

Gauche conformation of acyclic guest molecules appearing in the large cages of structure-H clathrate hydrates

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Abstract—In the present study, measurements and analyses were made of the High-Power Decoupling (HPDEC) solid-state ¹³C NMR spectra of structure-H (sH) methane hydrates with isopentane, one of the simplest and smallest acyclic large guest molecules, and methylcyclohexane (MCH), a commonly used cyclic guest molecule that is larger than isopentane. From the spectroscopic information, clear and definite evidence for the molecular conformation of acyclic guest molecules that are sufficiently small so as to be entrapped into the structure-H large cage (sH-L) was expected. The ¹³C NMR chemical shift change was additionally checked through the use of a hydrogen-hydrogen steric perturbation model. From the overall results, we concluded that one of the smallest acyclic guest molecules, isopentane, participating in the formation of a structure-H clathrate hydrate is engaged, confirming the gauche conformation in large cavities. The present results strongly suggest that the guest position and structure in hydrate cages are greatly influenced by both short-range interactions between guest molecules and cage frameworks and long-range interactions between small and large guests. Accordingly, cage dynamics must be carefully considered when a specific sH hydrate is designed and synthesized for the purpose of tuning material properties.

Key words: Structure-H, Clathrate Hydrate, Large Guest Molecule Substance

INTRODUCTION

Structure-H (sH) clathrate hydrates, first discovered by Ripmeester et al. [1], have been intensely studied because of their importance for storage and transportation of natural gas [2] in addition to their function as a strong hydrate promoter associated with rapid and favorable structure stabilization. However, most sH research has been more involved in the occupancy and corresponding stored amount of small guest molecules in small and medium cages in reference to heavy guest molecules occupying the largest cages [2-4]. However, molecular inclusion characteristics occurring in 5¹²6⁸ large cages (sH-L) have not yet been thoroughly examined in spite of the utility of such entities toward a clear understanding of sH hydrates. Recently, Lee et al. investigated *n*-pentane and *n*-hexane as co-guests incorporated with sH 2,2-dimethylbutane+CH₄ hydrates [5]. Though *n*-pentane and *n*-hexane are known not to form sH clathrate hydrates due to their large molecular size, Lee et al. were able to confirm the existence of a mixed sH hydrate simultaneously comprising both the co-guest and original guest through an analysis of X-ray diffraction (XRD) patterns and ¹³C NMR spectra. They also indicated that *n*-pentane (9.31 Å, molecular size [6]) may have one gauche interaction and that *n*-hexane may have more than one gauche interaction in order to fit the sH-L (8.62 Å, cavity diameter [6]). However, it must be noted that an actual phenomenon associated with short-range interaction between a heavy guest and cage framework can be only explored through structure identification, particularly for a heavy guest smaller than cage in size.

Accordingly, in the present study, measurements and analyses were

made of the High-Power Decoupling (HPDEC) solid-state ¹³C NMR spectra of sH methane hydrates with isopentane, one of the simplest and smallest acyclic large guest molecules, and methylcyclohexane (MCH), a commonly used cyclic guest molecule that is larger than isopentane [6]. From the spectroscopic information, clear and definite evidence for the molecular conformation of acyclic guest molecules that are sufficiently small so as to be entrapped into the sH-L was expected. The ¹³C NMR chemical shift change was additionally checked through the use of a hydrogen-hydrogen steric perturbation model [7].

EXPERIMENTAL SECTION

The CH₄ gas with a purity of 99.9 mol% used for this study was supplied by Praxair Technology (Danbury, CT). Isopentane (2-methylbutane) of 99.5% and methylcyclohexane (MCH) of 99% from Aldrich Chemical Co., Inc. were used without any further purification.

The isopentane (3.70 g, slightly in excess of 2.8 mol%)+water (30.0 g)+CH₄ (60 bar) and the MCH (5.00 g, slightly in excess of 2.8 mol%)+water (30.0 g)+CH₄ (60 bar) hydrate samples for sH were prepared in a mechanically stirred reactor with a volume of 150 cm³. A mechanical stirrer agitated the reactants during the entire formation process to provide a fresh surface to participate in the formation of gas hydrates. The temperature was decreased from room temperature to 272.15 K very slowly. When the formation processes of the hydrate samples were completed, the samples were crushed by using a mortar and pestle, and pulverized finely at the temperature of liquid nitrogen for the solid-state NMR measurement.

To analyze the structure of large guest molecule, a Bruker (Billerica, MA) AVANCE 400 MHz solid-state NMR spectrometer was

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used in this study. The powdered samples were placed in a 4 mm o.d. zirconia rotor loaded into a variable temperature probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) at approximately 5 kHz. A pulse length of 2 μs and a pulse repetition delay of 15 s under proton decoupling were employed with a radio frequency field strength of 50 kHz, corresponding to 5- μs 90° pulses. The downfield carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference.

RESULTS AND DISCUSSION

The chemical shifts of gaseous guest molecules in the ^{13}C NMR spectra tend to move downfield due to molecules captured in the cages of clathrate hydrates as a result of the short-range interaction between the guest and cage framework. For example, a chemical shift of CH_4 gas is observed at -11.1 ppm, but when CH_4 molecules are located in structure-I 5^{12} (sI-S) and $5^{12}6^2$ cages (sI-L) or in structure-II $5^{12}6^4$ cages (sII-L), the chemical shifts of CH_4 are moved to the downfield region of -4.3 , -6.7 and -8.3 ppm [8]. Clearly, the smaller the cage size, the more the chemical shift of the guest moves downfield. Fig. 1(a) shows the peaks in the HPDEC ^{13}C NMR spectrum of the sH MCH+ CH_4 clathrate hydrate, including a very small amount of coexisting sI CH_4 hydrate having the following chemical shifts: (δ_c/ppm : -6.56 (CH_4 in sI-L), -4.79 (CH_4 in 4^25^63 (sH-M)), -4.50 (CH_4 in 5^{12} (sH-S)), 23.36 (C^α), 26.67 (C^4), 26.97 (C^3), 33.36 (C^1), 35.86 (C^2) for $\text{H}_3\text{C}^\alpha\text{-cyclo-(C}^1\text{H}_2\text{-(C}^2\text{H}_2)_2\text{-(C}^3\text{H}_2)_2\text{-C}^4\text{H}_2$). Accordingly, a peak representing the sH-S CH_4 with a chemical shift of -4.50 ppm is obviously more deshielded, while the sH-M CH_4 peak with a chemical shift of -4.79 ppm and sI-L CH_4 peak with a chemical shift of -6.56 ppm are shielded. This chemical shift pattern can be attributed to the host/guest electron donating-withdrawing effects occurring between the guest and the framework. More specifically, oxygen atoms of the clathrate hydrate framework withdraw the electrons of carbon via hydrogen atoms of the guest. As the size of the cage increases, this “withdrawing effect” decreases. For comparison, the liquid MCH spectrum is sourced from our previous work [8]. Fig. 1(b) shows the HPDEC ^{13}C NMR peaks of the liquid MCH and sI CH_4 hydrate with the following chemical shifts: (δ_c/ppm : -6.55 (CH_4 in sI-L), 23.28 (C^α), 26.67 (C^4), 26.97 (C^3), 33.29 (C^1), 35.79 (C^2) for $\text{H}_3\text{C}^\alpha\text{-cyclo-(C}^1\text{H}_2\text{-(C}^2\text{H}_2)_2\text{-(C}^3\text{H}_2)_2\text{-C}^4\text{H}_2$) [8]. All of the hydrocarbon guests are not completely encaged into the sH-L; thus two different spectra of hydrated hydrocarbons and

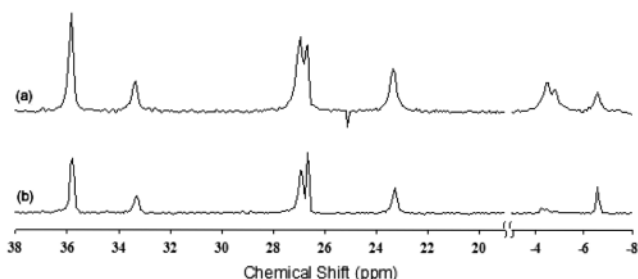


Fig. 1. HPDEC ^{13}C NMR spectra at 203.15 K: (a) mixed sH MCH + CH_4 and sI CH_4 clathrate hydrates, (b) liquid MCH and sI CH_4 clathrate hydrate (Yeon et al. [8]).

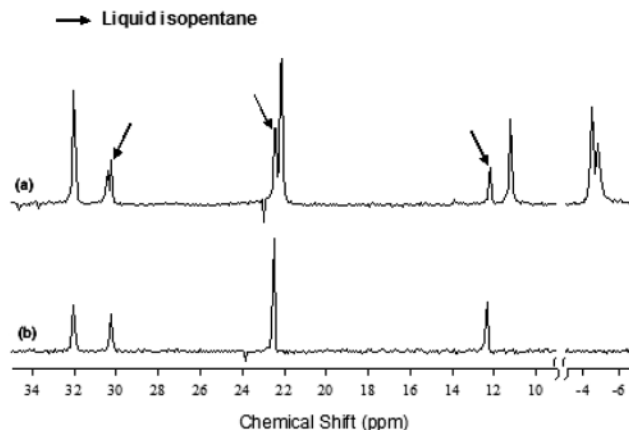


Fig. 2. HPDEC ^{13}C NMR spectra at 203.15 K: (a) sH isopentane+ CH_4 clathrate hydrate, (b) liquid isopentane+ice mixture.

remaining liquid hydrocarbons were observed [5]. However, only five peaks of MCH were observed in the downfield region in Fig. 1(a), which implies that the expected “withdrawing effect” becomes relatively small in the sH-L when compared to liquid MCH peaks in Fig. 1(b).

Interestingly, a fairly different pattern of chemical shift appears in the spectrum for the sH isopentane+ CH_4 hydrate. In the downfield region of Fig. 2, only four sharp peaks are observed for the liquid isopentane+ice mixture (b) (δ_c/ppm : 12.30 (C^4), 22.45 (C^1), 30.24 (C^2), 32.00 (C^3) for $(\text{C}^1\text{H}_3)_2\text{-C}^2\text{H-C}^3\text{H}_2\text{-C}^4\text{H}_3$), while seven peaks are shown in the spectrum for the sH isopentane+ CH_4 hydrate (a) (δ_c/ppm : -4.46 (CH_4 in sH-S), -4.83 (CH_4 in sH-M), 11.27 (C^4 in hydrate), 12.16 (C^4 in liq. isopentane), 22.08 (C^1 in hydrate), 22.37 (C^1 in liq. isopentane), 30.24 (C^2 in liq. isopentane), 30.39 (C^2 in hydrate), 32.00 (C^3) for $(\text{C}^1\text{H}_3)_2\text{-C}^2\text{H-C}^3\text{H}_2\text{-C}^4\text{H}_3$). The C^1 and C^4 chemical shifts are moved upfield, but the C^2 chemical shift is only slightly moved downfield. The isopentane has a one-gauche and one-anti (Anti) conformation. For isopentane, the anti conformer is known to be more stable than the two-gauche (Gauche) conformer by 0.79 kcal/mol [9]. Moreover, the isopentane is sufficiently small to be entrapped in the sH-L [6]. Thus, the Anti conformation appears to be naturally suitable for engagement, eliminating the possibility of a molecular shape change. In contrast, the HPDEC ^{13}C NMR spectrum confirms that the isopentane exists stably in sH-L with the gauche conformation. Methyl groups, located in a gauche-position, increase in electron density due to their steric effects, causing the chemical shifts of C^1 and C^4 to move upfield. A similar conformation pattern was also observed for *n*-pentane and *n*-hexane, which were also shifted upfield due to their gauche interactions [5].

The chemical shifts of a two-gauche rotational isomer were confirmed by applying the steric perturbation model [7]. Grant and Cheney proposed that the carbon-hydrogen bond was perturbed by the nonbonded hydrogen-hydrogen repulsive forces; furthermore, the conformational geometric difference between the conformational isomers was reflected by the resonance line shifting in the ^{13}C NMR spectrum. The resulting shift is expressed as follows:

$$\delta_c (\text{ppm}) = +1680 \cos\theta \exp(-2.671/r) \quad (1)$$

where r is the proximate proton-proton distance, θ the angle be-

Table 1. The Cartesian coordinates of isopentane with one-gauche and one-anti position (Å)

No.	Atom	x	y	z
1	C	-1.712	-1.247	-0.635
1'	C	-1.048	0.892	0.525
2	C	-0.704	-0.082	-0.616
3	C	0.739	-0.618	-0.518
4	C	1.822	0.458	-0.680
5	H	-1.660	-1.841	0.306
6	H	-2.758	-0.877	-0.745
7	H	-1.519	-1.939	-1.486
8	H	-0.917	0.409	1.520
9	H	-2.104	1.239	0.454
10	H	-0.412	1.805	0.500
11	H	-0.808	0.469	-1.586
12	H	0.880	-1.138	0.460
13	H	0.897	-1.384	-1.316
14	H	2.838	0.001	-0.687
15	H	1.804	1.196	0.152
16	H	1.698	1.013	1.638

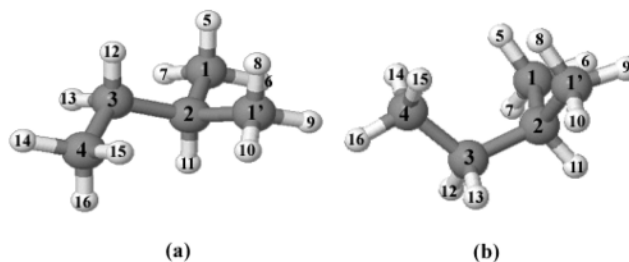
Table 2. The Cartesian coordinates of isopentane with two-gauche position (Å)

No.	Atom	x	y	z
1	C	1.549	-0.451	-0.619
1'	C	0.451	1.450	0.646
2	C	0.651	-0.074	0.573
3	C	-0.684	-0.848	0.579
4	C	-1.608	-0.583	-0.619
5	H	1.113	-0.118	-1.588
6	H	2.552	0.025	-0.529
7	H	1.707	-1.552	-0.674
8	H	-0.023	1.851	-0.278
9	H	1.426	1.976	0.769
10	H	-0.189	1.734	1.512
11	H	1.201	-0.375	1.503
12	H	-0.467	-1.943	0.623
13	H	-1.241	-0.603	1.515
14	H	-1.129	-0.866	-1.583
15	H	-1.910	0.486	-0.681
16	H	-2.544	-1.182	-0.532

tween the proton-proton axis and perturbed H-C bond, and δ_c represents the sterically induced ^{13}C chemical shift.

For the calculation, the Cartesian coordinates of two conformational isomers given in Tables 1 and 2 were obtained from ChemDraw software. In Fig. 3, the molecular coordinate information of Tables 1 and 2 is represented. From Tables 1 and 2, both the distances between hydrogen-hydrogen and angles between hydrogen-hydrogen-carbon were obtained by using the Jmol free software. The results are given in Tables 3 and 4.

The differences in the chemical shifts between two rotational conformers are given in Table 5. For C^1 , C^2 and C^3 , the differences in the chemical shifts were determined by the proximate hydrogen of C^4 , but for C^4 the difference was determined from the proximate

**Fig. 3. Rotational isomers of isopentane: (a) one-gauche and one-anti position, (b) two-gauche position.****Table 3. The distances between hydrogen and hydrogen and the angles between nonbonded hydrogen-hydrogen and bonded hydrogen-carbon of isopentane with one-gauche and one-anti position**

	Proximate hydrogen on C^4	hydrogen-hydrogen distance (Å)	Angle between hydrogen-hydrogen and hydrogen-carbon ($^\circ$)
C^1	$\text{H}^5(\text{C}^1)-\text{H}^{15}(\text{C}^4)$	4.61	69.9
$\text{C}^{1'}$	$\text{H}^{10}(\text{C}^{1'})-\text{H}^{15}(\text{C}^4)$	2.32	109.5
C^2	$\text{H}^{11}(\text{C}^2)-\text{H}^{16}(\text{C}^4)$	2.56	91.8
C^3	$\text{H}^{13}(\text{C}^3)-\text{H}^{14}(\text{C}^4)$	2.47	62.9
	$\text{H}^{15}(\text{C}^4)-\text{H}^5(\text{C}^1)$	4.61	66.4
$\text{C}^{4,a}$	$\text{H}^{15}(\text{C}^4)-\text{H}^{10}(\text{C}^{1'})$	2.32	107.5
	$\text{H}^{16}(\text{C}^4)-\text{H}^{11}(\text{C}^2)$	2.56	89.2
	$\text{H}^{14}(\text{C}^4)-\text{H}^{13}(\text{C}^3)$	2.47	60.9

^aSteric perturbation on C^4 was determined by the proximate hydrogens on the rest of carbons.

Table 4. The distances between hydrogen and hydrogen, and the angles between nonbonded hydrogen-hydrogen and bonded hydrogen-carbon of isopentane with two-gauche position

	Proximate hydrogen on C^4	Hydrogen-hydrogen distance (Å)	Angle between hydrogen-hydrogen and hydrogen-carbon ($^\circ$)
C^1	$\text{H}^5(\text{C}^1)-\text{H}^{14}(\text{C}^4)$	2.36	106.0
$\text{C}^{1'}$	$\text{H}^8(\text{C}^{1'})-\text{H}^{15}(\text{C}^4)$	2.36	105.9
C^2	$\text{H}^{11}(\text{C}^2)-\text{H}^{14}(\text{C}^4)$	3.90	23.7
C^3	$\text{H}^{13}(\text{C}^3)-\text{H}^{16}(\text{C}^4)$	2.49	61.4
	$\text{H}^{14}(\text{C}^4)-\text{H}^5(\text{C}^1)$	2.36	109.2
$\text{C}^{4,a}$	$\text{H}^{15}(\text{C}^4)-\text{H}^8(\text{C}^{1'})$	2.36	109.2
	$\text{H}^{14}(\text{C}^4)-\text{H}^{11}(\text{C}^2)$	3.90	62.6
	$\text{H}^{16}(\text{C}^4)-\text{H}^{13}(\text{C}^3)$	2.49	60.0

^aSteric perturbation on C^4 was determined by the proximate hydrogens on the rest of carbons.

hydrogens of C^1 , C^2 and C^3 . The peak shifting from the HPDEC ^{13}C NMR spectrum in Fig. 2(a) is nearly identical to that predicted by the model, implying that the rotational conformer of isopentane has two-gauche positions in sH-L, although the anti conformer is more stable and its size is smaller compared to the sH-L (Fig. 4).

Table 5. The chemical shift differences between two rotational conformers of isopentane ($\Delta\delta = \delta_{\text{Gauche}} - \delta_{\text{Anti}}$)

	$\Delta\delta_{\text{calc}}$ (ppm)	$\Delta\delta_{\text{obs}}$ (ppm)
C ^{1,2}	-0.28	-0.29
C ²	+0.10	+0.15
C ³	0.00	0.00
C ⁴	-1.03	-0.89

^aThe average between two C¹'s.

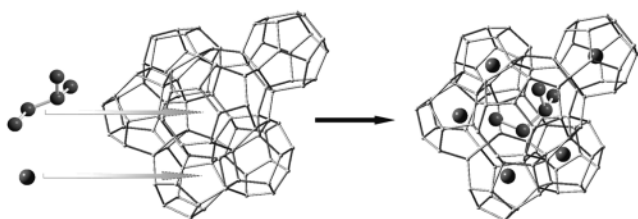


Fig. 4. View of sH isopentane+CH₄ clathrate hydrate. Gray atoms are carbons and vertexes in lattice cage are oxygen. Hydrogen atoms are omitted for clarity.

CONCLUSION

In summary, we analyzed ¹³C NMR spectra of sH CH₄ hydrate with isopentane, one of the simplest and smallest acyclic large guest molecule substances, and MCH, a commonly used cyclic guest molecule that is larger than isopentane in order to analyze the conformation of acyclic large guest molecules. From the comparison with liquid isopentane and MCH spectrum, it was detected that the chemical shifts of isopentane were changed as isopentane molecules were captured into the sH-L; on the other hand, those of MCH, cyclic guest molecule, were not changed. These differences in the chemical shift between two different types of isopentane were checked through the use of a hydrogen-hydrogen steric perturbation model, and from the results we drew the conclusion that one of the smallest acyclic guest molecules, isopentane, participating in the formation of a structure-H clathrate hydrate is encaged, confirming the gauche conformation in large cavities. The present results strongly suggest that the guest position and structure in hydrate cages are greatly in-

fluenced by both short-range interactions between guest molecules and cage frameworks and long-range interactions between small and large guests. Accordingly, cage dynamics must be carefully considered when a specific sH hydrate is designed and synthesized for the purpose of tuning material properties. Further studies will hopefully reveal actual inclusion phenomena of a variety of sH hydrates, particularly including their readily accessible stabilization over sI and sII hydrates.

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