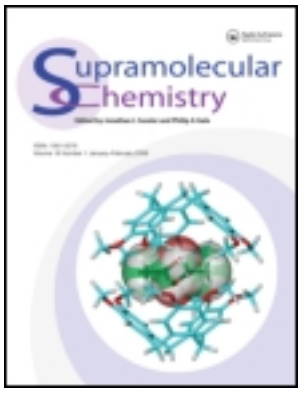

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Host-guest interactions of 6-benzyladenine with normal and modified cucurbituril: ^{1}H NMR, UV absorption spectroscopy and phase solubility methods

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Host–guest interactions of 6-benzyladenine with normal and modified cucurbituril: ^{1}H NMR, UV absorption spectroscopy and phase solubility methods

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Guest–host inclusion complexes between 6-benzyladenine (6-BA), cucurbit[7]uril (Q[7]), symmetrical tetramethylcucurbit[6]uril (TMeQ[6]) and meta-hexamethyl-substituted cucurbit[6]uril (HMeQ[6]) in aqueous solution were investigated by ^{1}H NMR, UV absorption spectroscopy and phase solubility studies. The ^{1}H NMR spectra analysis revealed that the hosts selectively bound the phenyl moiety of the guests. Absorption spectroscopic analysis defined the stability of the host–guest inclusion complexes. A host:guest ratio of 1:1 was measured quantitatively as $(5.63 \pm 0.26) \times 10^4$, $(1.94 \pm 0.17) \times 10^3$ and $(2.89 \pm 0.23) \times 10^3$ mol L^{-1} for the Q[7]-6-BA, TMeQ[6]-6-BA and HMeQ[6]-6-BA systems, respectively. Phase solubility diagrams were analysed through rigorous procedures to obtain estimates of the complex formation constants for Q[*n*]-6-BA complexation. The formation constants were $(1.29 \pm 0.24) \times 10^4$ L mol^{-1} for Q[7]-6-BA, $(3.20 \pm 0.17) \times 10^3$ L mol^{-1} for TMeQ[6]-6-BA and $(3.52 \pm 1.01) \times 10^3$ L mol^{-1} for TMeQ[6]-6-BA. Furthermore, phase solubility studies showed that 6-BA solubility increased as a function of Q[7], TMeQ[6] and HMeQ[6] concentrations. The thermodynamic parameters of the complex formation were also determined. The formation of inclusion complexes between 6-BA and Q[7] was enthalpy controlled, suggesting that hydrophobic and van der Waals interactions were the main driving forces. Our results demonstrated that the complexation of 6-BA with Q[*n*] could be used to improve the solubility of 6-BA.

Keywords: 6-benzyladenine; Q[7]; TMeQ[6] and HMeQ[6]; ^{1}H NMR; UV spectroscopy; phase solubility method

Introduction

6-benzyladenine (6-BA) is a common model compound for cytokinins, one of the most important classes of plant hormones. It can stimulate cell division, lateral bud emergence (apples, oranges), basal shoot formation (roses, orchids), flowering (cyclamen, cacti) and fruit set (grapes, oranges, melons) (*1–5*). Although the effects of cytokinins in plants are well known, the mechanisms of their actions are not well understood. 6-BA and its derivatives have strong potential in molecular medicine (*6*). However, the insolubility of 6-BA in distilled water could practically limit its biological application.

Cucurbit[*n*]urils are host molecules that can form inclusion complexes with a variety of drugs to improve drug solubility, stability and bioavailability (*7–11*). A hydrophobic cavity and two open hydrophilic portals are common characteristic features of each member in the Q[*n*] family. A series of Q[*n*] derivatives, such as fully substituted pentacyclohexano cucurbit[5]uril (Cy5Q[5]) (*12*), disubstituted cucurbit[6]uril (*13*) and diphenyl Q[6] (*14*), were synthesised and reported to overcome the generally poor solubility of the Q[*n*] family in common solvents. Using a dimer of glycoluril (*15*) that was synthesised in our laboratories along with a diether of alkylglycoluril, we were able to synthesise a series of new symmetrical and unsymmetrical substituted cucurbit[*n*]urils (*16–19*). Some Q[*n*] molecules showed surprising water solubility, which allowed us to investigate their host–guest chemistry in water.

In this work, inclusion between 6-BA, cucurbit[7]uril (Q[7]), two partial methyl-substituted cucurbit[6]uril, symmetrical tetramethylcucurbit[6]uril (TMeQ[6]) and meta-hexamethyl-substituted cucurbit[6]uril (HMeQ[6]) (Figure 1) in aqueous solutions was investigated by ^{1}H NMR, UV absorption spectroscopy and phase solubility studies. The stability constant of these complexes was estimated using electronic absorption spectroscopy and phase solubility methods. The phase solubility method was also used to examine the effect of three types of cucurbit[*n*]urils on the aqueous solubility of 6-BA.

Results and discussion

^{1}H NMR spectra analysis of the interactions between Q[n]s and 6-BA

When a guest interacts with Q[*n*]s, it experiences a cavity interaction, a portal interaction or a combined cavity and portal interaction with the host Q[*n*]. The proton's

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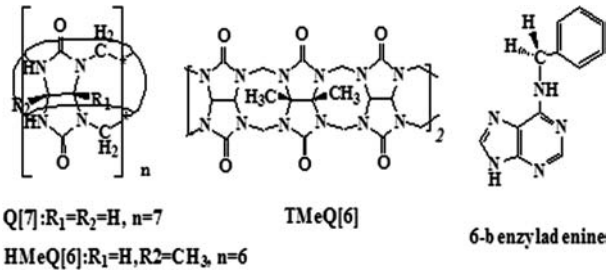

Figure 1. Structures of cucurbit[*n*]urils and 6-BA.

environment can be changed by the shielding effect of the cavity of the Q[*n*] or the deshielding effect of the portals of the Q[*n*]. Therefore, the ^{1}H NMR technique is a powerful method to investigate the interaction and structural characteristics of the guest and the host.

Figure 2 shows the ^{1}H NMR spectra of 6-BA (a) in the absence of Q[*n*] and (b) in the presence of 2.5 equiv. of Q[7], (c) 3.0 equiv. of TMeQ[6] and (d) 2.8 equiv. of HMeQ[6]. The undeuterated protons (H_a–H_f) of 6-BA were detected.

The protons H_a, H_b and H_c on the benzene ring moiety of 6-BA exhibited an upfield shift of ~0.8 ppm. Moreover, the methylene proton (H_d) merged in the 5–6 ppm region and the protons H_f and He showed little shift. These results suggest that Q[7] encapsulated the benzene ring and the methylene moiety into its cavity. Furthermore, the adenine ring was located at the deshielding portal of the host.

When complexed with host TMeQ[6] and HMeQ[6], the benzene ring and methylene moiety of guest 6-BA were entrapped in the cavity of the host. The ^{1}H NMR spectra of 6-BA in the absence and presence of TMeQ[6] and HMeQ[6] are shown in Figure 2(c) and (d), respectively. The protons H_a–H_c on the benzene ring moiety showed an upfield shift of ~0.8 ppm with ~3.0 equiv. of cucurbiturils. Moreover, the proton H_d on the methylene showed an upfield shift and merged in the 5–6 ppm region. These data suggested that the benzene ring and the methylene group were encapsulated into the cavity of the cucurbiturils and that the adenine ring was located at the deshielding portal of the host.

Spectrophotometric analysis of the interaction between Q[n]s and 6-BA

The ^{1}H NMR spectroscopy revealed that Q[*n*] bound the 6-BA and formed host–guest inclusion complexes. However, it was hard to conclude the ratio of host and guest in the complex. To analyse the interaction between Q[*n*] and the guest, electronic absorption spectra were recorded. The techniques are applicable to low concentrations of Q[*n*].

The UV spectra obtained from the aqueous solutions containing a fixed concentration of the guest (40 μM) and variable concentrations of Q[*n*] are shown in Figure 3. As shown, the absorption spectra of the guest exhibited a progressively lower absorbance with a slight red shift as the ratio of $N_{Q[7]}/N_{6\text{-BA}}$ increased. When complexed with TMeQ[6] and HMeQ[6], the absorption spectra of the guest exhibited a progressively lower absorbance with a slight red shift as the ratio of $N_{Q[n]}/N_{6\text{-BA}}$ increased. The hosts showed no absorbance in the range of > 210 nm. The absorbance (A) versus ratio curves were fitted into a 1:1 binding model for the Q[*n*]-6-BA systems. The simple isosbestic points at $\lambda = 270$, 272 and 272 nm for the Q[7], TMeQ[6] and HMeQ[6] systems, respectively, suggest that these three host–guest inclusion complexes are consistent with a simple interaction between Q[*n*] and the guest. The corresponding formation constants (K) are $(5.63 \pm 0.26) \times 10^4\,\mathrm{L\,mol^{-1}}$ for Q[7]-6-BA, $(1.94 \pm 0.17) \times 10^3\,\mathrm{L\,mol^{-1}}$ for TMeQ[6]-6-BA and $(2.89 \pm 0.23) \times 10^3\,\mathrm{L\,mol^{-1}}$ for HMeQ[6]-6-BA.

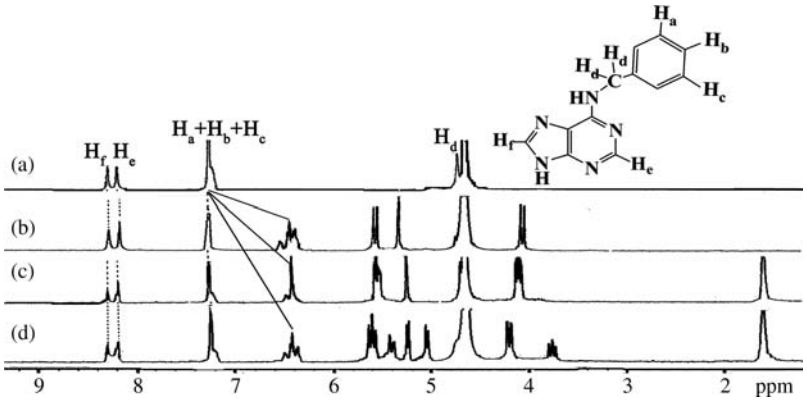

Figure 2. ^{1}H NMR spectra (400 MHz, D_2O) of 6-BA in (a) the absence of Q[*n*], (b) the presence of 2.5 equiv. of Q[7], (c) the presence of 3.0 equiv. of TMeQ[6] and (d) the presence of 2.8 equiv. of HMeQ[6].

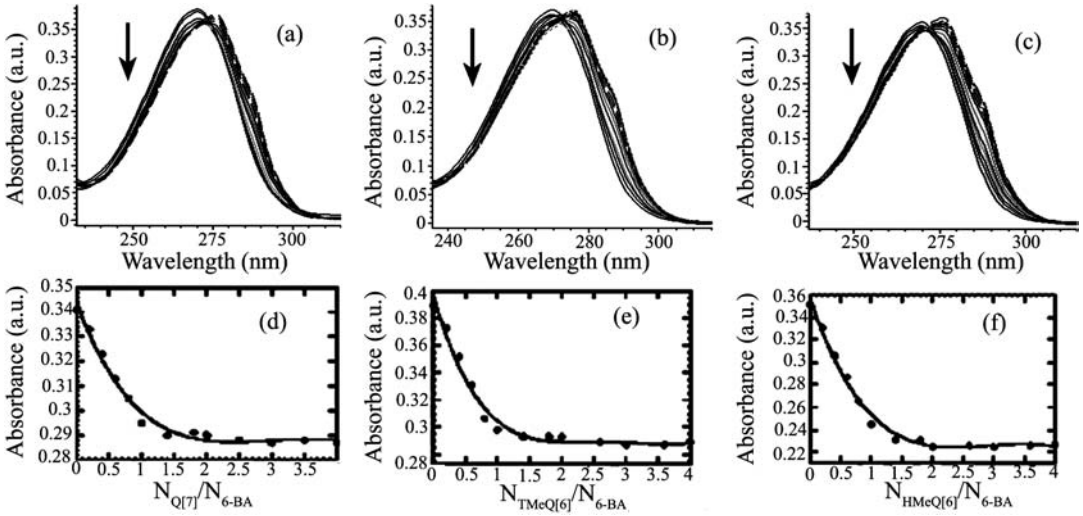

Figure 3. UV absorption spectrum of 6-BA in the presence of increasing concentrations of cucurbiturils (a) Q[7], (b) TMeQ[6], (c) HMeQ[6] and corresponding absorbance versus $N_{Q[n]}/N_{6\text{-BA}}$ at $\lambda_{max} = 268$ nm (d) Q[7], (e) TMeQ[6], (f) HMeQ[6].

Effects of Q[n] on the solubility of 6-BA

The effects of cucurbiturils on the aqueous solubility of 6-BA were evaluated using the phase solubility method. Figure 4 shows the phase diagrams of 6-BA with three different types of Q[*n*] in aqueous solutions at 20°C. The solubility of 6-BA increased linearly as a function of TMeQ[6] and HMeQ[6] concentrations. These phase solubility diagrams (PSDs) are classified as type A_L by Higuchi and Connors (*21*), which denotes a linear increase in solubility. In contrast, Q[7] showed a type B_S solubility curve, which denotes an initial increase in solubility and a later plateau in solubility (caused by the limited solubility of the complexes).

On the basis of the PSDs, the association constants (*K*) for the different inclusion complexes were determined using Equation (1), assuming a 1:1 stoichiometry (see Table 1). The association constants (*K*) of the 6-BA inclusion complexes are $(1.29 \pm 0.24) \times 10^4\ L\ mol^{-1}$ for Q[7]-6-BA, $(3.20 \pm 0.17) \times 10^3\ L\ mol^{-1}$ for TMeQ[6]-6-BA and $(3.52 \pm 1.01) \times 10^3\ L\ mol^{-1}$ for HMeQ[6]-6-BA.

In the aqueous solutions of Q[*n*]-6-BA, the free 6-BA molecules are in equilibrium with the 6-BA molecules entrapped within the cavity. Thus, with an increase in the concentration of Q[*n*], more 6-BA molecules will be captured from the aqueous solution into the hydrophobic cavities of the Q[*n*]. Therefore, more 6-BAs are dissolved in water and the solubility of 6-BA increases with the increased concentration of Q[*n*]. The concentration of 6-BA in the Q[7] solutions reached 12.40 mM, a 35-fold increase over that in water. A 32-fold and 36-fold increase in solubility was achieved when 14.00 mM TMeQ[6] and HMeQ[6] solutions were used, respectively. Q[7] was the most effective candidate to solubilise 6-BA (Tables 2–4).

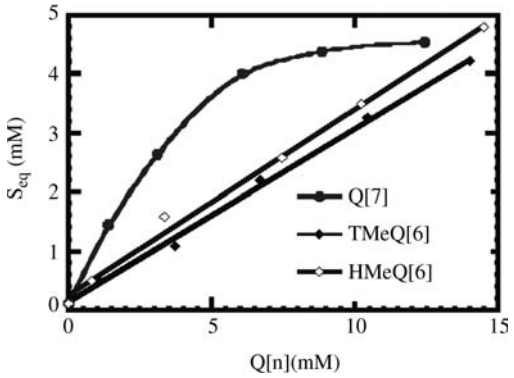

Figure 4. PSDs of 6-BA versus concentrations of Q[7], TMeQ[6] and HMeQ[6] obtained in water at 20°C.

Effect of temperature on the complex formation constant

In principle, evaluation of complex formation constants (*K*) over a significant temperature range can be used to calculate the enthalpy (ΔH) and entropy (ΔS) of association. These parameters can provide insight into the driving forces responsible for the binding interaction. Therefore, we measured the *K* values from the solubility measurements at 295, 299, 303, 310 and 315 K. The PSDs of 6-BA obtained at different temperatures are shown in Figure 5. A plot of ln *K* as function of 1/*T* is shown in Figure 6. The corresponding complex formation constants (ln *K*), the solubilities of 6-BA in the absence of Q[*n*] (So) and the calculated thermodynamic parameters (ΔH, ΔS and ΔG) are listed in Table 5.

Figure 5 shows the solubility of 6-BA with the concentration of Q[7] at different temperatures, indicating a B_s type of PSDS, according to Higuchi and Connors (*21*).

Table 1. Complex formation constants of 6-BA with Q[7], TMeQ[6] and HMeQ[6] calculated from PSDs (Figure 4).

	Equation	R	K (M^{-1})[a]	PSD type[b]
Q[7]	$Y = 0.628x + 0.411$	0.9854	$(1.29 \pm 0.24) \times 10^4$	B_S
TMeQ[6]	$Y = 0.294x + 0.149$	0.9980	$(3.20 \pm 0.17) \times 10^3$	A_L
HMeQ[6]	$Y = 0.314x + 0.283$	0.9970	$(3.52 \pm 1.01) \times 10^3$	A_L

[a] Standard deviations are calculated on triplicate trials.
[b] A_L stands for a linear PSD and B_S stands for PSDs with a descending portion, according to Higuch and Connors (*21*).

Table 2. Increases in 6-BA solubility after complexing with Q[7].

TMeQ[6] (mM)	0	1.06	3.72	6.67	10.40	14.00
S_{eq} (mM)[a]	0.13 ± 0.03	1.46 ± 0.02	2.65 ± 0.04	4.01 ± 0.08	4.34 ± 0.03	4.54 ± 0.06
S/S_0	1.00	11.23	20.38	30.85	33.38	34.92

[a] Standard deviations are calculated on triplicate trials.

Table 3. Increases in 6-BA solubility after complexing with TMeQ[6].

HMeQ[6] (mM)	0	0.794	3.32	7.46	10.20	14.50
S_{eq} (mM)[a]	0.13 ± 0.02	0.54 ± 0.05	1.08 ± 0.04	2.21 ± 0.07	3.26 ± 0.07	4.22 ± 0.05
S/S_0	1.00	4.15	8.31	17.00	25.08	32.46

[a] Standard deviations are calculated on triplicate trials.

Table 4. Increases in 6-BA solubility after complexing with HMeQ[6].

HMeQ[6] (mM)	0	0.794	3.32	7.46	10.20	14.50
S_{eq} (mM)[a]	0.13 ± 0.02	0.51 ± 0.05	1.59 ± 0.04	2.58 ± 0.07	3.50 ± 0.07	4.80 ± 0.05
S/S_0	1.00	3.92	12.23	19.85	26.92	36.92

[a] Standard deviations are calculated on triplicate trials.

Moreover, $\ln K$ values decreased with an increase in temperature, suggesting that the complex was less stable at higher temperatures. The changes in Gibbs-free energy and enthalpy were negative, and entropy was positive. These data suggest that complex formation ($\Delta G = -22.39 \pm 0.17$ to -23.20 ± 0.08) kJ/mol was largely driven by enthalpy ($\Delta H = -9.7 \pm 1.1$ kJ/mol) in the presence of a favourable entropy ($\Delta S = 42.7 \pm 3.8$ J/mol K). Therefore, complex formation was attributed to van der Waals and hydrophobic interactions.

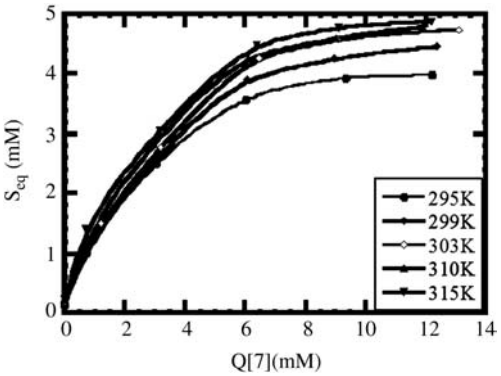

Figure 5. PSDs of the Q[7]-6-BA system at different temperatures (295, 299, 303, 310 and 315 K).

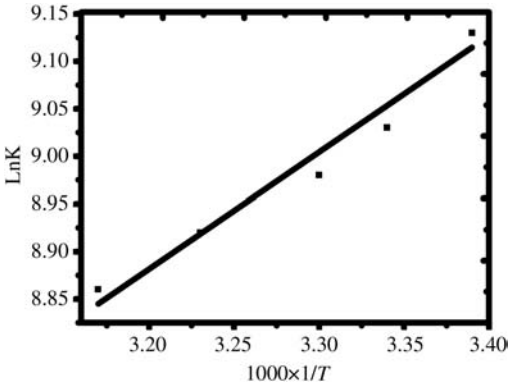

Figure 6. Plot of $\ln K$ as function of $1/T$ for the interaction of Q[7] with 6-BA.

Table 5. Complex formation constants (K_{11}) and the thermodynamic parameters of the Q[7]/6-BA system at pH 5.67.

T (K)	S_0 (mM)	ln K	ΔG (kJ/mol)	ΔH (kJ/mol)[a]	ΔS (J/mol K)[a]
295	0.10 ± 0.02	9.13 ± 0.07	−22.39 ± 0.17		
299	0.11 ± 0.01	9.03 ± 0.04	−22.45 ± 0.10		
303	0.12 ± 0.02	8.98 ± 0.05	−22.62 ± 0.14	−9.7 ± 1.1	42.7 ± 3.8
310	0.13 ± 0.01	8.92 ± 0.04	−22.99 ± 0.09		
315	0.22 ± 0.04	8.86 ± 0.03	−23.20 ± 0.08		

[a] The ΔH and ΔS values were calculated from the temperature dependence of ln K according to the integrated form of the Van't Hoff equation.

Conclusion

We investigated the inclusion complex formation between 6-BA, Q[7], TMeQ[6] and HMeQ[6] in aqueous solution by ^{1}H NMR, UV absorption spectroscopy and phase solubility studies. The ^{1}H NMR spectra analyses established that the benzene ring and the methylene group of 6-BA were encapsulated into the cavity of the cucurbiturils. Furthermore, the adenine ring was located at the portal of the hosts. Absorption spectroscopic analysis revealed that the host–guest inclusion complexes had a host:guest ratio of 1:1. The measured constants were $(5.63 \pm 0.26) \times 10^4\,\mathrm{mol\,L^{-1}}$ (Q[7]-6-BA), $(1.94 \pm 0.17) \times 10^3\,\mathrm{mol\,L^{-1}}$ (TMeQ[6]-6-BA) and $(2.89 \pm 0.23) \times 10^3\,\mathrm{mol\,L^{-1}}$ (HMeQ[6]-6-BA). Phase solubility studies showed that 6-BA solubility increased in a linear fashion as a function of TMeQ[6] and HMeQ[6] concentrations. Though 6-BA solubility initially increased, it levelled off as the Q[7] concentration increased. On the basis of the PSDs, the association constants for the different inclusion complexes were $(1.29 \pm 0.24) \times 10^4\,\mathrm{L\,mol^{-1}}$ for Q[7]-6-BA, $(3.20 \pm 0.17) \times 10^3\,\mathrm{L\,mol^{-1}}$ for TMeQ[6]-6-BA and $(3.52 \pm 1.01) \times 10^3\,\mathrm{L\,mol^{-1}}$ for HMeQ[6]-6-BA. The interaction between 6-BA and the cucurbituril weakened as the temperature increased. The formation of the inclusion complexes was found to be enthalpy controlled, suggesting that hydrophobic and van der Waals interactions were the main driving forces. Our results demonstrate that the complexation of 6-BA with Q[n] can be used to improve the solubility of 6-BA in aqueous solution.

Experimental

Materials

Cucurbit[n]urils (Q[7], TMeQ[6] and HMeQ[6]) were prepared and purified according to published methods (*15,18,20*). 6-BA was obtained from Sigma and used without further purification. The corresponding HCl salts were prepared by dissolving the related guests in 6 M HCl, followed by concentration, crystallisation and air drying. All other reagents were of analytical grade and were used as received.

^{1}H NMR measurements

To study the host–guest complexation of Q[n] and 6-BA, $2.0–2.5 \times 10^{-3}$ mmol samples of Q[7] in 0.5–0.7 mL D_2O with Q[7]:6-BA ratios of 2.5:1, TMeQ[6]:6-BA ratios of 3.0:1, and HMeQ[6]:6-BA ratios of 2.8:1 were prepared. The corresponding ^{1}H NMR spectra were recorded at 20°C on a VARIAN INOVA 400 spectrometer.

UV absorption spectroscopy measurements

The UV absorption spectra of the host–guest complexes were recorded on an Agilent 8453 Photospectrometer at room temperature. An aqueous solution of the HCl salt of 6-BA was prepared at a concentration of $1.00 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$. Aqueous solutions of Q[7], TMeQ[6] and HMeQ[6] were prepared with concentrations of $2.00 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ for absorption spectra determination. Samples of these solutions were combined to give guest:host ratios of 0, 0.5:1, 1:1, 2:1, 3:1 and 4:1. The pH values of the host–guest complexes in solution were monitored with a S-3C pH meter and the pH of the samples was adjusted with HCl and NaOH.

Phase solubility studies

Phase solubility was measured according to the method of Higuchi and Connors (*21*). Briefly, excess amounts of 6-BA were added to aqueous solutions containing various concentrations of Q[7], TMeQ[6] and HMeQ[6] (0–16.0 mM). Samples were maintained at 20°C, vibrated for 24 h and allowed to stay for 7 days until equilibrium was reached. Afterwards, samples were filtered (0.45 μm) and appropriately diluted with H_2O. The absorbances at 267 nm were measured on an Agilent 8453 spectrophotometer. The 6-BA calibration curve was generated at pH 10.50. Apparent 1:1 stability constants (K) were determined from the initial part of the straight-line of the PSDs:

$$K = \frac{\text{slope}}{S_0(1 - \text{slope})} \quad (1)$$

Where S_0 is the free 6-BA aqueous solubility. The molar ratios of the complexes were determined by UV absorbance at 267 nm. Each experiment was conducted in triplicate.

Gibbs and Van't Hoff equations were used to estimate the thermodynamic parameters ΔH, ΔS and ΔG according to the relation

$$\Delta G = -\mathrm{RT}\ln K \quad (2)$$

$$\ln K = \Delta S/R - \Delta H/\mathrm{RT}. \quad (3)$$

A plot of $\ln(K)$ versus $1/T$ produced slope $= -\Delta H/R$ and intercept $= \Delta S/R$.

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