iJRASET
International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 7 **Issue:** XII **Month of publication:** December 2019

DOI: http://doi.org/10.22214/ijraset.2019.12161

www.ijraset.com

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.177
Volume 7 Issue XII, Dec 2019- Available at www.ijraset.com

Comparative Structural and Vibrational Study of 8-Hydroxyquinoline and 8-Hydroxyquinoline Succinate Compounds: A DFT Study

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***Abstract:** Quinoline based compounds efficiently form molecular complexes with various organic acids through hydrogen bonding. These compounds are classified as electron-deficient heterocyclic in nature and exhibit acceptor-donor properties with intramolecular charge transfer. 8-Hydroxyquinolinesuccinate is a π donor-acceptor molecular compound in which 8-HQ acts as donor and succinic acid as electron acceptor. The present work deals with the interaction of title compounds using Density Functional Theory (DFT) implemented in Gaussian-09 software package. All geometry optimizations, the vibrational analysis, electronic transition study of UV and NMR spectra of title compounds were interpreted with aid of normal coordinate analysis based on DFT/B3LYP using 6-311G basis set. Dihedral angles of 8-HQ varies between 0° and 180°. This shows that the molecule of 8-HQ is practically planar. 8-HQSC crystal is stabilized by the hydrogen bonds N2-H13….O22 and O22-H12….O1 formed by the existence of complementary functional groups. The negative chemical shift values of -145.5869 ppm do exist for nitrogen atom in 8-HQ. Energy gap of 8-HQ is obtained theoretically by DFT method is 4.52 eV and from HOMO-LUMO diagram is 4.53 eV. From the Mulliken atomic charges confirms the extensive intermolecular charge transfer between adsorbate and adsorbent of the title compound during the interaction. The calculated results are found to be in good agreement with the previous investigations.*

***Keywords:** 8-Hydroxyquinoline, 8-Hydroxyquinoline Succinate, Vibrational spectra, Density Functional Theory (DFT), HOMO, LUMO.*

I. INTRODUCTION

8-Hydroxyquinoline is a bicycle compound and has typical phenolic properties. It consists of carbocyclic ring and pyridine ring with hydroxyl group substituted at position-8. Due to the unique chemical properties of 8-HQ, these compound derivatives have application in agricultural and medical fields.

The compound shows a variety of applications ranging from pharmacological and pharmaceutical agents to electron carriers in organic light emitting diodes and fluorescent chemo sensors for metal ions. In medical field, its derivatives can be used as insecticides, antibacterial, fungicidal, neuroprotective, and anti-HIV agents [1]. Organic functionalized NLO materials attracted a great deal of attention due to its extensive applications in harmonic generation, amplitude, phase modulation, switching and other signal processing devices [2-4].

A possible reason for the significant increase in the effective nonlinear optical response observed in organic molecules is due to the existence of π-conjugation between the appropriate electron donor and acceptor groups, chirality and hydrogen bonding. Functional modification in electron-donor systems affects the optical and electrical properties of the quinolone derivatives. 8-Hydroxyquinolinesuccinate is a π donor-acceptor molecular compound in which 8-HQ acts as donor and succinic acid as electron acceptor. Theoretical studies are valuable approaches to explore the mechanism of reactions in the molecules and their electronic structures levels in addition to electronic parameters that acquired by means of theoretical calculations employ the computational methods of quantum chemistry. The improvement in theoretical studies and applications have accomplish a point where predicted features of logical accuracy can be obtained from DFT (density functional theory) studies [5,6].

Geometry of the molecules in its ground state, as well as the nature of their molecular orbitals, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are involved in the properties of activity of molecules reaction. The object of the present paper is to carry out DFT calculations on 8-Hydroxyquinoline and 8-Hydroxyquinoline succinate and to determine a relationship between some quantum chemical parameters obtained from the structure of the compounds and experimental parameters of IR, Raman spectra, UV and NMR reported by the previous studies.

II. DFT CALCULATIONS

Molecular geometries of the singlet ground state of compounds 8-HQ and 8-HQSC were fully optimized at B3LYP/6-311G level using Gaussian09 program. In geometry optimizations every bond length, bond angle and dihedral angle was permitted to relax, free of constraints. For each compound frequency calculations were carried out, verifying that the optimized structure obtained corresponded to energy minimum, thus only positive frequencies were expected. Frontier molecular orbitals were used to identify the adsorption centers of the inhibitor molecule. For the simplest transfer of electrons, adsorption should occur at the part of the molecule where the softness (σ) has the highest value. Electronegativity, hardness and softness have conformed to be very useful quantities in quantum molecular description calculations [7]. Moreover, we have computed UV, Nuclear Magnetic Resonance (NMR), highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) energies in order to understand the properties of the molecules.

III. RESULTS AND DISCUSSION

We have computed the structures of 8-HQ and 8-HQSC compounds using DFT calculations and quantities of the spectroscopic interest for the two compounds and compared the results with previous studies.

A. Molecular Geometries

The optimized molecular structures of the 8-HQ and 8-HQSC with atomic labeling are shown in Fig. 1.

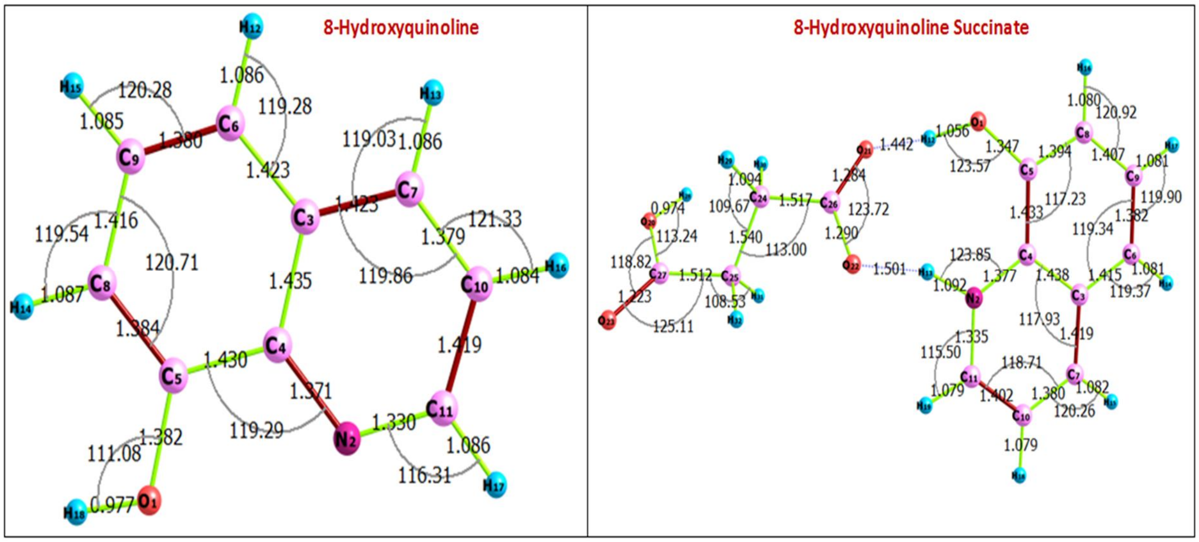

Fig. 1 optimized molecular structures of the 8-HQ and 8-HQSC with atomic labeling

The interatomic bond lengths and bond angles of 8-HQ and 8-HQSC derived from DFT study are listed in Table 1 and 2. 8-HQ consists of two rings, one phenol and other pyridine type ring. The angle between the phenolic and pyridine ring is only 1.382° [8]. The average C-C bond length in the rings is 1.456 Å whereas the average C-N bond is 1.387 Å. The observed C-C bond length in the two rings vary from 1.349 to 1.540 Å. Nearly identical C-C bonds indicate the complete delocalization of π -electrons in the individual hetero atom rings. The obtained C-O bond length is 1.43 Å. It is found that the C-C bonds and hetero atom C-N bond are nearly the same as that found in experimental result. The average value of the bond angles in the two benzene rings is 120°. The deviation from this ideal value is quite significant. Dihedral angles are useful to identify the molecular conformation. Dihedral angles of 8-HQ varies between 0° and 180°. This shows that the molecule of 8-HQ is practically planar. 8-HQSC single crystal growth and its characterization were reported by R.Thirumurugan et.al (2014). The N-site of the 8-HQ leads to the formation of cation and it is confirmed by the enhancement of the internal angle at N2 (N2-C11-C10 bond angle of 121.0427) compared with 122.12(2)° observed in 8-HQSC single crystal study [9]. The deprotonation occurs due to the succinic acid molecule and it leads to an anion. The variations of the carboxyl bond distances C26-O21 and C26-O22 are 1.3013 Å and 1.2584 Å respectively. The dihedral angle between 8-hydroxyquinolinium cation and succinate anion are 8.8499° coincide with the already existing report. It indicates that they are essentially planar. 8-HQSC crystal is stabilized by the hydrogen bonds N2-H13….O22 and O22-H12….O1 formed by the existence of complementary functional groups.

TABLE I
Optimized Geometrical Parameters[b] of 8-Hydroxyquinoline at b3lyp/6-311g level.

Definition [a]	8-HQ	Definition [a]	8-HQ	Definition [a]	8-HQ
r(1,5)	1.43	A(3,6,9)	119.9293	D(7,3,6,9)	180.0
r(1,18)	0.96	A(3,6,12)	120.0353	D(7,3,6,12)	0.0
r(2,4)	1.4759	A(9,6,12)	120.0353	D(4,3,7,10)	0.0
r(2,11)	1.2993	A(3,7,10)	118.812	D(4,3,7,13)	180.0
r(3,4)	1.3555	A(3,7,13)	120.594	D(6,3,7,10)	180.0
r(3,6)	1.5396	A(10,7,13)	120.594	D(6,3,7,13)	0.0
r(3,7)	1.5344	A(5,8,9)	120.0394	D(2,4,5,1)	0.0
r(4,5)	1.5403	A(5,8,14)	119.9803	D(2,4,5,8)	180.0
r(5,8)	1.3556	A(9,8,14)	119.9803	D(3,4,5,1)	180.0
r(6,9)	1.3549	A(6,9,8)	119.9704	D(3,4,5,8)	0.0
r(6,12)	1.07	A(6,9,15)	120.0148	D(1,5,8,9)	180.0
r(7,10)	1.3494	A(8,9,15)	120.0148	D(1,5,8,14)	0.0
r(7,13)	1.07	A(7,10,11)	119.2979	D(4,5,8,9)	0.0
r(8,9)	1.5401	A(7,10,16)	120.3511	D(4,5,8,14)	180.0
r(8,14)	1.07	A(11,10,16)	120.3511	D(3,6,9,8)	0.0
r(9,15)	1.07	A(2,11,10)	120.4693	D(3,6,9,15)	180.0
r(10,11)	1.5399	A(2,11,17)	119.7653	D(12,6,9,8)	180.0
r(10,16)	1.07	A(10,11,17)	119.7653	D(12,6,9,15)	0.0
r(11,17)	1.07	D(18,1,5,4)	180.0	D(3,7,10,11)	0.0
A(5,1,18)	109.4712	D(18,1,5,8)	0.0	D(3,7,10,16)	180.0
A(4,2,11)	121.4793	D(11,2,4,3)	0.0	D(13,7,10,11)	180.0
A(4,3,6)	120.2281	D(11,2,4,5)	180.0	D(13,7,10,16)	0.0
A(4,3,7)	119.4712	D(4,2,11,10)	0.0	D(5,8,9,6)	0.0
A(6,3,7)	120.3008	D(4,2,11,17)	180.0	D(5,8,9,15)	180.0
A(2,4,3)	120.4703	D(6,3,4,2)	180.0	D(14,8,9,6)	180.0
A(2,4,5)	119.7557	D(6,3,4,5)	0.0	D(14,8,9,15)	0.0
A(3,4,5)	119.774	D(7,3,4,2)	0.0	D(7,10,11,2)	0.0
A(1,5,4)	119.9706	D(7,3,4,5)	180.0	D(7,10,11,17)	180.0
A(1,5,8)	119.9706	D(4,3,6,9)	0.0	D(16,10,11,2)	180.0
A(4,5,8)	120.0589	D(4,3,6,12)	180.0	D(16,10,11,17)	0.0

[a] For atomic numbering scheme, see Fig. 1.

[b] Bond lengths (r) in Angstrom, bond angles (A) and dihedral angles (D) in degree.

Table II

Optimized Geometrical Parameters[b] of 8-Hydroxyquinoline Succinate At B3lyp/6-311g Level

Definition [a]	8-HQSC	Definition [a]	8-HQSC	Definition [a]	8-HQSC
R(1,5)	1.43	A(6,9,17)	120.0282	D(6,3,7,10)	-179.9999
R(1,12)	0.96	A(8,9,17)	120.0282	D(6,3,7,15)	0.0001
R(1,22)	1.8825	A(7,10,11)	119.8521	D(2,4,5,1)	0.0
R(2,4)	1.3428	A(7,10,18)	120.0739	D(2,4,5,8)	180.0
R(2,11)	1.3461	A(11,10,18)	120.0739	D(3,4,5,1)	-179.9999
R(2,13)	1.0	A(2,11,10)	121.0427	D(3,4,5,8)	0.0001
R(3,4)	1.3977	A(2,11,19)	119.4787	D(1,5,8,9)	179.9999
R(3,6)	1.4007	A(10,11,19)	119.4787	D(1,5,8,16)	-0.0001
R(3,7)	1.393	A(2,13,22)	148.4574	D(4,5,8,9)	-0.0001
R(4,5)	1.4016	A(27,20,28)	120.0	D(4,5,8,16)	179.9999
R(5,8)	1.4021	A(1,22,13)	70.0498	D(3,6,9,8)	-0.0001
R(6,9)	1.4012	A(1,22,26)	123.381	D(3,6,9,17)	180.0
R(6,14)	1.07	A(12,22,13)	91.8638	D(14,6,9,8)	-179.9999
R(7,10)	1.3966	A(12,22,26)	102.5442	D(14,6,9,17)	0.0002
R(7,15)	1.07	A(13,22,26)	165.2736	D(3,7,10,11)	0.0
R(8,9)	1.4019	A(25,24,26)	109.4712	D(3,7,10,18)	179.9998
R(8,16)	1.07	A(25,24,29)	109.4712	D(15,7,10,11)	180.0
R(9,17)	1.07	A(25,24,30)	109.4712	D(15,7,10,18)	-0.0003
R(10,11)	1.3588	A(26,24,29)	109.4712	D(5,8,9,6)	0.0001
R(10,18)	1.07	A(26,24,30)	109.4712	D(5,8,9,17)	-180.0
R(11,19)	1.07	A(29,24,30)	109.4712	D(16,8,9,6)	-179.9999
R(12,22)	2.281	A(24,25,27)	109.4712	D(16,8,9,17)	0.0
R(13,22)	2.2785	A(24,25,31)	109.4712	D(7,10,11,2)	-0.0001
R(20,27)	1.3013	A(24,25,32)	109.4712	D(7,10,11,19)	179.9999
R(20,28)	0.96	A(27,25,31)	109.4712	D(18,10,11,2)	-179.9999
R(21,26)	1.3013	A(27,25,32)	109.4712	D(18,10,11,19)	0.0001
R(22,26)	1.2584	A(31,25,32)	109.4712	D(2,13,22,1)	-10.4696
R(23,27)	1.2584	A(21,26,22)	120.0	D(2,13,22,12)	0.5153
R(24,25)	1.54	A(21,26,24)	120.0	D(2,13,22,26)	-167.6271
R(24,26)	1.54	A(22,26,24)	120.0	D(28,20,27,23)	-179.9999
R(24,29)	1.07	A(20,27,23)	120.0	D(28,20,27,25)	0.0001
R(24,30)	1.07	A(20,27,25)	120.0	D(1,22,26,21)	8.8499
R(25,27)	1.54	A(23,27,25)	120.0	D(1,22,26,24)	-171.1501
R(25,31)	1.07	D(12,1,5,4)	-150.0	D(12,22,26,21)	-4.9169
R(25,32)	1.07	D(12,1,5,8)	30.0	D(12,22,26,24)	175.0831
A(5,1,12)	109.4712	D(22,1,5,4)	-7.9361	D(13,22,26,21)	162.9376
A(5,1,22)	141.3484	D(22,1,5,8)	172.0639	D(13,22,26,24)	-17.0624
A(4,2,11)	121.1776	D(5,1,22,13)	8.773	D(26,24,25,27)	180.0
A(4,2,13)	119.4112	D(5,1,22,26)	-178.0139	D(26,24,25,31)	-60.0
A(11,2,13)	119.4112	D(11,2,4,3)	-0.0003	D(26,24,25,32)	60.0
A(4,3,6)	120.3662	D(11,2,4,5)	179.9999	D(29,24,25,27)	60.0
A(4,3,7)	118.9875	D(13,2,4,3)	179.9998	D(29,24,25,31)	180.0
A(6,3,7)	120.6463	D(13,2,4,5)	0.0	D(29,24,25,32)	-60.0
A(2,4,3)	120.194	D(4,2,11,10)	0.0003	D(30,24,25,27)	-60.0
A(2,4,5)	119.9813	D(4,2,11,19)	-179.9997	D(30,24,25,31)	60.0
A(3,4,5)	119.8247	D(13,2,11,10)	-179.9998	D(30,24,25,32)	180.0
A(1,5,4)	119.9988	D(13,2,11,19)	0.0002	D(25,24,26,21)	150.0
A(1,5,8)	119.9988	D(4,2,13,22)	7.8278	D(25,24,26,22)	-30.0
A(4,5,8)	120.0023	D(11,2,13,22)	-172.1721	D(29,24,26,21)	-90.0
A(3,6,9)	119.8369	D(6,3,4,2)	-179.9999	D(29,24,26,22)	90.0
A(3,6,14)	120.0816	D(6,3,4,5)	-0.0001	D(30,24,26,21)	30.0
A(9,6,14)	120.0816	D(7,3,4,2)	0.0001	D(30,24,26,22)	-150.0
A(3,7,10)	118.746	D(7,3,4,5)	179.9999	D(24,25,27,20)	30.0
A(3,7,15)	120.627	D(4,3,6,9)	0.0001	D(24,25,27,23)	-150.0
A(10,7,15)	120.627	D(4,3,6,14)	179.9999	D(31,25,27,20)	-90.0
A(5,8,9)	120.0263	D(7,3,6,9)	-180.0	D(31,25,27,23)	90.0
A(5,8,16)	119.9868	D(7,3,6,14)	-0.0002	D(32,25,27,20)	150.0
A(9,8,16)	119.9868	D(4,3,7,10)	0.0	D(32,25,27,23)	-30.0
A(6,9,8)	119.9436	D(4,3,7,15)	-180.0		

[a] For atomic numbering scheme, see Fig. 1.

[b] Bond lengths (r) in Angstrom, bond angles (A) and dihedral angles (D) in degree.

B. Vibrational Spectra

The 8-hydroxyquinoline has 18 atoms with 48 fundamental modes of vibration. These vibrations are divided into 33 in-plane and 15 out-of-plane vibrations. The detailed vibrational assignment of fundamental modes of frequencies of 8-HQ reported by Krishnakumar et al. [10] and calculated frequency using B3LYP/6-311G method are reported in Table 3. IR and Raman spectra of 8-HQ and 8-HQSC are shown in Fig. 2 and 3. The accurate position of the OH bond is based on the strength of the hydrogen bond. In 8-HQ, OH-N hydrogen bond absorption is found at 3688 cm^{-1}. The OH group in-plane and out-of-plane modes are found at 1518 cm^{-1} (δ OH) and 896 cm^{-1} (γ OH) respectively in agreement with the literature data [10,11]. In addition, a certain number of diatomic molecular fragments such as C2 and CN provide useful indications for identification of organic materials [12,13] and also the mixing of several bands are possible in this region. ν C11N2 and ν C9N1 are appeared at 1354 cm^{-1} and 1306 cm^{-1} respectively. In the IR spectra of 8-HQ, the non-linearity of hydrogen bond have an impact over the carbonyl group frequency. The IR band is observed at 1231 cm^{-1} and assigned to νC5O1 vibration. The frequencies at 591 cm^{-1} and 491 cm^{-1} are active due to δC5O and γC5O respectively. Generally, The presence of skeletal modes of semi-unsaturated C-C bonds vibrations are appeared in the 1650 - 1450 cm^{-1} frequency region [14]. Due to stretching modes, a change of dipole moment occurs in mono-substituted benzene. As a result of this, strong to medium intensity bands are expected for aromatic C-C modes. The medium intensity IR bands have been assigned to the ring stretching modes at 1657 cm^{-1} and 1551 cm^{-1}. The rest of bands are observed at 1475, 1441, 1394, 1294 and 1251 cm^{-1}. Table 3 shows that the results of observed and calculated IR and Raman frequencies yield good agreement.

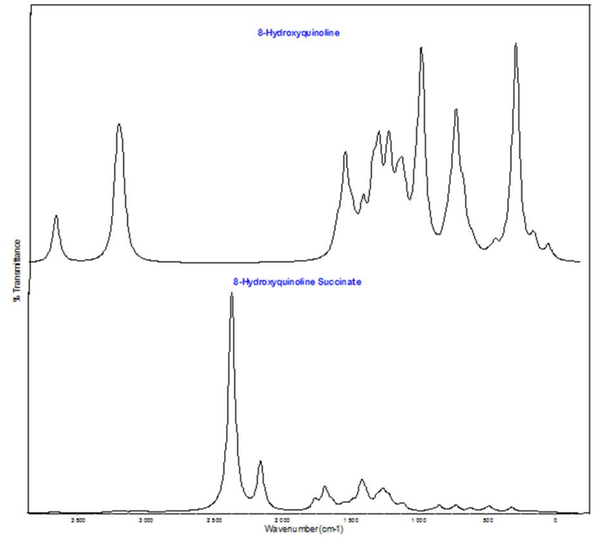

Fig. 2 IR spectra of 8-HQ and 8-HQSC

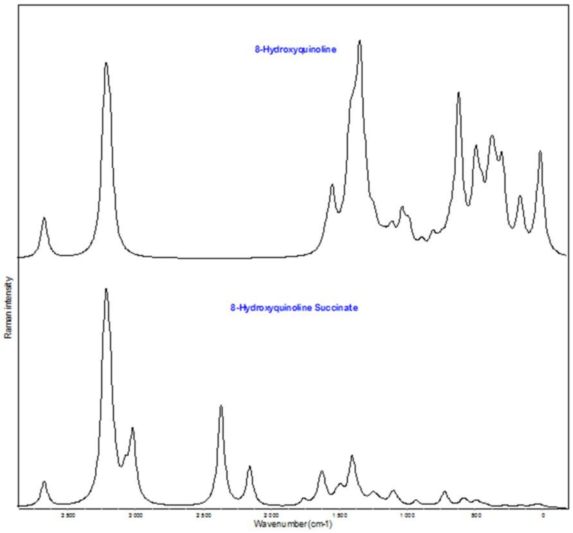

Fig. 3 Raman spectra of 8-HQ and 8-HQSC

Table III
Detailed Assignment Of Fundamental Vibrations Of 8-Hydroxyquinoline

No	Symmetry Species C_S	Observed frequency [Ref 10]		Calculated using B3LYP/6-311G method			Characterization of normal modes
		Infrared	Raman	Frequency (cm^{-1})	IR intensity	Raman activity	
1	A'	3418	--	3688	39.4493	174.2442	OH Stretch
2	A'	3097	--	3197	31.5145	307.2668	C10H Stretch
3	A'	3084	--	3192	36.7406	184.4129	C9H Stretch
4	A'	--	3066	3170	25.6162	143.3291	C7H, C8H Stretch
5	A'	3048	--	3167	10.3337	19.5749	C11H, C10H Stretch
6	A'	--	3019	3160	15.594	119.7586	C5H Stretch
7	A'	--	3003	3157	15.4611	91.6807	C8H, C11H Stretch
8	A'	--	1585	1657	10.6069	2.417	C11C10, C11N2 Stretch
9	A'	1577	--	1632	7.9544	10.349	C9C8, C10C7 Stretch
10	A'	1508	--	1595	54.174	38.5904	C5C3, C11C10 Stretch
11	A'	1472	1475	1551	17.919	3.2791	C5C9, C5C4 Stretch
12	A'	1454	--	1518	4.028	6.1479	OH In plane bending
13	A'	1434	1432	1475	24.5718	48.8213	C10H In plane bending
14	A'	1410	1404	1441	2.4819	32.7303	C11H In plane bending
15	A'	1381	1382	1394	43.874	116.1304	C8C5 Stretch
16	A'	1286	--	1354	57.3398	20.6337	C7H In plane bending
17	A'	1273	1276	1306	5.8492	11.8936	C9N1 Stretch
18	A'	--	1229	1294	63.3758	3.1707	C5C4, C7C3 Stretch
19	A'	1221	--	1251	9.4239	3.2718	C8H In plane bending
20	A'	1206	--	1231	19.0607	3.1143	C5O1, C4N2 Stretch
21	A'	1169	--	1198	32.0379	1.1901	C10H, C9H In plane bending
22	A'	--	1161	1176	6.3397	5.1521	C8H, C11H In plane bending
23	A'	1147	1141	1105	31.3946	16.7081	C5H In plane bending
24	A'	1093	1100	1065	112.562	2.4727	C11H, C8H In plane bending
25	A'	1059	1061	1054	11.922	7.2649	C7H In plane bending
26	A"	1034	--	1021	0.776	0.4964	C9H, C5H, C10H In plane bending
27	A"	974	--	997	0.4162	0.2262	C11H, C8H out of plane bending
28	A"	958	--	969	0.2897	1.3472	C5H, C10H out of plane bending
29	A'	--	951	897	11.6846	2.123	C9H, C7H out of plane bending
30	A"	896	891	896	0.9874	0.8258	OH out of plane bending
31	A"	867	866	849	23.1273	0.5872	C10H, C11H out of plane bending
32	A'	818	--	832	11.2632	0.9562	In plane bending
33	A"	--	808	827	79.5941	0.5774	C7H, C5H out of plane bending
34	A"	781	--	775	31.62	1.0173	C8H, C10H out of plane bending
35	A'	741	--	711	7.8229	30.3592	In plane bending
36	A"	710	707	665	0.7412	0.3332	Ring torsion out of plane
37	A"	636	--	603	0.6398	1.5936	Ring torsion out of plane
38	A'	575	579	591	1.4922	10.9747	C5O In plane bending
39	A'	545	548	551	7.1895	10.9747	In plane bending
40	A'	493	496	497	0.2951	5.2661	Ring torsion out of plane
41	A"	465	464	491	0.0504	0.1473	C5O out of plane bending
42	A'	440	--	472	0.6737	6.1355	C5O In plane bending
43	A"	422	423	444	2.7541	2.5516	In plane bending
44	A"	355	--	394	135.057	4.8773	In plane bending
45	A'	266	268	284	10.2579	1.6713	Butterfly, C5O out of plane bending
46	A"	194	195	268	4.7871	0.9137	Ring torsion out of plane
47	A"	137	--	180	9.7229	0.1523	Ring torsion out of plane
48	A"	98	--	136	0.769	1.3099	Ring torsion out of plane

The detailed frequencies of 8-HQSC with their assignments using B3LYP/6-311G method are reported in Table 4. Absorption bands are appeared at 3671.19 cm^{-1} for O-H stretching vibration and the peaks at 3179 cm^{-1} to 3234 cm^{-1} for C-H stretching. The C-N stretching vibration is observed at 1685 cm^{-1}. C-O-H plane bending vibration peak is assigned at 1476 cm^{-1}. The peaks at 1265, 1243 and 1109 cm^{-1} are found due to the absorption band for C-H in plane bending. The band near 788 cm^{-1} represents the C-H out of plane bending. These bands give significant information about the type of aromatic substitution. The carbonyl anti symmetric stretching vibration band of COO- group is reported at 1550 cm^{-1}. The ring C-C stretching vibration takes place in the region of 1685 cm^{-1} [15]. The band observed at 901 cm^{-1} is coincide with out of plane bending of C-O deformation reported by Dhanya et.al.[16] and Thirumurugan et. al.[9]. The ring breathing mode is assigned for frequencies vary from 1135 cm^{-1} to 1221 cm^{-1} which is in good agreement with the quinolone and isoquinoline. The vibrations 573 cm^{-1}, 588 cm^{-1} and 596 cm^{-1} are assigned to C-O in plane bending vibration which is similar to the quinoline vibrations [17]. The C-C in plane and out of plane bending was observed at 1094 cm^{-1} and 811 cm^{-1}. The ring stretching vibration of quinoline is appeared at 1388 cm^{-1} due to CH_2 deformation. The in plane bending vibrations of quinoline was reported between 500 and 750 cm^{-1} [9]. 763, 726, 712, and 517 cm^{-1} are the observed vibrational frequencies and it represents the position of in plane bending vibrations of quinoline [18].

Table IV
Detailed Assignment Of Fundamental Vibrations Of 8-Hydroxyquinoline Succinate

No	Symmetry Species C_S	Calculated using B3LYP/6-311G method			Characterization of normal modes
		Frequency (cm^{-1})	IR intensity	Raman activity	
1	A	17.704	4.7703	2.1324	
2	A	20.1561	0.0849	4.2526	
3	A	43.3615	1.2506	2.1156	
4	A	53.0698	1.5074	2.3815	
5	A	60.2886	6.3626	0.6632	
6	A	78.7225	4.4232	0.9685	
7	A	98.4331	1.7687	0.9418	
8	A	149.7372	14.0647	1.7833	Ring torsion out of plane
9	A	158.376	2.042	1.4286	
10	A	168.6823	9.1345	1.2512	
11	A	189.3775	0.4449	0.4868	Ring torsion out of plane
12	A	211.9531	17.2501	1.3824	
13	A	261.482	1.2386	1.9407	Ring torsion out of plane
14	A	284.4859	0.4151	2.337	Butterfly, C-O out of plane bending
15	A	315.4841	124.4251	0.8878	
16	A	419.5327	5.2182	5.2244	
17	A	444.755	9.0316	3.0373	In plane bending
18	A	473.7569	71.8554	1.8973	C-O In plane bending
19	A	483.7636	27.8823	8.0535	
20	A	489.0768	2.3909	0.5339	
21	A	493.2749	59.1196	4.4129	Ring torsion out of plane
22	A	517.1057	17.804	2.9363	
23	A	557.5937	0.9324	6.168	
24	A	573.2466	8.77	3.3844	C-O In plane bending
25	A	588.9931	4.213	14.1451	C-O In plane bending
26	A	596.047	6.7392	2.5574	C-O In plane bending
27	A	618.7497	82.0213	0.493	
28	A	648.4574	3.2074	0.184	
29	A	670.6983	0.808	0.2296	Ring torsion out of plane
30	A	712.0108	28.5188	12.0959	In plane ring bending
31	A	726.3639	135.3893	30.7011	In plane ring bending
32	A	763.458	22.4179	0.8622	In plane ring bending
33	A	788.6721	6.0965	0.4678	C-H out of plane bending
34	A	811.1474	3.2219	0.6847	C-C out of plane bending
35	A	829.7912	4.6196	0.4663	C-H In plane bending
36	A	845.3951	78.4139	0.06	C-H out of plane bending
37	A	848.6118	68.1817	3.741	C-H out of plane bending

38	A	901.049	44.5341	0.391	C-O deformation
39	A	921.5914	1.8191	0.74	OH out of plane
40	A	931.972	4.2592	14.9542	C-C Stretch
41	A	982.1853	1.4416	0.5616	C-H out of plane bending
42	A	1012.1852	0.0239	0.7336	C-H twisting
43	A	1032.50	0.8316	0.3784	C-H twisting
44	A	1055.3228	2.883	1.2055	
45	A	1061.79	0.2874	1.848	
46	A	1064.718	5.5046	5.2345	
47	A	1094.3708	2.2443	20.628	C-C in plane bending
48	A	1109.5658	137.8005	19.6538	C-H In plane bending
49	A	1135.8563	62.4353	1.6332	In plane bending ring
50	A	1165.4514	35.669	2.2518	In plane bending ring
51	A	1186.2482	4.5663	6.451	In plane bending ring
52	A	1212.8627	256.9344	7.4529	In plane bending ring
53	A	1221.7421	1.8444	1.7833	In plane bending ring
54	A	1243.6844	128.5237	20.8728	C-C Stretch; C-H in plane bending
55	A	1259.9714	67.7117	3.2453	C-C Stretch; C-H in plane bending
56	A	1261.1842	151.9825	1.6521	C-H In plane bending
57	A	1265.0347	93.747	6.1412	C-H In plane bending
58	A	1297.9659	253.547	3.031	C-C Stretch
59	A	1315.1723	5.4672	0.9914	CH_2 Wagging
60	A	1342.1056	20.0742	13.3958	CH_2 Twisting
61	A	1347.2734	19.1216	4.0157	C-C Stretch
62	A	1373.6268	80.3438	12.0537	Asymmetry COO^- Stretching
63	A	1388.1458	156.8427	8.1857	Ring stretch
64	A	1399.9736	73.0545	58.3957	C-C Stretch
65	A	1409.7217	73.2905	61.9312	In plane bending
66	A	1419.2441	542.7768	0.8832	Wagging
67	A	1476.6181	76.4168	13.015	C-O-H plane bending
68	A	1487.4443	78.0765	18.6307	In plane bending ring
69	A	1508.5421	0.738	16.2588	CH_2 symmetry stretch
70	A	1520.6674	30.8446	9.3289	In plane bending ring
71	A	1524.4133	20.6308	1.199	CH_2 symmetry stretch
72	A	1550.4135	121.8452	2.5442	Anti-symmetry COO^- group
73	A	1612.6288	42.7094	36.8778	C-C Stretch
74	A	1631.0969	13.9091	56.5387	C-C Stretch
75	A	1638.6294	136.6119	9.6169	C-C Stretch
76	A	1685.2279	575.2508	3.9248	C-C, C-N Stretch
77	A	1759.0941	257.989	18.2197	COO Stretch
78	A	2157.0276	1235.975	106.9134	COO Stretch; OH Stretch
79	A	2369.0515	5683.2459	277.3536	OH Stretch
80	A	3017.2281	5.2265	150.2304	CH_2 rocking
81	A	3027.6895	17.1555	39.0364	CH_2 Symmetrical Stretching
82	A	3073.2668	19.3408	64.8093	CH_2 Symmetrical Stretching and rocking
83	A	3141.1116	2.4908	26.9589	CH_2 Asymmetrical Stretching
84	A	3179.1	3.8786	55.3858	CH Stretch
85	A	3184.2364	3.9848	85.8094	CH Stretch
86	A	3197.6576	20.2462	177.0382	CH Stretch
87	A	3217.8745	9.8881	60.2354	CH Stretch
88	A	3218.2467	0.594	236.2681	CH Stretch
89	A	3234.2359	1.1029	164.5032	CH Stretch
90	A	3671.1951	15.5036	68.4411	OH Stretch

C. NMR spectral analysis

NMR chemical shifts calculations of 8-HQ have been carried out by using B3LYP/6-311G GIAO (Gauge Including Atomic Orbital) method. GIAO method is somewhat superior since it exhibits a faster convergence of the calculated properties upon extension of the basis set used [19]. GIAO method is one of the most common approaches for calculating isotropic nuclear magnetic shielding tensors [20]. The chemical shifts are used to identify the organic compounds and ionic species. It is helpful to recognize the accurate predictions of optimized molecular geometrics for the reliable calculations of magnetic properties [21]. The NMR spectrum of 8-HQ and 8-HQSC is presented in Fig. 4.

In 8-HQ, the observed chemical shift of the carbon atoms was identified from 17.8577 ppm to 70.1716 ppm. The chemical shift value of hydrogen atoms was reported from 23.4832 ppm to 28.9341 ppm. The chemical shift of oxygen atom is 185.9363 ppm. The negative chemical shift values of -145.5869 ppm do exist for nitrogen atom. This is due to the strong shielding effect of the macrocyclic aromatic ring current on protons inside the macrocycle oppose the protons outside the macrocycle.

In the case of 8-HQSC, the observed chemical shift of the carbon atoms was identified from 0.0939 ppm to 154.041 ppm. The peak appeared in 154.041 ppm clearly indicates the presence of imine carbon. An imine is a functional group of C-N double bond. The chemical shift value of hydrogen atoms was reported from 25.686 ppm to 31.802 ppm. The chemical shift of oxygen atom varies from -198.067 to 127.993ppm. The chemical shift value nitrogen atom appears at 82.095 ppm. It is interesting to note that the NMR signals for 8-HQSC which was found in the experimental spectrum showed its presence in the computed NMR spectrum.

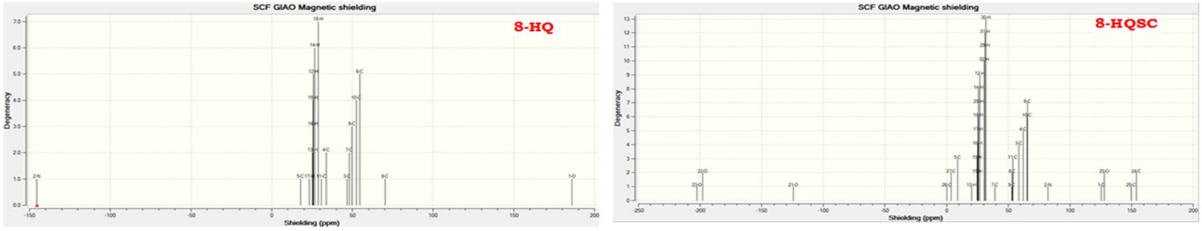

Fig. 4 NMR spectrum of 8-HQ and 8-HQSC

D. UV Spectral Analysis

Computation of UV spectra using B3LYP/6-311G is able to detect accurate absorption wavelengths at a relatively small computing time which is correspond to vertical electronic transitions computed on the ground state geometry. The UV-VIS spectrum of 8-HQ and 8-HQSC is shown in Fig. 5. The experimental and theoretical excitation energies, absorption wavelength and oscillator strength are noted in Table 5. These transitions are on the basis of major contribution of molecular orbitals. The orbitals contributions ≤ 10% are neglected [22]. Experimentally measured absorption wavelengths of 8-HQ are good in agreement with the theoretical wavelengths 274, 315, 340, and 408 nm. Energy gap of 8-HQ is obtained theoretically by DFT method is 4.52 eV and from HOMO-LUMO diagram is 4.53 eV.

Optical transmission range and the cutoff wavelength are very important factor for optical application. The energy gap of the 8-HQSC corresponding to the cutoff wavelength 434.39 nm, 241.7 nm, 192.87 nm is 2.85 eV, 5.13 eV and 6.43 eV respectively. The group contributions to the molecular orbital and the density of state (DOS) are calculated using Gauss-sum 2.2 program [23]. The calculated TDOS diagram of 8-HQ and 8-HQSC is shown in Fig. 6. The DOS spectra were produced by convoluting the molecular orbital information with Gaussian cures of unit height [24].

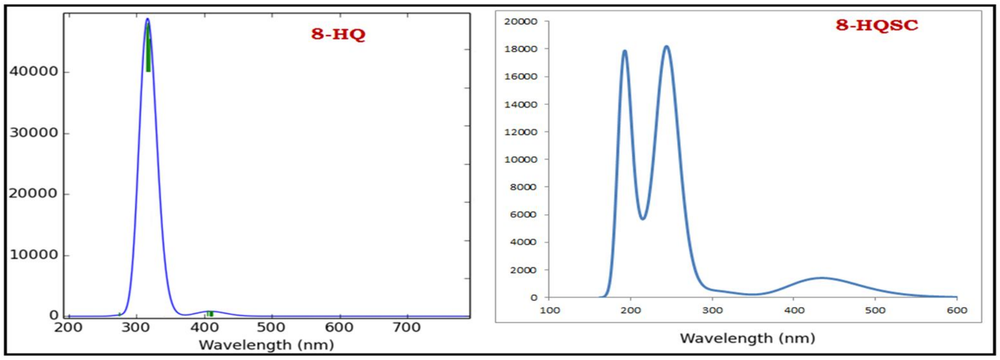

Fig. 5 UV-VIS spectrum of 8-HQ and 8-HQSC

Table V
The Experimental and Theoretical Excitation Energies, Absorption Wavelength and Oscillator Strength.

λmax (nm)	Band gap (eV)	Energy (cm-1)	f
8-Hydroxyquinoline			
274.03	4.52	36492	0.0024
315.43	3.93	31701	0.0747
340.35	3.64	29381	0.0024
408.84	3.03	24458	0.0014
8-Hydroxyquinoline Succinate			
192.87	6.43	50830.26	0.0226
241.7	5.13	6297.554	0.0028
434.39	2.85	78269.6	0.0348

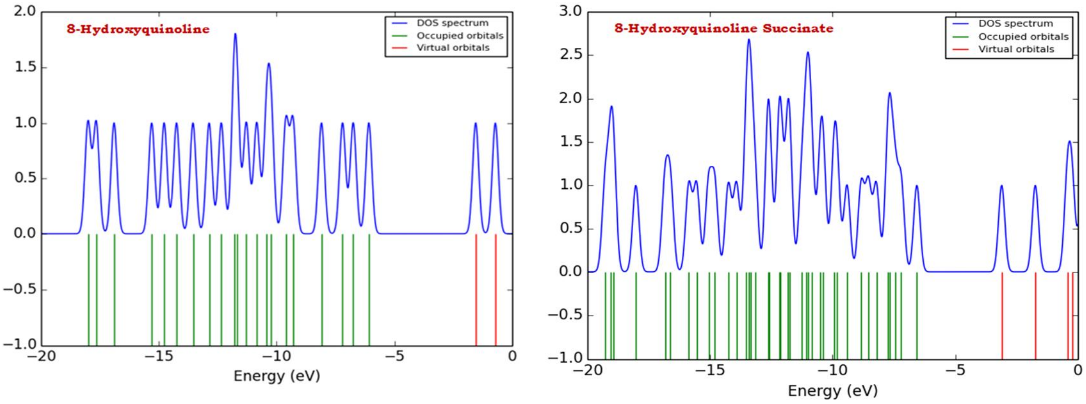

Fig. 6 The calculated TDOS diagram of 8-HQ and 8-HQSC

E. Chemical Reactivity Studies

The highest occupied molecular orbitals and the lowest unoccupied molecular orbitals are the main orbital taking part in chemical reactions of the molecules called as Frontier molecular orbitals (FMOs) [25]. The HOMO behaves as an electron donor and LUMO acts an electron acceptor. The molecular orbital analysis provides a platform for understanding the phenomenon of charge transfer through optical molecular excitations [26]. The chemical hardness and reactivity of 8-Hydroxyquinoline (8-HQ) and 8-Hydroxyquinolinium succinate (8-HQSC) can be predicted from HOMO-LUMO energy gap. Calculated quantum molecular descriptors of 8-HQ and 8-HQSC compounds are presented in Table 6.

The HOMO and LUMO energies of 8-Hydroxyquinoline are -6.08 eV and -1.55 eV respectively. The energy gap between the HOMO and LUMO shows the molecular chemical stability [27]. The energy gap of 8-HQ is 4.53 eV. The ionization energy (I) and electron affinity (A) can be expressed through HOMO and LUMO orbital energies as $I = -E_{HOMO} = 6.08$ eV and $A = -E_{LUMO} = 1.55$ eV. The global hardness (η) is predicted by the relation $\eta = (I-A)/2 = 2.265$ eV. The electron affinity can be used in combination with ionization energy to give electronic chemical potential $\mu = -(E_{HOMO} + E_{LUMO})/2 = 3.815$ eV. Considering the chemical hardness, if one molecule has large HOMO-LUMO gap, it is a hard molecule or small HOMO-LUMO gap it is a soft molecule. The global electrophilicity index (ω) is calculated in terms of chemical potential and the hardness as $\omega = -(\mu^2/2\eta) = -3.212$ eV and assess the lowering of energy due to maximal electron flow between donor and acceptor. The inverse of the hardness is expressed as the global softness $S=(1/\eta) = 0.441$. $\Delta N_{max} = -\mu/\eta = -1.68$ is the maximum amount of electronic charge that the electrophile system may accept.

In the 8-HQSC compound, the HOMO and LUMO energies are -6.56 eV and -3.1 eV respectively. The energy gap of 8-HQSC is 3.46 eV. The ionization energy (I) and electron affinity (A) of the 8-HQSC is $I = -E_{HOMO} = 6.56$ eV and $A = -E_{LUMO} = 3.1$ eV. The global hardness (η) is $\eta = (I-A)/2 = 1.73$ eV. The electronic chemical potential is found to be $\mu = 4.83$ eV. The global electrophilicity index (ω) of 8-HQSC is -6.74 eV. The global softness is calculated using the relation $S=(1/\eta) = 0.578$. The maximum amount of electronic charge ΔN_{max} is -2.79.

Table VI
Calculated Quantum Molecular Descriptors Of 8-HQ and 8-HQSC Compounds

S.No.	Parameters	Values	
		8-HQ	8-HQSC
1	E_{HOMO} (a.u)	-6.08	-6.56
2	E_{LUMO} (a.u)	-1.55	-3.1
3	IA: Ionization energy = - E_{HOMO} (eV)	6.08	6.56
4	EA: Electron affinity = - E_{LUMO} (eV)	1.55	3.1
5	E_g: Energy gap = E_{HOMO} - E_{LUMO} (eV)	4.53	3.46
6	η: Hardness =Energy gap/2 (eV)	2.265	1.73
7	μ: Electronic chemical potential = (E_{HOMO} + E_{LUMO})/2 (eV)	3.815	4.83
8	ω: Electrophilicity index=$\mu^2/2\eta$	-3.212	-6.74
9	S: softness =(1/ η)	0.441	0.578
10	χ: Electro negativity = -μ	-3.815	-4.83
11	ΔN_{max}=-μ/η	1.68	-2.79

F. Mulliken Atomic Charges

The binding capacity and the molecular conformation are greatly depending on the electric charges of the atoms [28-30]. The bar diagram of Mulliken charge distribution is shown in Fig. 7. In the case of 8-HQ, the atom O1 and N2 presents a strong electronegativity. All hydrogen atoms have a net positive charge. In particular, the hydrogen atom H18 has large net positive charge. In the 8-HQSC, Totally 13 carbon atoms are present. Among these atoms, six atoms have positive charge value and seven have negative charge value. The atoms C3 (-0.135) and C10 (-0.263) enforce a small positive charge on C7 (0.004). All the hydrogen atoms present less positive charge except H13 which confirms the electron movement through the nitrogen atom to the quinoline ring. The atom N2 shows the largest electronegativity and the atom C27 shows the largest electro positivity. Negative charge is observed for oxygen atoms and highest negative value of oxygen (-0.628) is observed in quinoline ring. Thus analysis of Mulliken atomic charges reveals the extensive intermolecular charge transfer in the molecule.

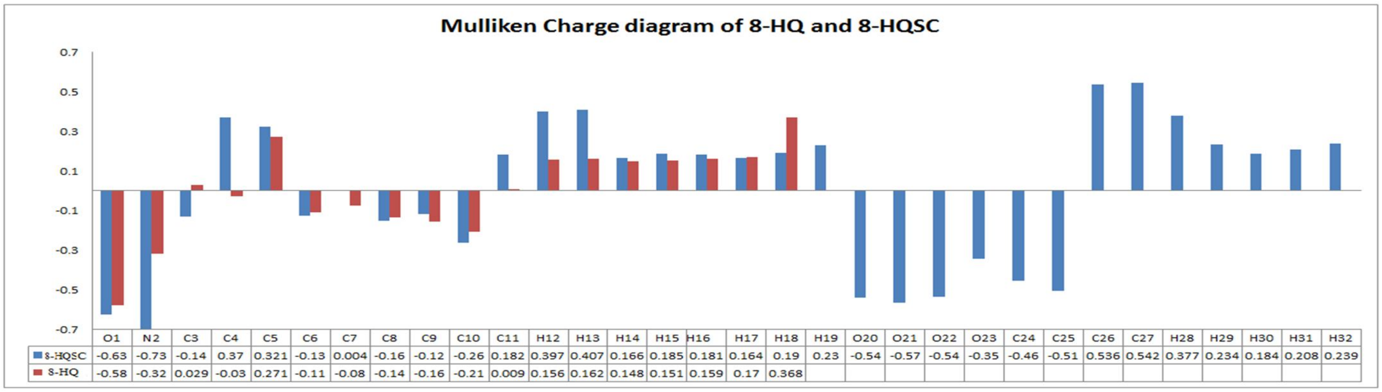

Fig. 7 The bar diagram of Mulliken charge distribution

IV. CONCLUSIONS

The optimized stable molecular structure of 8-HQ and 8-HQSC were calculated using B3LYP/6-311G basis set. Nearly identical C-C bonds indicate the complete delocalization of π -electrons in the individual hetero atom rings. The dihedral angle between 8-hydroxyquinolinium cation and succinate anion are 8.8499° coincide with the already existing report. It indicates that they are essentially planar. 8-HQSC crystal is stabilized by the hydrogen bonds N2-H13….O22 and O22-H12….O1 formed by the existence of complementary functional groups. The results of observed and calculated IR and Raman frequencies yield good agreement. The negative chemical shift values of -145.5869 ppm do exist for nitrogen atom in 8-HQ. This is due to the strong shielding effect of the macrocyclic aromatic ring current on protons inside the macrocycle oppose the protons outside the macrocycle. In the case of 8-HQSC, the peak appeared in 154.041 ppm clearly indicates the presence of imine carbon. An imine is a functional group of C-N double bond. Energy gap of 8-HQ is obtained theoretically by DFT method is 4.52 eV and from HOMO-LUMO diagram is 4.53 eV. The energy gap of the 8-HQSC corresponding to the cutoff wavelength 434.39 nm, 241.7 nm, 192.87 nm is 2.85 eV, 5.13 eV and 6.43 eV respectively. All the hydrogen atoms in 8-HQSC present less positive charge except H13 which confirms the electron movement through the nitrogen atom to the quinoline ring.

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