

Crystal engineering of nonporous organic solids for methane sorption†

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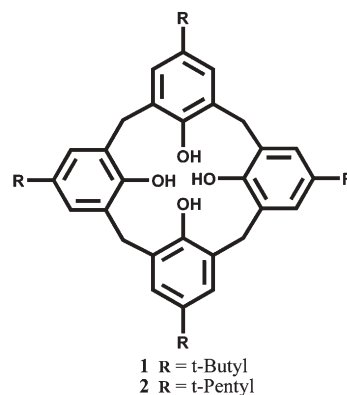
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The low density polymorph of the well-known host *p*-tert-butylcalix[4]arene absorbs more methane than *p*-tert-pentylcalix[4]arene at room temperature and 1 atm pressure, but the order of absorption is reversed at 38 atm with *p*-tert-pentylcalix[4]arene absorbing more.

Finding an inexpensive way to store hydrogen will be crucial for establishing hydrogen as a fuel for the next generation. However, the problems associated with the facile storage of hydrogen have not been solved, nor are they likely to be solved in the near term.¹ There is a well-recognized need for alternate fuels to bridge the gap between the current oil-based economy and the future hydrogen economy. Methane, a major component of natural gas, is a prime candidate to function as such an energy bridge.² Although extensive effort has been directed towards synthesizing metal-organic frameworks with large pore volumes in an attempt to enhance the sorption capacities for gases such as methane,³ relatively little attention has been focused on organic solids.⁴ Historically, organic compounds have been ignored in the context of gas sorption because such compounds generally adhere to close-packing principles which do not lead to conventionally porous structures. However exceptions to this phenomenon are known to exist.⁵

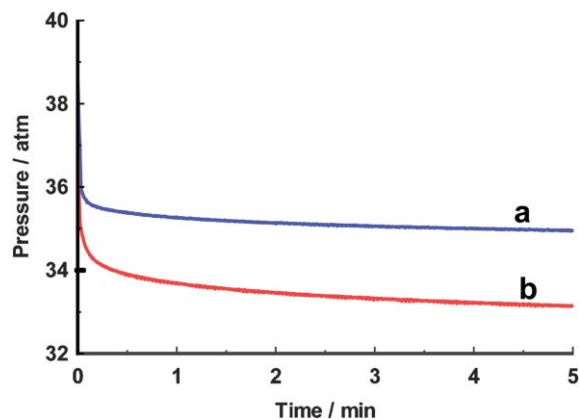
In this context, calix[4]arenes have been found to exhibit interesting and unexpected behaviour. For example, calix[4]arene has the ability to trap highly volatile guests such as CF₃Br, CF₄ and CH₄ well beyond their normal boiling points.⁶ Similarly, *p*-tert-butylcalix[4]arene, **1** (Scheme 1) is an extremely versatile inclusion compound with several guest-induced structural motifs.⁷ Our previous studies on a low density polymorph of **1**, obtained under sublimation at 280 °C, revealed absorption of N₂, O₂, CO and CO₂ under ambient temperature and pressure. This same polymorph can be used in the purification of hydrogen from gas mixtures.⁵ Further, immersion of crystals of this polymorph in liquid vinyl bromide for 15 minutes results in a single-crystal to single-crystal phase transition in which vinyl bromide diffuses through the crystal to achieve the thermodynamically most stable form.⁸ Very recently, we have shown that 14% of the capsules in **1** are occupied by two molecules of methane at 0.54 atm.⁹ In a continuation of this work, we have sought to use principles of



Scheme 1

crystal engineering¹⁰ to extend our sorption experiments on **1** to the related host *p*-tert-pentylcalix[4]arene, **2** (Scheme 1).

In order to record the absorption isotherms, we constructed a device which has been outlined elsewhere.⁹ A sample of **1** (1.4 g) was placed in a sample chamber and evacuated for 1 h at room temperature to remove any trace amount of gas. Methane was introduced into the sample chamber ($V_s = 7.35 \text{ cm}^3$) at an initial pressure of 38 atm. Fig. 1 presents the absorption isotherm, which shows the pressure in sample **1** decreasing with time. After approximately 30 min, equilibrium was reached at ca. 35 atm. The calculated uptake value of methane is 1.7 wt%. Similar experiments were conducted on a freshly sublimed sample of **2** (1.23 g). At room temperature equilibrium was reached at ca. 32 atm (after 30 min). Surprisingly, the nonporous network of **2** has a significantly higher storage capacity for methane (2.2 wt%) than does **1** at an initial pressure of 38 atm. Even more surprisingly, when the sorption experiments were repeated at relatively low

Fig. 1 High pressure sorption of methane on (a) **1** and (b) **2** at 298 K.

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† Electronic supplementary information (ESI) available: ORTEP diagram of **2** and overlay of **2** and **2**-toluene. See <http://dx.doi.org/10.1039/b507406a>

pressure (*ca.* 1 atm), the amount of methane uptake by **2** at room temperature is very small when compared to **1** (Fig. 2).

As has been described before, the crystal structure of **1** shows calixarene molecules arranged in an up-down bilayer packing motif.⁷ Fig. 3 shows that, across the bilayer, the calixarene molecules are offset from one another and exist in what may be described as skewed capsules, each with a free volume of *ca.* 235 Å³. The sublimed crystals of **2** have now been subjected to a single-crystal X-ray diffraction analysis.[‡] The molecules in **2** are also arranged to form bilayers as in **1**, but the packing is quite different. Fig. 4 shows a packing diagram of **2** in which all calixarene molecules are stacked in columns along [001] and each column consists of molecules facing the same direction. Each column is surrounded by four nearest-neighbor columns running in the opposite direction. Within the column the packing of one calixarene molecule on top of the next affords *ca.* 88 Å³ of free

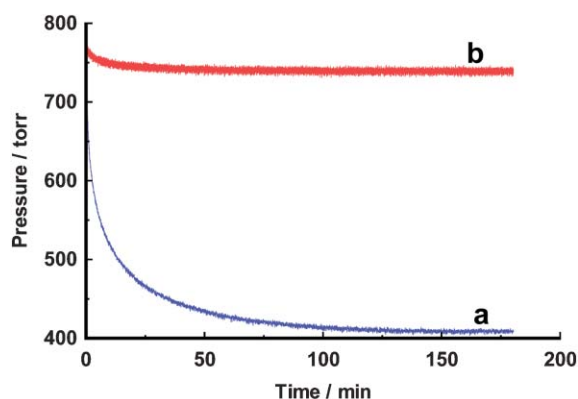


Fig. 2 Low pressure sorption of methane on (a) **1** and (b) **2** at 298 K.

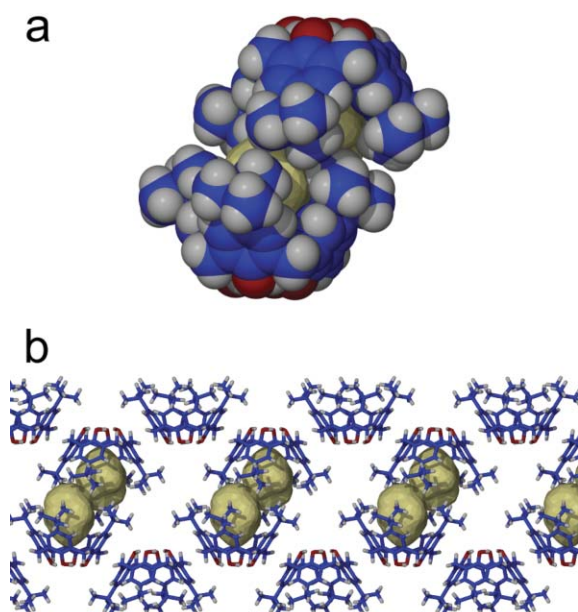


Fig. 3 X-Seed¹¹ representation of (a) a slightly offset face-to-face calixarene dimer of **1** with the void shown as a yellow surface and (b) the bilayer packing mode of the molecules. The yellow surface was generated using Connolly's Molecular Surface¹² software (probe radius = 1.5 Å).

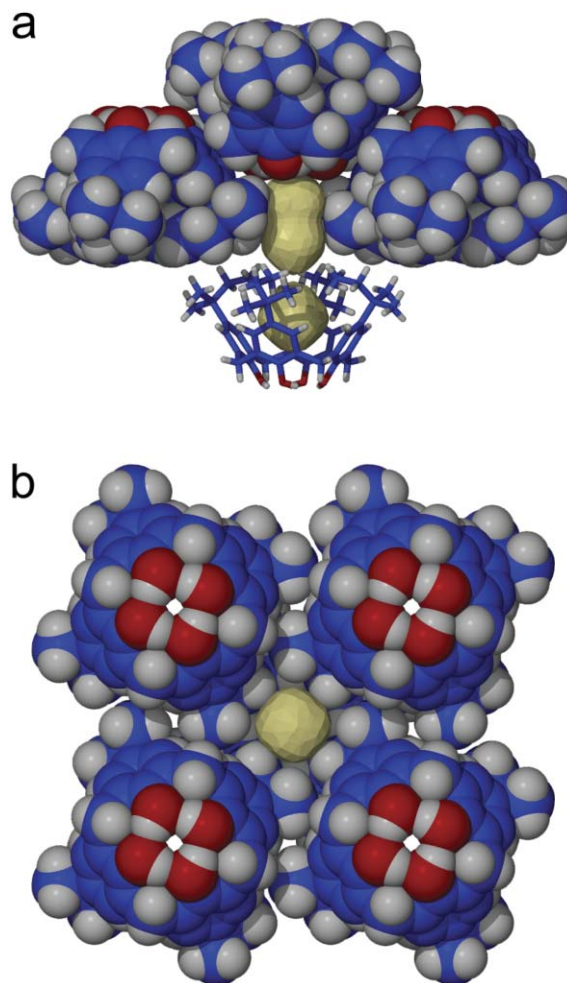


Fig. 4 (a) Small voids (yellow surfaces, probe radius = 1.5 Å) of 34 and 54 Å³ are formed between adjacent calixarenes in columns of **2** stacked along [001]. Neighboring calixarenes are removed for clarity. (b) Calixarene columns in **2** viewed along [001].

volume. Moreover, observation of Fig. 4a and 4b reveals that there are two chambers of void space, one (34 Å³) which is the cavity of the *p*-*tert*-pentylcalix[4]arene and the other (54 Å³) which results from the packing of one calixarene on the other.

Close scrutiny of apohost crystal structures of **1** and **2** reveals that neither structure possesses pores. However, in both cases gas molecules flow into the seemingly nonporous crystals. As noted earlier,⁹ it is plausible to assume that the upper rim *tert*-butyl groups of the calixarenes play a critical role in gas uptake for structure **1**. In the solid-state, the aromatic and hydroxyl groups at the lower rim of the calixarene have well-defined thermal ellipsoids and appear to be rigid, while the *tert*-butyl groups of the upper rim may rotate about the C(ar)–C(sp³) bond, as evidenced by crystallographic disorder. We have previously postulated that a cooperative rotation of the *tert*-butyl groups may produce a 'turnstile' effect which would allow the gas molecules to diffuse through the crystals.

To the best of our knowledge, this is the first structural report of apohost **2**. However, the crystal structure of **2**·toluene has been reported, and it is isostructural to apohost **2**.^{†13} As noted above, the packing of calixarene molecules is quite different for **1** and **2**.

The postulated mechanism for the diffusion of gas molecules through crystals of **1** is likely to be different from that for **2**. This expectation is based on the crystal structures, and since the 'turnstiles' noted for **1** do not exist in **2**, it is therefore reasonable to expect a different mechanism of gas diffusion to be operative in **2**. This expected difference in the mechanisms of gas diffusion appears to be supported by the sorption data presented in Fig. 1 and 2. It is clear that at 1 atm methane pressure, **1** absorbs more methane than does **2**. However, at 38 atm methane pressure, **2** absorbs more than does **1**. This is consistent with the major portion of the space available for housing methane in **2** to be either inaccessible at 1 atm methane pressure, and/or there are two pathways for methane sorption in **2**. Experiments in progress at this time are aimed at clarifying the mechanism of methane sorption in these nonporous organic solids.

Although much is known about the organic solid-state, it is abundantly clear that there is yet much more to be learned.

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Notes and references

‡ Crystal data for **2**: C₄₈H₆₄O₄, *M* = 704.99, colorless prism, 0.30 × 0.20 × 0.15 mm³, tetragonal, space group *P4/n* (No. 85), *a* = *b* = 12.717(3), *c* = 13.457(6) Å, *V* = 2176.2(11) Å³, *Z* = 2, *D*_c = 1.076 g cm⁻³, *F*₀₀₀ = 768, Bruker SMART Apex CCD diffractometer, MoK α radiation,

λ = 0.71073 Å, *T* = 173(2)K, $2\theta_{\max}$ = 54.3°, 14207 reflections collected, 2398 unique (*R*_{int} = 0.0860). Final GooF = 1.072, *R*1 = 0.0823, *wR*2 = 0.2016, *R* indices based on 1488 reflections with *I* > 2 σ (*I*) (refinement on *F*²), 150 parameters, 2 restraints. Lp and absorption corrections applied, μ = 0.066 mm⁻¹. CCDC 273602. See <http://dx.doi.org/10.1039/b507406a> for crystallographic data in CIF or other electronic format.

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