

Study of Density Functional Theory on Hydrogen Bonding Interaction of 7-Hydroxyquinoline-(MeOH)_n (n = 1,2)

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7-Hydroxyquinoline-methanol interactions have been employed to investigate 7-HQ-(MeOH)_n (n = 1,2) complexes using density functional theory B3LYP method at 6-311G* basis, obtaining 8 and 10 minima of ground states for 7-hydroxyquinoline-methanol and 7-hydroxyquinoline-(methanol)₂ complexes, respectively. The fully optimized geometries and binding energies $\Delta E''$ are reported, including corrections of the basis set superposition error and zero point energies for various stable points. The most stable configuration is the six-membered ring complex that consist of O-H¹...O and C-H...O H-bonds for 7-hydroxyquinoline-methanol complex. The most stable configuration is the complex that consists of three ring and five H-bonds for 7-hydroxyquinoline-(methanol)₂ complexes. Their corresponding binding energies are 26.85 and 65.60 kJ/mol, respectively, after the basis set superposition error and zero-point vibrational energy corrections.

Key Words: Density functional theory, 7-Hydroxyquinoline, H-Bond, BSSE.

INTRODUCTION

Intermolecular force exists in all chemical and biologic system, by which some specific physiological functions are realized. H-Bond is one of the most popular intermolecular chemical interaction forces¹⁻⁴. Aromatic molecules, for example, have both acidic and basic functional groups which involve in two proton acceptors of N atom with π -electron in it and O atom with isolated paired electron in it and thus they can form H-bond networks which play an important role in transferring substances such as protons and ions in polar solvents such as water, ammonia or methanol^{5,6}. 7-Hydroxyquinoline is a typical aromatic compound having such kind of acidic and basic functional groups.

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Nakagawa *et al.*⁷ ever reported that protons can be transferred in excited state in methanol solution. Kwon *et al.*⁸ studied the tautomerization dynamics of 7-hydroxyquinoline in excited-state in reverse micelles. Experimentally, proton transference was also extensively explored along with formation of H-bond⁹⁻¹³.

In methanol, 7-hydroxyquinoline is no longer symmetrical in configuration between methyl and hydrogen atoms in hydroxyl. There are some new characteristics in formation of H-bond complexes, such as steric effect. It is a valuable subject for 7-hydroxyquinoline-methanol [7-HQ-(MeOH)_n (n = 1,2)] interactions. There is no literature about how to form complexes between 7-hydroxyquinoline and methanol. In this paper, we will report the results when the 7-hydroxyquinoline-methanol [7-HQ-(MeOH)_n (n = 1, 2)] interactions are employed to investigate 7-HQ-(MeOH)_n (n = 1, 2) complexes using density functional theory B3LYP method at 6-311G* basis.

Calculation methodology

Density functional theory was applied with Gaussian 03 program¹⁴. The geometries of monomers and all possible complexes between 7-hydroxyquinoline and methanol were fully optimized at B3LYP/6-311G* levels. The result is illustrated in Fig. 1 (A to O). For each species, zero point energies, corrections of the basis set superposition error and zero-point vibration energy corrections were computed for various stable points. Boys and Bernardi's Counterpoise procedure was applied to calculate BSSE, obtaining binding energies of complexes between 7-hydroxyquinoline and methanol¹⁵. After corresponding binding energies, the calculating formula is:

$$\Delta E_c = E_{AB} - E_A(B) - E_B(A) \quad (1)$$

with E_{AB} , $E_A(B)$ and $E_B(A)$ for the binding energies of complex AB, binding energy of monomer A of all atom nuclear B as ghost atom involving virtual orbit and binding energy of monomer B of all atom nuclear A as ghost atom involving virtual orbit, respectively. Then atoms in molecules (AIM) analysis^{16,17} were studied to clarify the properties and characteristics of hydrogen bond in all these complexes.

RESULTS AND DISCUSSION

The fully optimized geometries and computed frequency are obtained for all monomers and possible complexes between 7-hydroxyquinoline and methanol, obtaining 8 and 10 minima of ground states for the 7-HQ-(MeOH) and 7-HQ-(MeOH)₂ complexes, respectively. Their geometries configuration and structure parameter are shown in Fig. 1. AIM analysis was carried out to calculate the charge densities of critical points of H-bond, as shown in the circle brackets in Fig. 1. H-bond is present in all the 18 complexes

between 7-hydroxyquinoline and methanol. Bond lengths and bond angles of all the H-bonds ranged from 0.17 to 0.27 nm and from 110° to 180°, respectively. Total energy (E/a.u.), zero-point energy (a.u.), BSSE (a.u.), interaction energy ΔE , $\Delta E'$, $\Delta E''$ (KJ/mol) and dipole moments (10^{-30} C·mol) are listed in Table-1 for all the monomers and complexes between 7-hydroxyquinoline and methanol. Here the relationships between the energies are expressed by

$$\Delta E = E_{\text{complex}} - E_{\text{methanol}} - E_{7\text{-Hydroxyquinoline}} \quad (2)$$

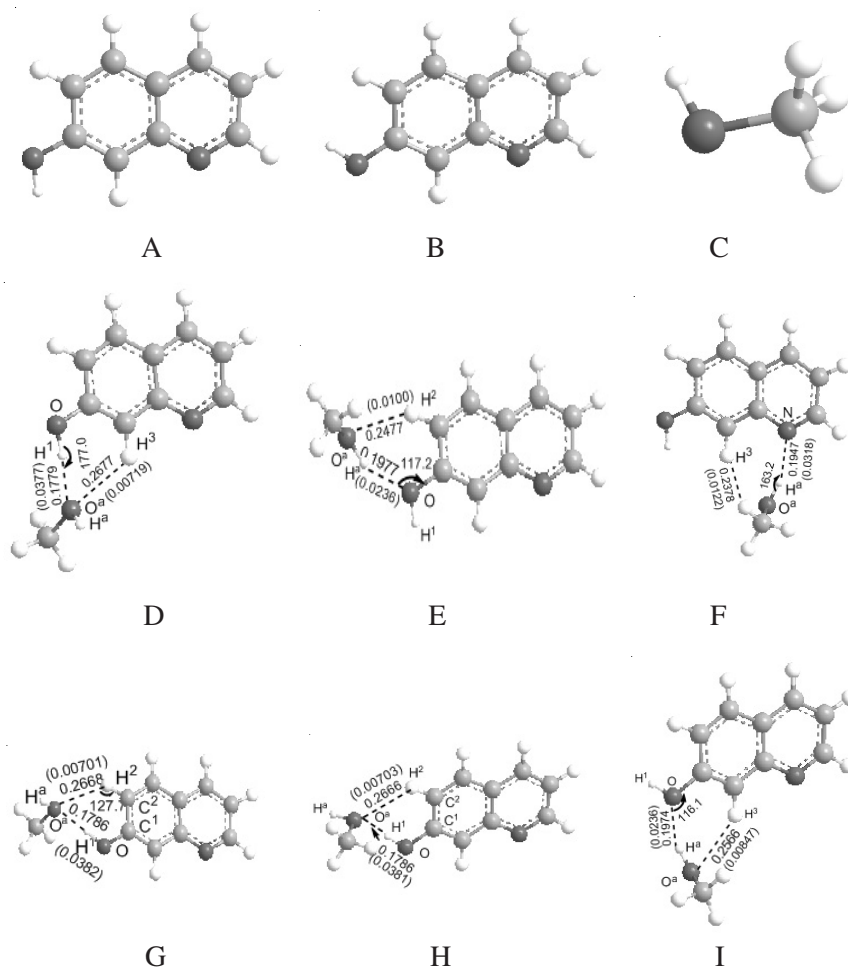
and

$$\Delta E' = \Delta E + \text{BSSE} \quad (3)$$

Binding energies corrections of the basis set superposition error.

$$\Delta E'' = \Delta E + \text{BSSE} + \Delta ZPE \quad (4)$$

Binding energies corrections of the basis set superposition error and zero-point vibrational energy corrections.



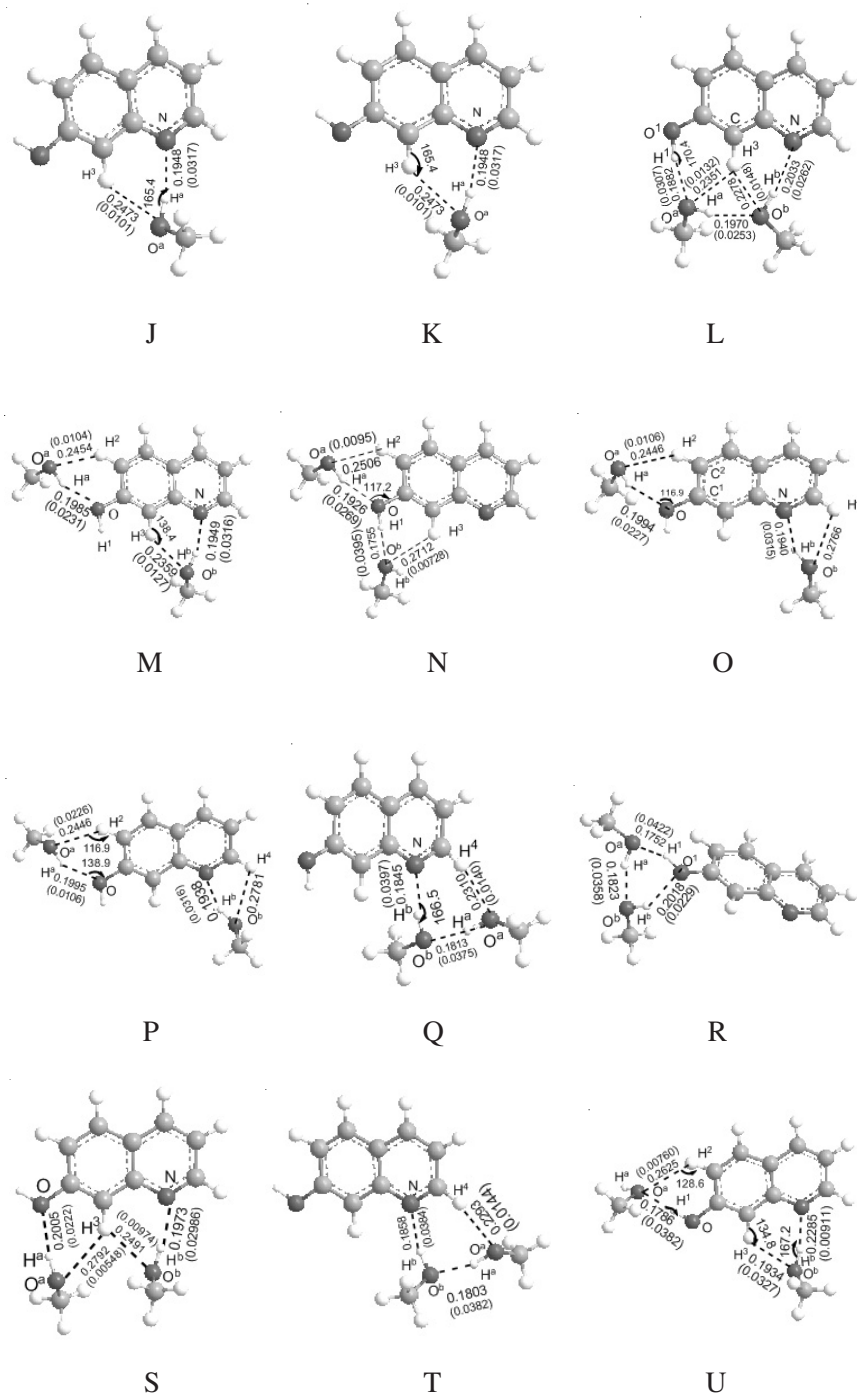


Fig. 1. Hydrogen bonding structure for ground state of 7-HQ-(MeOH)_n

Stability analysis of 7-HQ-(MeOH)_n

D, G and H are stable structures in all 7-hydroxyquinoline-(methanol)₁ [7-HQ-(MeOH)] complexes. Hydroxy group of 7-hydroxyquinoline is combined with oxygen atom in methanol to form H-bond. Their common characteristics are to form six-members ring with C-H bond in 7-hydroxyquinoline ring, in which hydrogen and methyl in methanol are outside of upper side and underside of the ring, respectively, to reduce repulsion with H-bond. The corresponding binding energy (D) is 26.85 KJ mol⁻¹, the lowest in all complexes. For the coplane of hydroxy group in methanol with 7-hydroxyquinoline ring, methyl in methanol is above the H-bond plane in I, resulting in repulsion with H-bond and the corresponding binding energy of complex I is the largest one and complex I is the most unstable in all 7-HQ-(MeOH) complexes. The corresponding binding energy of J is approximately equal to that of K owing to their similar structure. The relationship between G and H is the same as that between J and K. The average corresponding binding energy of all 7-HQ-(MeOH) complexes is 19.28 KJ mol⁻¹. The results presented in Table-1 and Fig. 2 show that the sequence in stability of the above-mentioned complexes is D > G ≈ H > F > K ≈ J > E > I.

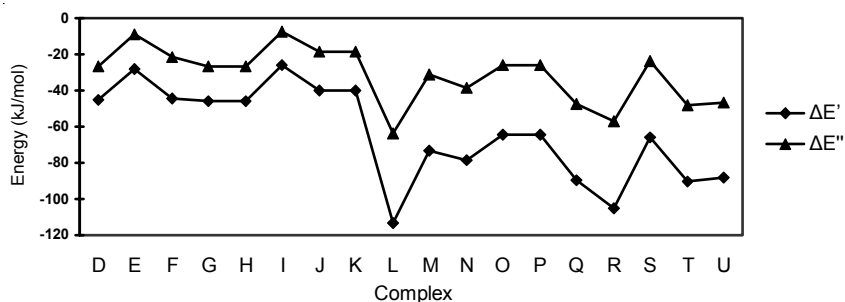


Fig. 2. Energy of complex

The corresponding binding energy of L, which consists of five H-bonds and three rings (one four-members ring and two six-members ring), is 63.60 KJ mol⁻¹. L can form hydrogen bridge bond networks and it is the most stable configuration in all 7-HQ-(MeOH)₂ complexes. On contrast, S is the most unstable configuration in all 7-HQ-(MeOH)₂ complexes, which consists of two six-members rings due to its steric effect. O, P, Q and T have the same relationship as that of J and K. The average binding energy of all 7-HQ-(MeOH)₂ complexes is 40.94 KJ mol⁻¹. For all the 7-HQ-(MeOH)₂ complexes, the sequence of the stability is L > R > T > Q > U > N > M > P ≈ O > S.

TABLE-1
 CALCULATED TOTAL ENERGY (E/a.u.), ZERO-POINT ENERGY (a.u.), BSSE
 (a.u.), INTERACTION ENERGY ΔE , $\Delta E'$, $\Delta E''$ (KJ/mol) AND DIPOLE MOMENT
 (10^{-30} C.mol) FOR MONOMER AND 7-HQ-(MeOH)_n, $\Delta E' = \Delta E + \text{BSSE}$,
 $\Delta E'' = \Delta E + \text{BSSE} + \Delta \text{ZPE}$

No.	E	ΔE	BSSE	ZPE	$\Delta E'$	$\Delta E''$	Dipole moment
A	-477.2539706	–	–	0.139511	–	–	0.9016
B	-477.2517154	–	–	0.139217	–	–	3.5914
C	-115.7465130	–	–	0.051312	–	–	1.8061
D	-593.0176618	-45.10	0.0048596	0.192915	-32.34	-26.85	2.9419
E	-593.0113150	-28.44	0.0052279	0.192945	-14.71	-9.14	1.5895
F	-593.0174834	-44.63	0.0060651	0.193440	-28.71	-21.84	3.0599
G	-593.0158589	-46.29	0.0051292	0.192981	-32.82	-26.38	6.0732
H	-593.0158589	-46.29	0.0051346	0.192990	-32.81	-26.35	6.0685
I	-593.0080935	-25.90	0.0051624	0.192487	-12.35	-7.21	5.2752
J	-593.0135604	-40.25	0.0059279	0.192983	-24.69	-18.25	5.5731
K	-593.0135603	-40.25	0.0059244	0.192982	-24.70	-18.26	5.5701
L	-708.7900499	-113.04	0.0126846	0.248278	-79.73	-63.60	2.8339
M	-708.7748760	-73.20	0.0112810	0.246901	-43.58	-31.07	3.0119
N	-708.7767999	-78.25	0.0105847	0.246597	-50.46	-38.74	3.9973
O	-708.7715445	-64.45	0.0102845	0.246466	-37.45	-26.08	2.4984
P	-708.7715765	-64.53	0.0102417	0.246458	-37.64	-26.29	1.5808
Q	-708.7811792	-89.75	0.0111756	0.247079	-60.40	-47.42	3.2440
R	-708.7848010	-105.18	0.0122458	0.247894	-73.03	-57.13	3.1760
S	-708.7698853	-66.02	0.0116120	0.246238	-35.53	-23.98	6.6431
T	-708.7792855	-90.70	0.0110837	0.246853	-61.60	-48.44	5.8878
U	-708.7782770	-88.05	0.0108619	0.246730	-59.53	-46.69	7.4398

After comparison between the binding energies of all the 7-HQ-(MeOH)₂ complexes and those of all the 7-HQ-(MeOH) complexes, it should be noted that: (1) the ratio of corresponding binding energies of the most stable configuration is 63.60/26.85 \approx 2.37; (2) the ratio of average corresponding binding energies is 40.94/19.28 \approx 2.12; (3) the complexes will become more stable with increasing methanol mass.

Characteristics of hydrogen bond

There are five kinds of H-bonds in all the complexes. Their average bond lengths are 0.1815 nm for O–H \cdots O, 0.1903 nm for H–O \cdots H, 0.1984 nm for C–O \cdots H, 0.2033 nm for O–H \cdots N and 0.2521 nm for C–H \cdots O, respectively. They become weaker and weaker in the above-mentioned. It is obvious that interaction of O–H \cdots O H-bond is the strongest and that of C–H \cdots O H-bond is the weakest. The length of C–H \cdots O H-bond is in the

range of 0.24 to 0.27 nm. But the bond lengths of C-H^a...O^a and C-H^b...O^b H-bond are 0.2351 and 0.2278 nm in L, respectively. The reason may be that there are bridge H-bond networks in them.

AIM analysis

AIM analysis is carried out to calculate the charge density of critical points of H-bond. The results are shown in the circle bracket by H-bond in Fig. 1. Based on Propelier's criterion of H-bond^{18,19}, with the charge density of critical points of H-bond $\rho_b \approx 0.002 \sim 0.035$ au, it can be safely concluded that H-bonds are present in all the 7-HQ-(MeOH)_n (n = 1, 2) complexes.

In all the 7-HQ-(MeOH)_n (n = 1, 2) complexes, the average charge densities of critical points of O-H...O, H-O...H, O-H...N, C-O...H and C-H...O H-bonds are 0.0363, 0.0280, 0.0327, 0.0234 and 0.0148 au, respectively. It is primarily in accordance with interaction of five H-bonds in all the 7-HQ-(MeOH)_n (n = 1, 2) complexes.

The interaction between two H-bonds also exists in all the [7-HQ(MeOH)] complexes. There are two new (3, -1) bond critical points and a (3, +1) ring critical point in each complex. The charge density of (3, +1) ring critical point ranged from 0.0067 to 0.0084 au. The average charge density of (3, +1) ring critical points is 0.0071 au. As a result, all [7-HQ(MeOH)] complexes are six-member ring complexes consisting of two H-bonds.

It is more complicated to compare the structures of [7-HQ(MeOH)₂] with that of [7-HQ(MeOH)]. L is a complex with three rings. In this complex, the charge densities of the ring critical points of the left ring, the middle ring and the right ring are 0.0094, 0.010 and 0.0094 au, respectively. All the three rings are stable. The interaction of H-bond is the strongest one in all the [7-HQ(MeOH)₂] complexes. Two-rings complexes are also present and each complex has six-members ring. The charge densities of critical points of (3, +1) rings, such as M, N, S and U, are in the range of 0.0052 to 0.0084 au. The charge densities of ring critical points of Q and T are 0.0039 and 0.0043 au, respectively. Both are a ring complex with seven-members ring. They are more stable than S because of their less steric effect. R is a complex with six-members ring, combined hydroxy in 7-hydroxy quinoline with two hydroxy groups in methanol. Its charge density of ring critical points is 0.0088 au.

Conclusion

7-Hydroxyquinoline-(methanol)_n (n = 1, 2) interaction was employed to prove the presence of H-bonds in complexes using density functional theory B3LYP method at 6-311G* basis, obtaining 8 and 10 minima of ground states for 7-hydroxyquinoline-methanol and 7-hydroxyquinoline-(methanol)₂ complexes, respectively. The fully optimized geometries and

binding energies $\Delta E''$ are reported, including corrections of the basis set superposition error and zero point energies for various stable points. The stable configuration is the six-membered ring complex that consists of O–H¹...O and C–H...O H-bond among 7-hydroxyquinoline-methanol complexes. Among 7-hydroxyquinoline-methanol complexes, the sequence of stability is D > G \approx H > F > K \approx J > E > I. The most stable configuration is the complex that consists of three ring and five H-bonds among 7-hydroxyquinoline-(methanol)₂ complexes. Among 7-hydroxyquinoline-(methanol)₂ complexes, the sequence of stability is L > R > T > Q > U > N > M > P \approx O > S. The corresponding binding energies of the most stable configurations in the series of 7-hydroxyquinoline-methanol and 7-hydroxyquinoline(methanol)₂ complexes are 26.85 and 65.60 kJ/mol, respectively, after the basis set superposition error and zero-point vibrational energy corrections. The stability of complexes becomes stronger with increasing methanol mass.

ACKNOWLEDGEMENT

The authors are thankful for the support from the National Natural Science Foundation, China (account number 20503018).

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