490	1535	1481	1560	11.87	bOH(30) bCH(18) CO(10)
10	A	1466	1505	1459	1501	1453	1523	190.03	bCH(20) CO(16) CC(12)
11	A	1404	1459	1435	1457	1387	1480	100.26	bOH(31) CC(22) bCH(11)
12	A	1370	1432	1374	1428	1364	1454	74.48	bCH(25) CO(14) CC(10)
13	A	1364	1418	1368	1417	1329	1419	14.21	bCH(77) CC(14)
14	A	1335	1389	1331	1388	1268	1412	28.16	CN(47) CC(23)
15	A	1275	1306	1271	1304	1243	1305	257.80	CN(51) CC(14) R <sub>asymd</sub> (10)
16	A	1229	1279	1214	1282	1201	1281	59.84	CC(64) R <sub>asymd</sub> (20)
17	A	1205	1247	1202	1240	1188	1216	34.75	CO(20) bCH(14) CC(12)
18	A	1193	1235	1173	1231	1134	1208	71.21	CC(59) bCH(26)
19	A	1143	1174	1138	1167	1116	1187	22.29	bCH(56) CC(23)
20	A	1090	1118	1086	1114	1042	1115	22.22	bCH(63) R <sub>asymd</sub> (31)
21	A	1050	1072	1026	1069	1042	1093	75.88	CC(62) bCH(12)
22	A'	-	1000	0.40	1005	980	1068	9.22	$\omega$ CH(92)
23	A'	959	968	962	971	950	1005	16.04	$\omega$ CH(90)
24	A'	951	965	935	945	924	997	0.31	$\omega$ CH(49) CC(23)

Abbreviations used: R- ring, b- bending, symd- symmetric deformation, asymd- asymmetric deformation, trigd- trigonal deformation,  $\omega$ -out-of-plane bending, t- torsion, sciss- scissoring, rock- rocking  
<sup>a</sup> For the notation use Table 2.



**Table 5 (continued)** Detailed assignment of fundamental vibrations of DCIHQ, DBrHQ, DIHQ by normal modes analysis based on SQM force field calculations.

No.	symm. Spec. $C_s$	DCIHQ		DBrHQ		DIHQ		Characterization of normal modes with PED (%)
		observ. freq.	Calculated freq. scaled	observ. freq.	Calculated freq. scaled	observ. freq.	Calculated freq. scaled	
25	A	883	883	872	941	874	969	CC(62) $\omega$ CH(26)
26	A	861	888	859	871	845	854	CC(62) $R_{asymd}(53)$
27	A'	812	822	808	850	813	850	$\omega$ CH(82)
28	A	787	783	783	813	789	817	$R_{trigd}(86)$
29	A	656	745	562	622	555	637	CX(62) $R_{asymd}(20)$
30	A'	-	735	653	735	662	748	t $R_{asymd}(50)$ tOH(22) $\omega$ CX(12)
31	A	628	667	-	694	612	740	$R_{asymd}(32)$ $R_{trigd}(20)$ $\omega$ CO(10)
32	A	603	660	616	681	608	667	$R_{symd}(64)$ CX(24)
33	A	597	631	500	571	496	634	CX(45) $R_{trigd}(14)$ CO(10)
34	A	530	609	-	632	480	611	t $R_{asymd}(43)$ $\omega$ CX(26)
35	A	499	587	494	516	476	515	$R_{trigd}(72)$ $R_{asymd}(12)$
36	A	472	508	406	506	404	526	t $R_{asymd}(70)$ $\omega$ CX(23)
37	A'	-	507	-	442	355	485	t $R_{trigd}(46)$ $t_{asym}(17)$ CX(12)
38	A'	-	437	-	367	310	440	CX(40) $\omega$ CX(28)
39	A'	-	385	-	320	286	391	$\omega$ CO(52) $R_{asymd}(12)$
40	A'	-	365	-	294	236	319	$\omega$ CX(59) CX(25)
41	A'	-	358	-	245	224	291	Butterfly(45) t $R_{trigd}(32)$
42	A	-	296	-	242	166	271	bCX(88)
43	A	-	244	-	173	143	253	bCX(90)
44	A'	-	219	-	165	131	183	t $R_{asymd}(45)$ t $R_{trigd}(22)$
45	A'	-	190	-	146	124	159	t $R_{asymd}(90)$
46	A'	-	156	-	133	119	130	t $R_{symd}(86)$
47	A'	-	135	-	120	116	109	t $R_{asymd}(53)$ Butterfly(32)
48	A'	-	82	-	71	65	82	t $R_{asymd}(83)$

Abbreviations used: R- ring, b- bending, synd- symmetric deformation, asymd- asymmetric deformation, trigd- trigonal deformation,  $\omega$ -out-of-plane bending, t- torsion, sciss- scissoring, rock- rocking

$\alpha$  For the notation use Table 2.

**Table 6** Detailed assignment of fundamental vibrations of HQ and DNHQ by normal modes analysis based on SQM force field calculations.

No.	Symm. Spec. $C_s$	HQ		Characterization of normal modes with PED (%)		obs. frq.	DNHQ		obs. frq.	Characterization of normal modes with PED (%)		IR inte.
		observed frq.	Calculated scaled	IR inte.	observed frq.		unscaled	scaled		IR inte.		
1	A	3386	3521	3401	89.24	OH(100)	3380	3622	3410	132.45	OH(100)	
2	A	3088	3220	3088	8.74	CH(98)	3110	3238	3093	4.91	CH(99)	
3	A	-	3213	3082	21.84	OH(95)	3086	3237	3092	2.65	CH(100)	
4	A	-	3202	3071	25.48	CH(100)	-	3320	3075	6.13	CH(100)	
5	A	-	3187	3057	7.48	CH(100)	2987	3189	3046	15.98	CH(100)	
6	A	-	3185	3055	3.48	CH(100)	1643	1689	1631	23.61	CC(39) bOH(20) CN(15)	
7	A	-	3172	3043	23.09	CH(100)	1582	1658	1529	264.92	NO <sub>2</sub> ass(69) CC(10)	
8	A	1623	1689	1629	8.45	CC(47) bOH(20) R <sub>asymd</sub> (15)	1548	1654	1550	58.59	NO <sub>2</sub> ass(89)	
9	A	1593	1651	1580	6.57	CC(68) CH(24)	1515	1637	1522	117.95	CC(54) NO <sub>2</sub> ass(21)	
10	A	1579	1631	1564	23.14	CC(32) CN(21) CH(10)	-	1627	1493	73.38	CC(53) CH(21)	
11	A	1507	1560	1506	141.12	bOH(32) bCH(16) CC(10)	1462	1551	1461	121.42	CC(32) bOH(16) CO(14)	
12	A	1427	1520	1465	76.96	bCH(33) CO(22) CC(12)	-	1513	1434	51.19	CC(37) NO <sub>2</sub> ass(28)	
13	A	1409	1489	1448	10.68	CC(35) bOH(24) CH(17)	1404	1477	1392	90.61	bCH(89)	
14	A	-	1458	1403	37.18	bCH(65) CC(22)	-	1449	1378	26.96	bCH(49) CC(20) NO <sub>2</sub> ass(9)	
15	A	1379	1418	1371	29.77	bCH(35) CC(23) R <sub>asymd</sub> (15)	1340	1429	1358	53.35	NO <sub>2</sub> ss(41) NO <sub>2</sub> ass(31)	
16	A	1339	1408	1346	46.44	CN(54) CC(29)	1326	1421	1331	130.96	NO <sub>2</sub> ss(41) CN(20) CC(12)	
17	A	1286	1324	1290	128.10	CN(43) CO(20) R <sub>asymd</sub> (12)	1300	1412	1310	182.69	CN(43) CC(21) NO <sub>2</sub> ss(9)	
18	A	-	1315	1265	22.81	bCH(35) CO(17) CC(10)	1279	1396	1276	238.27	CN(63) bCH(34)	
19	A	1222	1263	1217	38.10	CO(41) CH(28) R <sub>trig</sub> (12)	1256	1316	1251	63.20	CN(53) CO(39)	
20	A	1206	1244	1194	33.41	CC(44) CH(23)	1204	1298	1226	34.22	CC(58) CO(28)	
21	A	-	1151	1202	13.05	bCH(87)	1175	1272	1188	68.09	bCH(63) CC(19)	
22	A	-	1169	1117	0.56	bCH(68) CC(18)	1155	1236	1143	8.53	bCH(57) CC(24)	
23	A	1090	1118	1085	17.02	R <sub>symd</sub> 925 bOH(15) CO(15)	1112	1191	1101	2.51	R <sub>sym</sub> (39) bCH(36)	
24	A	1052	1081	1036	3.41	CC(65) bCH(26)	1057	1135	1041	9.08	CC(53) bCH(31)	

Abbreviations used: R- ring, b- bending, symd- symmetric deformation, asymd- asymmetric deformation, trigd- trigonal deformation  
 $\omega$ -out-of-plane bending, t- torsion, sciss- scissoring, rock- rocking  
<sup>a</sup> For the notation use Table 2.

**Table 6 (continued)** Detailed assignment of fundamental vibrations of HQ and DNHQ by normal modes analysis based on SQM force field calculations.

No.	Symm. Spec. $C_s$	obs. freq.	HQ		IR inte.	Characterization of normal modes with PED (%)	obs. freq.	DNHQ		IR inte.	Characterization of normal modes with PED (%)
			unscaled	scaled				unscaled	scaled		
25	A	-	1054	1011	0.19	CC(85)	1012	1079	1007	2.32	CN(45) $R_{asymd}(22)$
26	A'	-	994	996	0.76	$\omega$ CH(95)	-	1024	990	0.79	$\omega$ CH(97)
27	A'	974	971	975	0.71	$\omega$ CH(90)	939	1006	943	0.12	$\omega$ CH(94)
28	A	-	960	954	0.31	$\omega$ CH(90)	930	973	923	0.08	CN(54) $R_{trigid}(23)$
29	A'	-	905	885	1.76	$\omega$ CH(93)	852	951	860	19.58	$\omega$ CH(93)
30	A	-	887	883	0.89	$R_{asymd}(65)$ $R_{trigid}(23)$	-	898	853	13.39	$\omega$ CH(86)
31	A	818	834	814	44.60	$R_{asymd}(62)$ $R_{symd}(31)$ $\omega$ CH(13)	831	868	843	12.48	$NO_2$ sciss(58) $R_{trigid}(12)$
32	A	804	820	798	2.76	$R_{trigid}(74)$ CC(20)	798	828	796	22.17	$NO_2$ rock(36) $R_{trigid}(34)$
33	A'	782	793	767	10.82	$\omega$ CH(94)	762	812	754	42.94	$\omega$ CH(32) $R_{trigid}(26)$ $tNO_2(10)$
34	A	742	767	726	17.62	$R_{asymd}(44)$ $tR_{sym}(23)$ $tOH(15)$	745	791	731	19.96	$\omega$ CH(33) $R_{trigid}(14)$ $tNO_2(11)$
35	A	637	726	641	17.48	$R_{trigid}(60)$ CN(24)	702	777	722	12.08	$NO_2$ sciss(60) $\omega$ CO(22)
36	A	-	660	607	91.51	$tR_{asym}(63)$ $tOH(35)$	-	764	712	7.88	$NO_2$ sciss(59) $\omega$ CO(32)
37	A	-	644	594	22.17	$tR_{trig}(90)$	683	735	681	14.64	$tR_{trigid}(50)$ $NO_2$ sciss(45)
38	A	578	592	575	0.678	$R_{symd}(50)$ $tR_{trig}(32)$	658	696	656	24.24	$\omega$ NO <sub>2</sub> (62) $R_{asymd}(19)$
39	A	552	587	547	0.71	CC(52) $tR_{asym}(25)$	619	685	621	2.06	$\omega$ CN(75) $R_{trigid}(32)$
40	A	542	554	541	3.48	$R_{asymd}(77)$ $tR_{trigid}(20)$	592	672	605	113.65	$tOH(71)$ $\omega$ CO(12)
41	A'	491	498	489	0.21	CC(59) $\omega$ CO(22)	580	656	583	10.57	$tR_{asymd}(63)$ $R_{trigid}(21)$ $tR_{asym}(42)$ $\omega$ CO(31)
42	A'	465	477	455	0.02	$tR_{trig}(48)$ $tR_{asymd}(37)$	-	606	536	7.53	$\omega$ CN(69) $tR_{asymd}(41)$
43	A'	-	446	432	11.00	$\omega$ CH(49) $tR_{sym}(33)$	517	569	506	3.37	$R_{asymd}(46)$ $R_{symd}(41)$
44	A'	-	432	396	0.76	$\omega$ CO(69) $R_{trig}(46)$	-	541	497	9.75	$tR_{trig}(89)$
45	A	-	284	278	4.42	Butterfly(57) $\omega$ CH(30)	440	508	449	1.76	$tR_{asym}(58)$ $\omega$ CH(30)
46	A	-	271	250	0.79	$tR_{trig}(69)$ butterfly(28)	417	476	400	6.63	Butterfly(57) $\omega$ CN(32)
47	A'	-	177	162	1.95	$tR_{trig}(70)$ butterfly(20)	-	427	368	0.26	$R_{asymd}(59)$ $\omega$ CN(31)
48	A'	-	156	142	0.10		-	397	335	0.32	$R_{asymd}(63)$ CN(30)

Abbreviations used: R- ring, b- bending, symd- symmetric deformation, asymd- asymmetric deformation, trigd- trigonal deformation,  $\omega$ -out-of-plane bending, t- torsion, sciss- scissoring, rock- rocking  
<sup>a</sup> For the notation use Table 2.

**Table 6 (continued)** Detailed assignment of fundamental vibrations of HQ and DNHQ by normal modes analysis based on SQM force field calculations.

No.	Symm. Spec. $C_s$	obs. freq.	HQ		obs. freq.	Characterization of normal modes with PED (%)		DNHQ		obs. freq.	Characterization of normal modes with PED (%)	
			unscaled	scaled		IR inte.	unscaled	scaled	unscaled		scaled	IR inte.
49	A'	-	345	310	-	NO <sub>2</sub> sciss(59)	R <sub>trigid</sub> (29)	345	310	-	NO <sub>2</sub> sciss(59)	R <sub>trigid</sub> (29)
50	A	-	318	271	-	$\omega$ CN(59)	butterfly(29)	318	271	-	$\omega$ CN(59)	butterfly(29)
51	A	-	278	251	-	bCN(80)		278	251	-	bCN(80)	
52	A'	-	278	223	-			278	223	-		
53	A	-	278	223	-			278	223	-		
54	A'	-	236	194	-			236	194	-		
55	A'	-	214	185	-			214	185	-		
56	A'	-	185	152	-			185	152	-		
57	A'	-	164	148	-			164	148	-		
58	A'	-	148	128	-			148	128	-		
59	A'	-	119	119	-			119	119	-		
60	A'	-	73	98	-			73	98	-		

Abbreviations used: R- ring, b- bending, symd- symmetric deformation, asymd- asymmetric deformation, trigd- trigonal deformation,  $\omega$ -out-of-plane bending, t- torsion, sciss- scissoring, rock- rocking

<sup>a</sup> For the notation use Table 2.