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Interaction Between Cucurbit[8]uril and HCl Salts of 3,4,7,8-Tetramethyl-1,10-phenanthroline

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To explain ^{1}H NMR results where two different inclusion orientation isomer complexes of cucurbit[8]urils (Q[8], host) and protonated 3,4,7,8-tetramethyl-1,10-phenanthroline (guest) were observed. The STO-3G and B3LYP/3-21G* calculations were performed on the inclusion complexes of cucurbit[8]urils (Q[8], host) and protonated or free 3,4,7,8-tetramethyl-1,10-phenanthroline (guests). The results of ab initio and DFT energy calculations reveal that the "*anti*-" orientation was a preponderant alternative structure in 1:2 complexes of Q[8] and the guest, and the inclusion complexes were stabilized by protonation of the guest. The pH influence was investigated which further confirmed these calculation results by electronic absorption spectroscopy.

Keywords: Cucurbiturils; Inclusion complexes; ^{1}H NMR; Quantum chemistry calculations; UV-vis spectra

INTRODUCTION

Since the unique structure of the cucurbituril (Q[6]) was reported by Mock and co-workers in 1981 [1], Kim and Day have contributed to substantive studies on full characterization of a series of new Cucurbit[n, $n = 5 \sim 8$, 10]urils, (Q[5], Q[7], Q[8] and Q[10]) [2–5], which are macrocyclic cagelike oligomers synthesized from glycoluril and formaldehyde with acid catalysis. These macrocyclic display a range of novel properties and potential applications including gas encapsulation by Q[5] [6,7], interaction of Q[7] with some small cage compounds [8,9], viologen and its derivatives [10–13], and the special ability of Q[8] to simultaneously bind two aromatic guests [14–17]. The Q[n]s chemistry has expanded dramatically with these new members of the Qs family [18–24].

Kim and co-workers have studied the relative stabilities of the cucurbituril homologues and their methyl derivatives by using *ab initio* method and density functional theory (DFT) calculation, which predicted and confirmed the synthetic outcome of cucurbit[n]urils [25]. In a recent publication, Pichierri reported molecular structures of cucurbituril, its sulfur analogue and tubular molecular formation by the *thia*-cucurbit coordination with transition metal ions using theoretical methods [26,27].

In this paper, we illuminate the stability of double guest inclusion of two isomers of "*syn*-" and "*anti*-" of protonated 3,4,7,8-tetramethyl-1,10-phenanthroline (Scheme 1) in Q[8] [28–31] and also illustrate the influence of the protonation of the guest on the stability of the inclusion complexes by using *ab initio* methods, DFT calculations and experimental evidence. The *ab initio* energy calculations reveal that the "*anti*-" orientation isomer was a preponderant alternative structure in 1:2 complexes of Q[8] and the guest, and the inclusion complexes were stabilized by protonation of the guest, such as the fully protonated guest **1**, partially protonated guest **2** (**3** is free guest). The pH influence investigation by electronic absorption spectroscopy further confirmed these calculation results.

RESULTS AND DISCUSSION

^{1}H NMR Study on Host-guest System

Figure 1 shows the ^{1}H NMR spectra of the guest(HCl salt) in D_2O recorded in the absence (top) and in the presence (bottom) of 2 equivalents of Q[8]. The spectrum shows a complex set of resonances with as many as eight aromatic proton resonances and eight CH_3 resonances. A likely explanation based upon the

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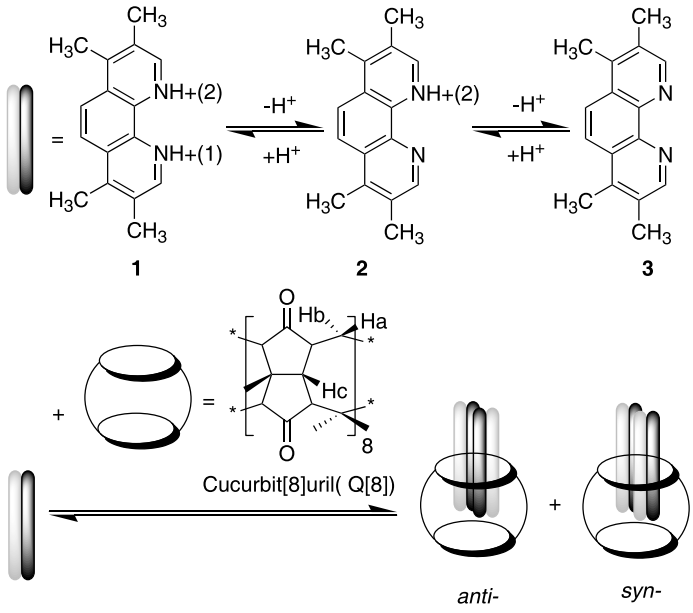

SCHEME 1 Models of Q[8], Guests and inclusion complexes.

number of resonances suggests the existence of orientation isomers of a type shown in Scheme 1. The two isomers in the Q[8]-guest system originate from the formation of orientation isomers of the guest as "*anti-*" or "*syn-*" π−π stacked pairs [31].

The signals marked with "*" for the major isomer appear at δ1.63, 1.93, 2.43 and 2.61 for four methyl groups, and the aromatic protons at δ6.91, 7.21, 7.92 and 8.96 ppm, while the signals marked with "#" for the minor isomer appear at δ1.81, 1.86, 2.43 and 2.82 for the four methyl groups, and the aromatic protons at δ7.33, 7.61, 7.78 and 8.52. The H5 protons are coupled to each other in both major and minor isomers because one sits just now in the cavity while the other sits at or near the portal, and as a result they both experience different magnetic environments. These isomers are formed in a ratio of 2:1 according to integral but it has not been determined which isomer predominates.

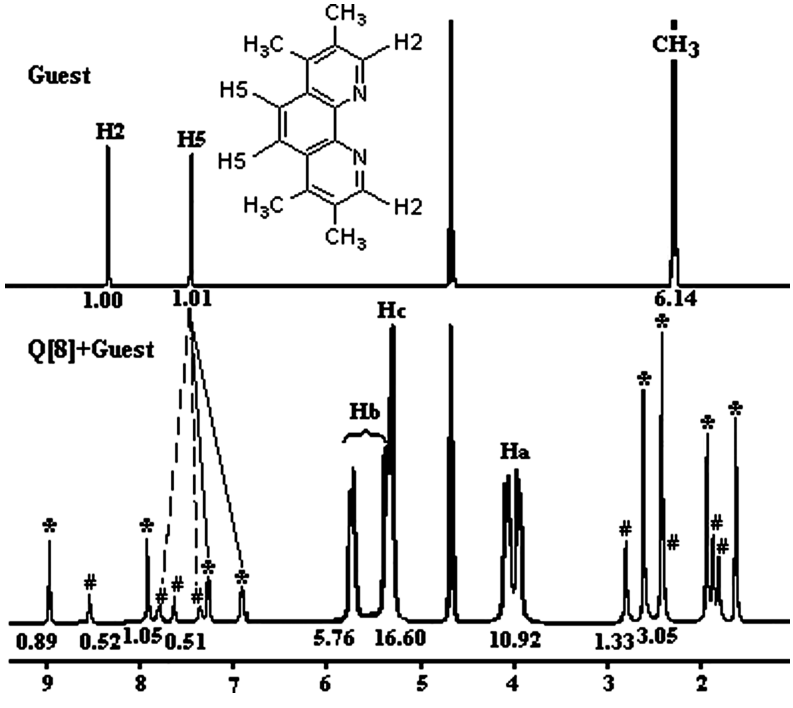

FIGURE 1 ^{1}H NMR spectra of Guest and Q[8] + Guest in D_2O.

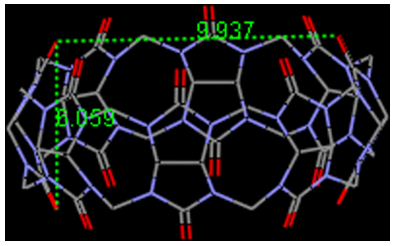

FIGURE 2 X-ray crystal structures of Q[8]. Color codes: carbon, gray; nitrogen, blue; oxygen, red.

TABLE I Stabilization energy of "anti-" and "syn-" orientation π−π stack complexes of Q[8] with 1–3 (in KJ/mol)[1]

1:2 Complex	HF/STO-3G		B3LYP/3-21G*	
	In vacuum	In water	In vacuum	In water
anti-Q[8] + 1	−142.02	−210.10	−182.84	−229.11
anti-Q[8] + 2	−181.31	−208.44	−184.12	−219.49
anti-Q[8] + 3	1.62	7.70	−39.08	−44.99
syn-Q[8] + 1	−45.80	−117.36	−157.70	−195.98
syn-Q[8] + 2	−125.61	−141.15	−153.85	−163.85
syn-Q[8] + 3	16.89	3.41	−21.04	−22.56

Notes: [1]The calculations showed a significant difference between the two *syn-* versus *anti*-orientation isomers in energy, and the conclusion that the *anti-* form is the predominant isomer is quality only, because the experimental results based on the ^{1}H NMR analysis showed that the isomers are formed in a ratio of 2:1.

Calculations of Inclusion Complexes of Q[8] and Guest

Q[8] was built based on its crystal structure (Fig. 2), and the binding models of Q[8] with the guest are established based on the ^{1}H NMR analyses, where the two stacked guests are partially included by the host Q[8], furthermore, the effect of protonation on nitrogen of the guest is considered in *ab initio* and DFT calculations. Table I shows the energy calculations at HF/STO-3G and B3LYP/3-21G* level for both the gas phase and the inclusion complexes immersed in a solvent dielectric continuum. Figure 3 shows the HF/STO-3G optimized geometries of "*anti-*" and "*syn-*" isomers.

In aqueous solution, the stabilization energy of the "*anti-*" 1:2 complexes are always more negative than that of the "*syn-*" isomer, which suggests that the "*anti-*" orientation should be more preponderant than "*syn-*", and clarity also explains two sets of different isomers observed in ^{1}H NMR spectra, the electrostatic repulsion effect of positive NH^+ and steric hindrance of methyl groups would disfavor π−π stacked pairs for *syn*-Q[8]-guest [32–34]. Moreover, the protonation of the guest is important in the interaction with Q[8], the energies of the inclusion complexes for both **1** and **2** with Q[8] are much lower than that of the inclusion complexes of free guest **3** with Q[8] and the energies of the inclusion complexes of fully protonated guest **1** are slightly lower than that of partially protonated guest **2**. The calculation results confirm that "*anti-*" orientation is preferred and the protonation on nitrogen of the guest can be an important driving force for the inclusion complex.

The calculation results also reveal that the protonated nitrogen of the guest and the oxygen of the portal carbonyl of the host Q[8] can be linked by hydrogen bond(s) (directed with arrows in Fig. 2), and the more the protonated N in a guest, the lower the energy of the inclusion complex. For the fully protonated guest **1,** the related data of hydrogen bonds are 1.157 nm (O…H), 1.231 nm (H–N), 2.387 (O…H–N), and 176.36° (O–H–N) in *anti*-Q[8]-**1**; 1.170 nm, 1.398 nm and 1.203 nm (O…H), 1.223, 1.109 nm and 1.200 nm (H–N), 2.391 nm, 2.479 nm and 2.389 nm (O…H–N), 175.29°, 162.87°, 167.98° (O–H–N), respectively, in *syn*-Q[8] + **1**. For the partially protonated guest **2,** the related data of hydrogen bonds are 1.252 nm (O…H), 1.168 nm (H–N) and 2.399 nm (O…H–N), 165.24° (O–H–N) in *anti*-Q[8] + **2**; 1.244 nm and 1.292 nm (O…H), 1.169 nm and 1.065 nm (H–N), 2.478 and 2.260 nm (O…H–N), 172.70° and 151.61° (O–H–N) in *syn*-Q[8] + **2**. Thus, hydrogen bonds between the host and guest play an impotent role formation of inclusion complexes.

Moreover, the bond lengths of the carbonyls related with the hydrogen bonding in the coordinated Q[8] are longer than that of the uncoordinated Q[8]. For example, at the HF/STO-3G level, the bond length of the carbonyl in the uncoordinated Q[8] is 1.215 nm, while the bond lengths of the carbonyl in the coordinated Q[8] are 1.312 nm for *anti*-Q[8] + **1**, 1.273 nm, 1.251 nm and 1.267 nm for *syn*-Q[8] + **1**, 1.253 nm for *anti*-Q[8] + **2**, and 1.246 nm, 1.242 nm for *syn*-Q[8] + **2**, respectively. Generally, the bond length of the carbonyl interacted with the fully protonated guest are longer than that of the carbonyl interacted with the partially protonated guest, however, the bond lengths of the carbonyl for *anti-* or *syn*-Q[8]-3 is the same as that of the carbonyl in the uncoordinated Q[8].

It is noted that the calculated carbonyl bond distance related to the hydrogen bond for the *anti*-Q[8] + **1** model is 1.31 nm, about 0.09 nm longer than the normal C = O distance, and almost the same length as the normal C = C distance (1.34 nm). In addition, comparison with the unbound carbonyl of Q[8] (Fig. 4), the atomic charges were distinctly more positive on the carbon atom and more negative on the oxygen atom.

Acidity Effect on Interaction of Q[8] With Guest

In Fig. 5, the curve B and C present the absorbance *vs.* pH for the guest·HCl and the inclusion complex with a ratio of 1:2 (host:guest), respectively. One can see a

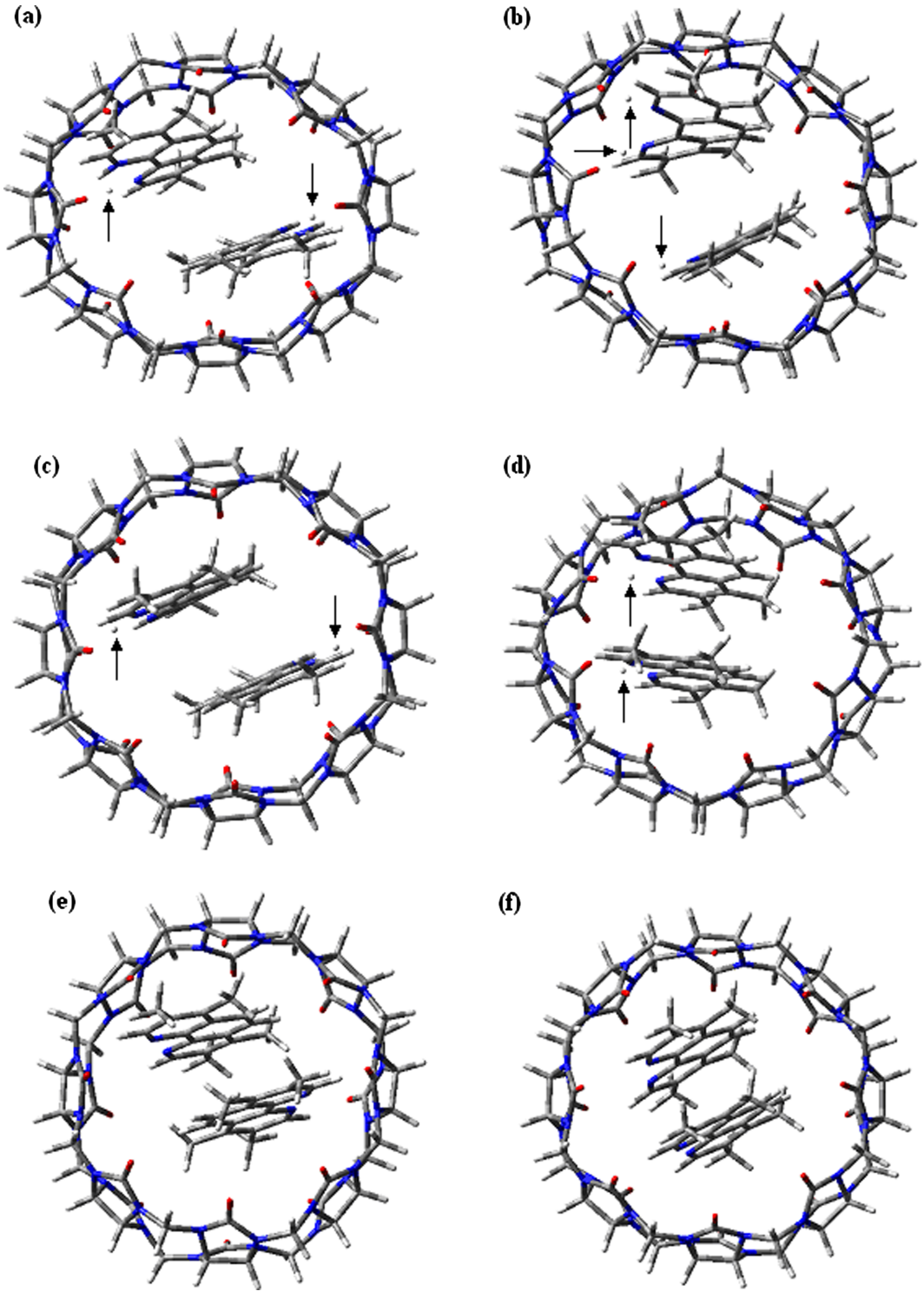

FIGURE 3 HF/STO-3G optimized structure of the 1:2 inclusion complexes of Q[8] with 1–3. Color codes: carbon, gray; nitrogen, blue; oxygen, red; hydrogen, white. *anti*-Q[8] + 1; (b) *syn*-Q[8] + 1; (c) *anti*-Q[8] + 2; (d) *syn*-Q[8] + 2; (e) *anti*-Q[8] + 3; (f) *syn*-Q[8] + 3.

significant absorbance difference between the guest and the inclusion complex in the acidic and the neutral aqueous solution ($2 < pH < 8$), while the curve C inclines to be above the curve B, which means that the bound guest could leave the host Q[8] in the basic aqueous solution ($pH > 11$). This experimental results suggest that combination of Q[8] and guest would be favorable in acidic aqueous solution, which is consistent with the calculation result, that is, the energies of the inclusion complexes of Q[8] + **1** or Q[8] + **2** are much lower than those of Q[8] + **3**.

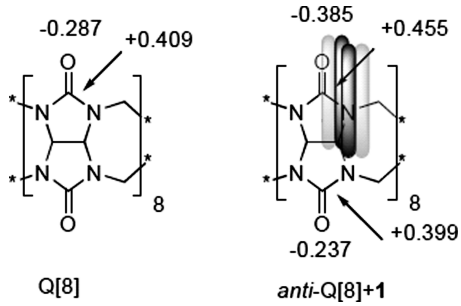

FIGURE 4 Calculated atomic charges on the carbonyl of Q[8] and anti-Q[8] + **1** at HF/STO-3G level.

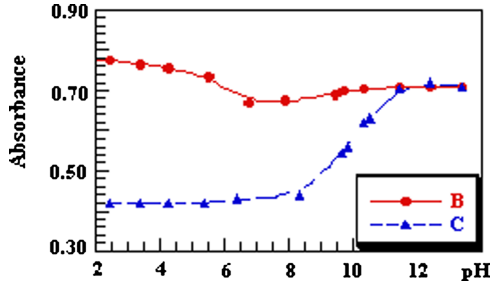

FIGURE 5 Maximum absorbance change following different pH of 3,4,7,8-tetramethyl-1,10-phenanthroline (curve B) and inclusion complex (curve C).

CONCLUSIONS

According to the calculation results, the two observed double guest inclusion isomers of the protonated 3,4,7,8-tetramethyl-1,10-phenanthroline in Q[8] could be consistent with the suggested formation of orientation isomers of the guest as "*anti-*" or "*syn-*" π−π stacked pairs, and the "*anti-*" complex should be the predominant species which was observed in the ^{1}H NMR spectrum of the host-guest systems. In addition, the two stacked guests partially included by the host Q[8] with a ratio of 1:2 of "*syn-*": "*anti-*" would be the case of partially protonated under the determination condition(pD ≈ 6.0).

MATERIALS AND METHODS

General

NMR spectra were recorded at 293 K on a VARIAN INOVA-400 spectrometer in DCl/D_2O, D_2O and NaOD/D_2O respectively.

UV-vis absorption spectra of the guest and the host-guest complexes were recorded on an Aglient 8453 Photospectrometer at room temperature. A solution of HCl salt of the guest was prepared with a concentration of 5.40×10^{-4}mol/L, this solution was combined with Q[8] to give a solution with a guest:Q[8] ratio of 2:1. Sodium hydroxide and hydrochloric acid have been used for adjusting pH to give a series of solutions of the guest or the host-guest with a certain pH values.

Materials

Q[8] was prepared and purified according to the methods developed in our laboratory [28]. 3,4,7,8-tetramethyl-1,10-phenanthroline were obtained from Shenzhen Meryer Chemical Technology Co., Ltd. and used without further purification. The corresponding HCl salt was prepared by dissolving 3,4,7,8-tetramethyl-1,10-phenanthroline in 5M HCl followed by crystallization with ethanol or acetone, collecting them by filtration and drying.

Computational Methods

All calculations have been processed on an Intel Pentium 3.0G PC with Gaussian 03W (Revision C.02) software package [29]. The initial geometries of all structures were constructed with the aid of Hyperchem Release 7.52 package [30]. Both "*syn-*" and "*anti-*" orientations were considered as 1:2 complexes of Q[8] and guests. The minimal basis set STO-3G was used for full geometry optimization with Hartree-Fock (HF) method. Beck's three-parameter hybrid functional with the correlation functional of Lee, Yang, and Parr (B3LYP) was used for single point calculations with 3-21G* basis set to give a better estimation of HF/STO-3G geometry.

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