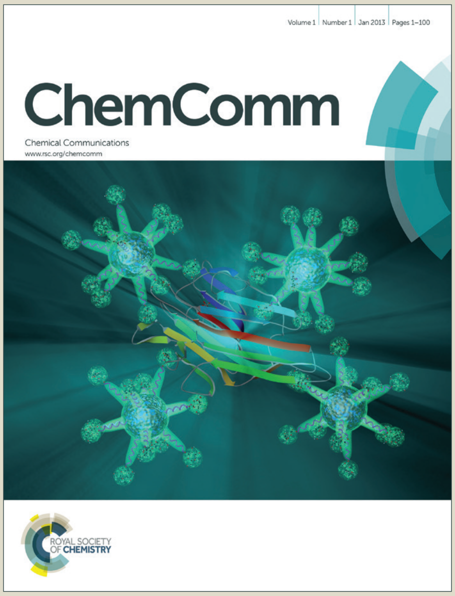
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On the Encapsulation of Hydrocarbon Components of Natural Gas within Molecular Baskets in Water. The Role of C–H···π Interactions and the Host's Conformational Dynamics in the Process of Encapsulation

Y. Ruan, P. W. Peterson, C. M. Hadad and J. D. Badjić*

We examined the encapsulation of CH_4, C_2H_6, C_3H_8 and *iso*-C_4H_{10} in water, using four molecular baskets [1]–[4]. The baskets were shown to bind to hydrocarbon gases by forming favourable C–H---π contacts and, concurrently, adjusting the size of their cup-shaped platform.

In the quest for sustainable and alternative sources of energy,[1] natural gas plays an important role.[2] The world reserves of this important resource are vast and maintained within the earth's crust, permafrost regions or at the bottom of the oceans.[3] The dominant constituent of natural gas is methane (70–90%), while ethane, propane and butane (natural gas liquids, NGLs) represent minor components (0–20%).[4] Indeed, small hydrocarbons are used for the generation of heat and electricity but also as a feedstock in the chemical industry whereby steam cracking, steam reforming, catalytic dehydrogenation and Fischer-Tropsch synthesis constitute important methods for obtaining valuable raw materials.[5, 6] Over the last decade, the exploitation of shale reserves of natural gas in North America, via so-called hydraulic fracturing, has spurred an additional interest toward developing effective and environmentally friendly ways for converting C1 through C4 hydrocarbons into functional chemicals.[6, 7] For instance, selective oxidation of methane into methanol[8] will allow more effective utilization of this abundant and potent greenhouse gas in the future.[9] Indeed, homogeneous catalytic methods[10] for promoting this exothermic process have already been developed, but the experimental procedures require additional optimizations for an industrial setting.[11] Given that methane monooxygenase (MMO) enzymes promote the selective oxidation of CH_4,[12] we reason that positioning a molecule of hydrocarbon gas in the proximity of a catalytic center ought to facilitate the activation of methane's strong C–H bonds;[13] note that chelation-assisted activation of a C–H group[14] is emerging as an important methodology in synthetic organic chemistry.[15] In this way, trapping a molecule of hydrocarbon gas in the cavity of an artificial concave host,[16, 17] containing a catalytic center, should permit the C–H activation. The caveat, though, is that a limited number of hosts[18-22] capable of trapping small gases are difficult to furnish with a catalytic center without perturbing their concave structure and thereby the process of molecular recognition.[23] Molecular baskets of type [**1**]–□**4**] (Figure 1A) are, however, C_3 symmetric and modular compounds with a flat aromatic base fused to three bicyclo[2.2.1]heptane rings forming a curved unit.[24] Three phthalimides extend this semi-rigid structure into a bowl-shaped cavitand capable of trapping guests.[25] Importantly, various amino acids can be conjugated to the framework for enhancing solubility in aqueous media and providing functionality.[26] As the baskets coordinate to transition metal cations (Cu(I)/(II)),[27, 28] at the top of their cavity, the construct provides a platform for developing a generation of supramolecular catalysts capable of oxidizing small hydrocarbons. In this vein, we hereby report on the encapsulation of the principal components of natural gas CH_4, C_2H_6, C_3H_8 and *iso*-C_4H_{10} with baskets [**1**]–□**4**] in water (Figure 1A/B). Importantly, these hosts were found to hold a hydrocarbon molecule in their interior, thereby placing it alongside the amino-acid residues at the rim.

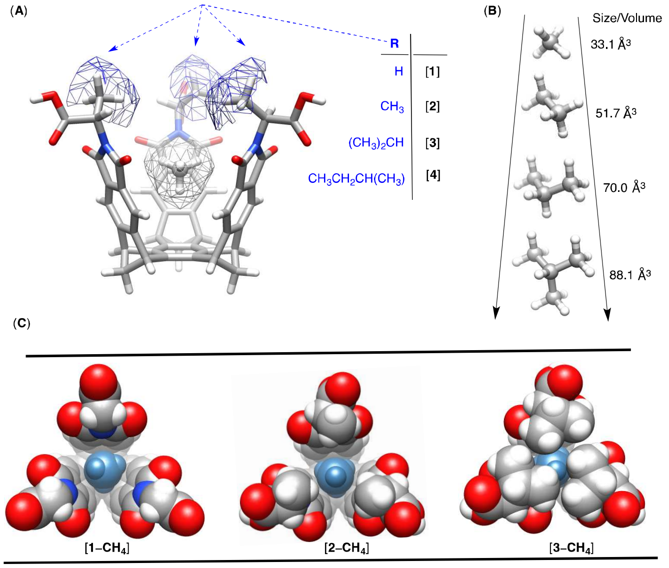

Figure 1. (A) Molecular baskets with three amino-acid residues, of the same kind, at the rim (R = H, glycine **1**; R = CH_3, alanine **2**; R = $(CH_3)_2CH$, valine **3**; and R = $CH_3CH_2CH(CH_3)$, isoleucine **4**. (B) Energy-minimized structures (MMFFs, Spartan) of the principal hydrocarbon components of natural gas and their corresponding volumes. (C) Top view of energy-minimized (DFT: M06-2X/6-31G*) structures of [**1**–CH_4], [**2**–CH_4] and [**3**–CH_4].

Baskets [**1**]–□**4**] were prepared following already published protocols.[26] These tri-anionic hosts stayed monomeric in aqueous phosphate buffer at pH = 7.0 ± 0.1 with, as we posit, three nonpolar R groups pointing to the inner side of each host and negatively charged carboxylates in the polar aqueous environment (Figure 1C).[26] The selected R groups were, in [**1**]–□**4**], deliberately chosen to vary in size so that [**1**] encompasses a practically open aperture at its northern side, while [**3**] has this portal almost completely blocked with the aliphatic groups (Figure 1C). With the assistance of the 3V modelling software,[29] we estimated the volume of the inner space of basket [**3**] to 113 Å^3 (Figure 2B).[30] The following questions arose: would cavitands [**1**]–□**4**] (113 Å^3) encapsulate CH_4 (33 Å^3), C_2H_6 (52 Å^3), C_3H_8 (70 Å^3) and *iso*-C_4H_{10} (80 Å^3) in water on the account of the hydrophobic effect[31] and host-guest complementarity?[32] Would there be any selectivity toward trapping hydrocarbon gases that have different sizes and shapes?[33]

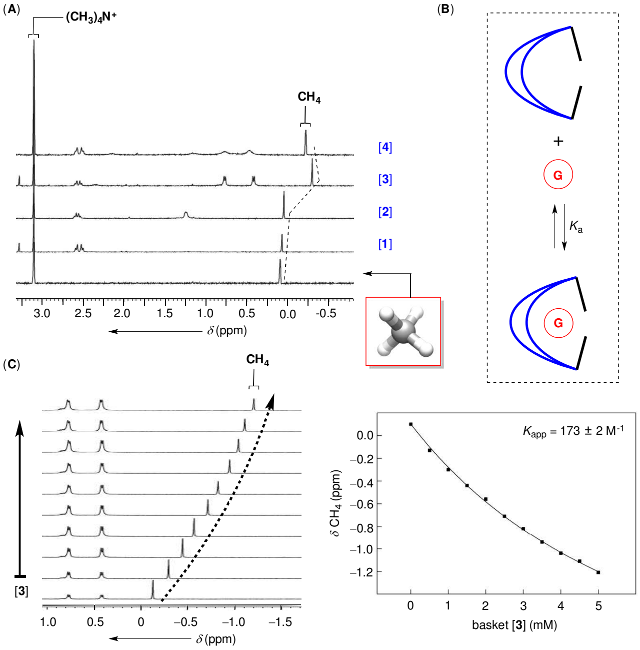

Figure 2. (A) Regions of ^{1}H NMR spectra (400 MHz, 298.2 K) for CH_4 (1.3 mM) dissolved in phosphate buffer at pH = 7.0 ± 0.1 (bottom) and with baskets [**1**], [**2**], [**3**] and [**4**], each at 1.0 mM (top); $(CH_3)_4N^+$ served as an internal concentration standard. (B) A schematic representation for the formation of 1:1 stoichiometric basket-guest complex. (C) An incremental addition of basket [**1**] (from 0.1 to 5.0 mM) to a saturated solution of CH_4 (1.3 mM) in phosphate buffer at pH = 7.0 ± 0.1 was monitored with ^{1}H NMR spectroscopy (400 MHz, 298.2 K). (Right) Nonlinear least-square analysis of the binding data (1:1 binding stoichiometry) gave the apparent association constant K_{app} = 173 ± 2 M^{-1} (R^2 = 0.999, SigmaPlot) for the formation of [**3**–CH_4].

We used ^{1}H NMR spectroscopy to investigate the process of encapsulation (Figure 2). In a typical experiment, an aqueous solution (10 mM phosphate buffer at pH = 7.0 ± 0.1) of [**3**] (1.0 mM) was saturated with CH_4 (1.3 mM) by bubbling the gas for an extended period of time (30 min). The ^{1}H NMR spectrum was then recorded (Figure 2A), and the procedure was repeated with differently concentrated solutions of the host (0.1–5.0 mM, Figure 2B). Thus far, we presumed that the aromatic framework of [**1**]–□**4**] surrounding CH_4 (Figure 1A) should diamagnetically shield the guest's nuclei.[34] Indeed, the ^{1}H NMR singlet at $\delta = 0.1$ ppm (Figure 2A), corresponding to "free" CH_4, shifted upfield with the addition of hosts [**1**]–□**4**] (Figure 2A). In particular, ^{1}H NMR spectra of [**1–4**⊂CH_4] showed a set of resonances corresponding to C_3 symmetric species interconverting at a fast rate on the NMR time scale. A greater chemical shift ($\Delta\delta$ (CH_4) = $\delta_{free}-\delta_{complexed}$, Figure 2A) of the guest, however, residing inside [**3**] or [**4**] suggested a higher affinity of such "more enclosed" baskets for binding CH_4; note that the packing coefficient ($PC = V_{guest}/V_{host}$) for CH_4 is 0.29 (Table 1).[35] Furthermore, an incremental addition of the strongest binder [**3**] to a saturated solution of CH_4 in water caused a steady perturbation of the magnetic environment of the methane proton nuclei (Figure 2C). We evaluated the binding data with a nonlinear least-square analysis for a model describing 1:1 stoichiometric complexation (Figure 2B).[36] The computed binding isotherm (298.2 K) fit well to the experimental data (R^2 = 0.999), with the apparent association constant of K_{app} = 173 ± 2 M^{-1} (Table 1); the NMR titration was incomplete, with a limited solubility of basket [**3**] permitting the formation of only 10–50% of the [**3**–CH_4] complex (Figure 2B).[37] The formation of a 1:1 complex was additionally probed with diffusion NMR measurements (DOSY NMR, Table 1).[26] As a result of the fast exchange of chemical species, on the ^{1}H NMR time scale, the experimentally observed translational diffusion coefficient of methane ($D_{CH4}^{observed}$ = 1.32 · 10^{-9} m^2 s$^{-1,}$ Figure S7) becomes a weighted average of the diffusion coefficients of free (D_{CH4}^{free}) and bound (D_{CH4}^{bound}) gas molecules within basket [**3**] and in line with the following equation: $D_{CH4}^{observed} = f_{CH4}^{free} D_{CH4}^{free} + f_{CH4}^{bound} D_{CH4}^{bound}$. As we obtained D_{CH4}^{free} = 1.84 · 10^{-9} m^2 s^{-1} from a separate measurement (Figure S11), the fractions of free and complexed methane (f_{CH4}^{free} = 0.62, f_{CH4}^{bound} = 0.38) were calculated using the experimental conditions: $[CH_4]_0$ = 1.3 mM, $[\mathbf{3}]_0$ = 4.0 mM and K_a = 173 ± 2 M^{-1} = [**3**–CH_4]/([CH_4] [**3**]). In this way, we determined that D_{CH4}^{bound} = 4.7 · 10^{-10} m^2 s^{-1} is akin to $D_{[3]}^{free}$ = 3.4 · 10^{-10} m^2 s^{-1} (Table 1) denoting that the apparent sizes of bound gas and free basket are comparable (Figure 3A). The result is reasonable, thereby providing an additional support for the formation of a 1:1 binding complex!

Table 1. The apparent equilibrium constants K_{app} (M^{-1}, 298.2 K), corresponding to the encapsulation of the four hydrocarbon gases in baskets **1** and **3**, were obtained from nonlinear least-square analysis of the ^{1}H NMR titration data (Figures S1–S4). Packing coefficients (*PC*) were calculated as $PC = V_{guest}/V_{host}$. Diffusion coefficients of free baskets **1** and **3** ($D_{[1]/[3]}^{free}$) and free/bound gas molecules ($D_{gas}^{free}/D_{gas}^{bound}$) were obtained from DOSY NMR (600 MHz) spectroscopic measurements at 298.2 K (Figures S5–S14).

	CH_4	C_2H_6	C_3H_8	C_4H_{10}
K_{app} (M^{-1})	173 ± 2^a	353 ± 11^a	91 ± 1^b	93 ± 4^b
PC	0.29	0.46	0.62	0.78
D_{gas}^{free} (10^{-10} m^{2}s^{-1})	18.4	14.4	12.7	10.7
$D_{[1]/[3]}^{free}$ (10^{-10} m^{2}s^{-1})	3.4^a	3.4^a	3.5^b	3.5^b
D_{gas}^{bound} (10^{-10} m^{2}s^{-1})	4.7^a	4.8^a	6.3^b	4.5^b

^{a}Basket **3**; ^{b}Basket **1**.

Interestingly, the selectivity of baskets [**1**]–□**4**] for trapping the slightly larger C_2H_6 guest (*PC* = 0.46, Figure 3B) was found to be similar to the one observed for smaller CH_4 (Figure 2A). The apparent thermodynamic stability of [**3**–C_2H_6] was, however, determined to be K_{app} = 353 ± 11 M^{-1} (Figure S2). The largest hydrocarbons, C_3H_8 (PC = 0.62) and *iso*-C_4H_{10} (PC = 0.78), showed a comparable affinity for complexing all four baskets (Figure 3C/D). In addition, we found that these guests possess a reduced affinity for populating the cavity of basket [**1**] (K_{app} ~ 90 M^{-1}, Figure S3–S4 and Table 1). Markedly, the results of diffusion NMR study of [**3**–C_2H_6], [**1**–C_3H_8] and [**1**–C_4H_{10}] were, in each case (Figures S5–S14), conforming with the formation of 1:1 stoichiometric complexes with D_{gas}^{bound} ~ D_{basket}^{free} (Table 1).

To sum up the experimental findings, CH_4 and C_2H_6 prefer residing in baskets [**3**] or [**4**] while C_3H_8 and *iso*-C_4H_{10} have similar affinity for occupying any host [**1**]–□**4**] in the series. Moreover, ethane is the strongest binder, followed by methane, propane and isobutane (Table 1).

To inspect the nature of host-guest interactions and account for the experimental observations, we used density functional theory at the M06-2X/6-31G* level to complete energy minimizations of baskets [**1**]–[**3**], each containing a molecule of hydrocarbon gas methane, ethane or propane (Figure 4).[38] The Minnesota Functionals are useful for quantifying molecular dispersion interactions[39] and particularly valuable for studying attractive C–H---π noncovalent interactions.[40] The structures of energy-minimized [**1**–CH_4], [**2**–CH_4] and [**3**–CH_4] show a molecule of methane placing three hydrogen atoms against four surrounding aromatic rings of the host (Figure 4A). The shortest C–**H**---**C**sp^2 distances (I–IV, Table 2) apparently fall off on going from basket [**1**] to [**3**], with a concomitant contraction of the cup-shaped platform (see N---N spans in Figure 4A and Table 2)! The cut-off distance for the C–H---π interaction is commonly taken as 3.05 Å,[41] which is within the sum of the van der Walls radii of hydrogen (1.2–1.4 Å) and sp^2 hybridized carbon (1.7 Å) atoms.[42] Evidently, the computational results agree with our experimental measurements by which the stability of the [**3**–CH_4] complex is the greatest (Figure 2A). For the binding of ethane, however, the C–H---π contacts are somewhat shorter within [**3**–C_2H_6] complex, in addition to smaller N---N distances (Table 2). Apparently, the valine-based basket "compresses" its aromatic "side walls", thereby assisting the formation of "tighter" C–H---π contacts and the complexation of CH_4/C_2H_6. We assume that the computed contraction is likely a result of the isopropyl groups at the rim of [**3**] getting closer for solvating each other (in vacuum), and in water, by escaping polar solvent molecules. Two additional C–H---π contacts (*d* = 2.853/2.953 Å, Figure 4B) contribute to the encapsulation of ethane in **3**, which in this way becomes more effectively trapped than methane (Table 1).[39] A molecule of propane occupying baskets [**1**]–[**3**] was computed to form seven C–H---π contacts with all three baskets irrespective of the amino acids at the rim. The experiments suggest a somewhat greater affinity of propane for residing within the glycine-based basket [**1**] (Figure 3C) with the computational results showing the shortest C–**H**---**C**sp^2 contacts corresponding to this complex (Table 2). Actually, a terminal CH_3 group of the entrapped propane within [**3**–C_3H_8] (Figure 4C), is in a close proximity (d ~ 2.4 Å, H---H distance) of the valines' CH_3 groups at the host's rim, thereby preventing the contraction of the basket (via van der Waals strain) and the formation of stronger C–H---π contacts. The fact that propane's affinity for occupying molecular baskets is lower than for methane/ethane (Table 1) is, however, difficult to elucidate without further experimentation. For bigger guest molecules, there ought to be solvation and entropic effects that play a significant role in the binding.

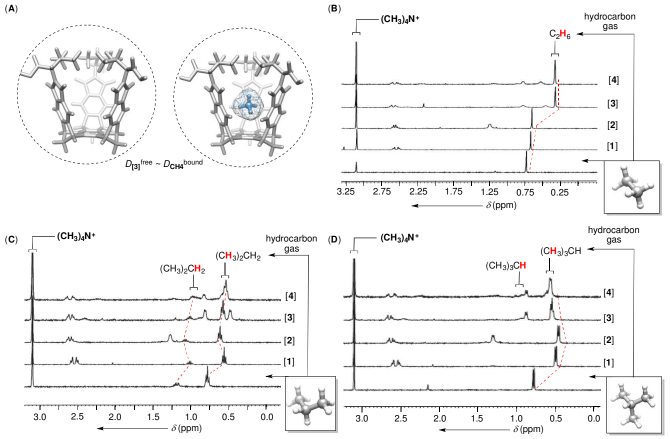

Figure 3. (A) When probed with diffusion NMR spectroscopy, the apparent sizes of "free" basket **3** (left) and methane gas trapped in **3** (right) should be comparable. (B) Selective regions of ^{1}H NMR spectra (400 MHz, 298.2 K) of C_2H_6 (1.8 mM) dissolved in phosphate buffer at pH = 7.0 ± 0.1 (bottom) and containing baskets [**1**], [**2**], [**3**] and [**4**], with each at 1.0 mM. (C) Selective regions of ^{1}H NMR spectra (400 MHz, 298.2 K) of C_3H_8 (1.4 mM) dissolved in phosphate buffer at pH = 7.0 ± 0.1 (bottom) and containing baskets [**1**], [**2**], [**3**] and [**4**], with each at 1.0 mM. (D) Selective regions of ^{1}H NMR spectra (400 MHz, 298.2 K) of *iso*-C_4H_{10} (0.8 mM) dissolved in phosphate buffer at pH = 7.0 ± 0.1 (bottom) and containing baskets [**1**], [**2**], [**3**] and [**4**], with each at 1.0 mM.

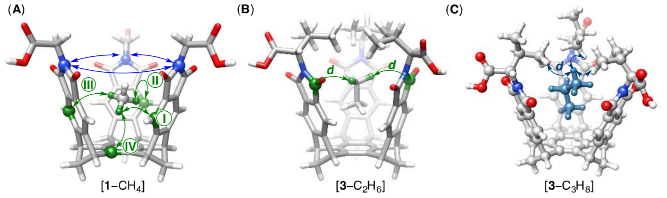

Figure 4. (A) A molecule of methane having four C–H---π contacts (I–IV, green) with surrounding aromatics of basket **1**. Three N---N distances (blue) report on the flexing of the basket. (B) Two additional C–H---π contacts are proposed to improve the stability of complex [**3**–C_2H_6]. (C) Short H---H contacts (d ~ 2.4 Å) within complex [**3**–C_3H_8].

Table 2. Four short C–**H**--**C**sp^2 distances (I–IV, Figure 4A) from [**1**/**3**–guest] complexes were obtained from the energy-minimized structures (DFT: M06-2X/6-31G*). The mean value of three N---N distances (Figure 4A), within each [**1**/**3**–guest] complex, is reported.

	C–H--π (I, Å)	C–H--π (II, Å)	C–H--π (III, Å)	C–H--π (IV, Å)	N–N (Å)
[**1**–CH_4]	2.770	2.996	3.012	3.058	7.515
[**2**–CH_4]	2.965	2.990	3.003	3.028	7.497
[**3**–CH_4]	2.832	2.892	2.916	2.919	7.231
[**1**–C_2H_6]	2.715	2.779	2.927	2.989	7.344
[**2**–C_2H_6]	2.798	2.837	2.919	3.049	7.352
[**3**–C_2H_6]	2.735	2.738	2.742	2.968	6.886
[**1**–C_3H_8]	2.761	2.772	2.781	2.943	7.049
[**2**–C_2H_8]	2.795	2.803	2.804	2.919	7.244
[**3**–C_2H_8]	2.815	2.880	2.909	2.913	7.459

In conclusion, molecular baskets encapsulate the principal components of natural gas in water by positioning these molecules against their aromatic cavity via numerous C–H---π interactions, and with an association constant as high as 353 ± 11 (at 298 K).[43] The basket expands or constricts its cup-shaped platform to accommodate the aliphatic groups at the rim and concurrently a hydrocarbon molecule in the inner-space; in this way, the consideration of the hosts' volumes are, perhaps, becoming less important. As the encapsulation of small alcohols (CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$ and $(CH_3)_3COH$) does not occur (Figure S15-S18), our study sets a good foundation for examining the oxidation of hydrocarbons in confined environments of molecular baskets.

Notes and references

[a] Department of Chemistry and Biochemistry, 100 West 18th Avenue, Columbus, Ohio USA. Fax: 614-292-1685; Tel: 614-247-8342; E-mail: badjic@chemistry.ohio-state.edu.

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Table of Contents

Text: Molecular baskets encapsulate hydrocarbon components of natural gas by forming C–H---π contacts and adjusting the size of their cup-shaped platform.