A crystalline organic substrate absorbs methane under STP conditions

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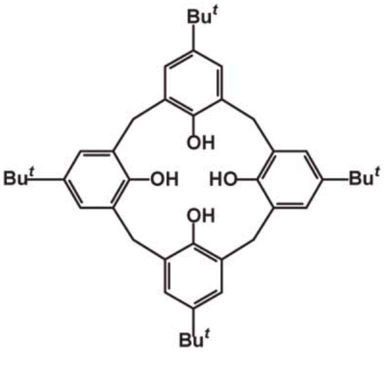
A well-known host compound readily absorbs methane at room temperature and pressures of one atmosphere and lower.

Our long-standing interest[1] in the host–guest chemistry of calixarenes has recently evolved into studies of the solid–gas sorption phenomena exhibited by these fascinating compounds. For example, we have shown that calix[4]arene has the ability to entrap highly volatile gases such as halons, freons and methane within lattice interstices.[2] Although the crystals are primarily stabilised by van der Waals interactions, guests such as CF_3Br, CF_4 and CH_4 are retained at temperatures of up to 260, 370 and 320 °C, respectively, above their normal boiling points. In this system, the host lattice must be disassembled thermally in order to release the guest molecules. While such tenacious host–guest stability is useful for gas sequestration, topical applications involving gas-uptake (*e.g.* temporary storage and separation) generally require readily reversible sorption reactions such as those observed for activated carbons and zeolites. Furthermore, to minimize the expenditure of energy during either sorption or release of the gas, the ideal crystalline host matrix should not undergo a significant phase transformation during these processes.

Although a particular apohost phase of the well-known host compound *p-tert*-butylcalix[4]arene, **1** (Scheme 1), obtained by sublimation, undergoes a transition concomitant with the uptake of organic vapors such as vinyl bromide and toluene,[3] this apparently does not occur when the guest is a gas. In a recent study we revealed that **1** selectively includes CO_2 from a mixture of H_2 and CO_2, and that this phenomenon can be exploited to purify either gas.[4] Whereas it is known that **1** will undergo subtle, thermally-induced phase changes,[5,6] no discernable phase transition of the host lattice occurs during the CO_2 sorption process. Until now our studies of the gas inclusion properties of **1** have been confined to a limited selection of gases. Here we show that a previously described[4] low-density phase of **1** is capable of absorbing methane at room temperature and pressures of one atmosphere or lower.



p-tert-butylcalix[4]arene (**1**)

Scheme 1

In order to record gas sorption isotherms, we constructed the device shown schematically in Fig. 1. The apparatus was installed inside an insulated cabinet which could be thermostated at a constant temperature. A powdered sample (1.403 g) of sublimed **1** was placed in chamber B (volume V_B = 12.6 cm^3). Chambers A and B were evacuated through valve V_3 with V_2 open and V_1 closed. Chamber B was then sealed under vacuum by closing V_2 and V_3. The pressures in A and B were recorded automatically by means of electronic transducers P_A and P_B (Wika ECO series) interfaced to a computer equipped with an analog-to-digital converter. A known amount (P_A = 1503 torr) of methane was introduced into chamber A (V_A = 15.4 cm^3) through valve V_1. Valve V_2 was opened for approximately one second in order to equalise the methane pressure in chambers A and B (*i.e.* $P_{AB} = [P_A \times V_A]/[V_A + V_B - V_{sample}]$). After closing V_2, the pressure in B began to decrease rapidly as the gas was absorbed by the calixarene crystals (Fig. 2). After approximately 2.5 hours, the pressure in chamber B reached an equilibrium value of 410 torr. At this pressure, the molar ratio of methane to calixarene is calculated to be 0.14 : 1.

Although the room temperature crystal structure of the low-density polymorph of **1** has been described elsewhere,[5] it is useful to readdress some salient features of this remarkable material. The structure consists of dimeric capsules composed of facing, but slightly offset calixarene molecules. Since the crystals are formed

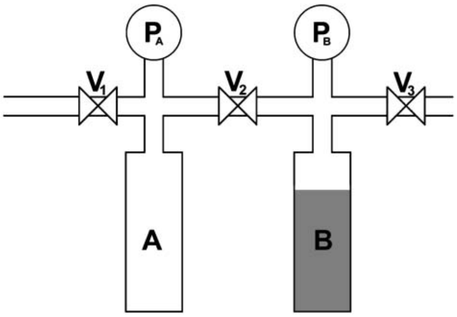


Fig. 1 Schematic diagram of a device for the measurement of gas sorption isotherms. With the exception of the pressure transducers P_A and P_B, the apparatus consists of modular brass components manufactured by Swagelok®. The solid sample (grey) is placed in chamber B.

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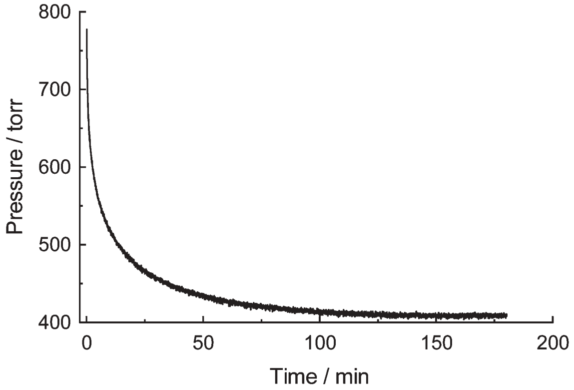

Fig. 2 Isothermal sorption of methane by *p-tert*-butylcalix[4]arene at 298 K.

by sublimation under vacuum, each capsule encloses 235 Å^3 of unoccupied space.[3] After exposure of newly sublimed crystals to air for several hours, X-ray structural analysis revealed significant residual electron density within the confines of the capsule. This observation implies the presence of O_2 and N_2 as a result of sorption of these gases under ambient conditions. Indeed, subsequent sorption experiments involving these gases confirmed this hypothesis.[4]

Inspection of a static model of the capsule and its immediate molecular surroundings reveals no atomic-scale pores that breach the capsule walls. At face value, this implies that the capsule should be impervious even to small linear molecules such as CO_2, N_2 and O_2. However, since these gas molecules clearly display a significant degree of mobility in the seemingly nonporous crystal lattice, and even force their way into the capsule voids, we can conclude that the static model derived from crystal structure analysis does not comport accurately with reality.

It is reasonable to assume that the *tert*-butyl moieties at the upper rims of the calixarene molecules play a key role in facilitating gas uptake. In the solid state the aromatic and hydroxyl regions of the molecules are generally considered to be structurally rigid, while the *tert*-butyl groups can conceivably rotate about the C(ar)–C(sp^3) bond. At 298 K all four of the *tert*-butyl groups of the calixarene are each rotationally disordered over two relatively well-defined positions. This disorder appears to be primarily static, although a significant degree of dynamic displacement of the methyl groups is also evident (as inferred from thermal ellipsoid models). The *tert*-butyl groups form a broad equatorial band encircling the capsule void and it therefore seems plausible that they might rotate cooperatively to create transient windows of opportunity during which gas molecules are able to diffuse through.

In our recent study[4] of CO_2 uptake by **1** we showed that only a single molecule of the gas can be accommodated within each void formed by two calixarene molecules (*i.e.* host : guest = 2 : 1). For a given temperature the proportion of lattice voids occupied by the guest is dependent on pressure; at 298 K, 100% occupancy is only reached under approximately three atmospheres of CO_2 pressure. A molecule of CO_2 is *ca.* 5.2 Å long with a maximum radial diameter of *ca.* 3.4 Å (Fig. 3). In contrast, a molecule of methane is more isotropically shaped with an average diameter of *ca.* 3.8 Å. Thus, according purely to size–shape considerations (Fig. 4), it should be possible to accommodate at least two CH_4 molecules within each dimeric capsule (*i.e.* host : guest = 1 : 1). Based upon this assumption, our preliminary result indicates that 14% of the capsules are, on average, each occupied by two molecules of methane at 0.54 atm.

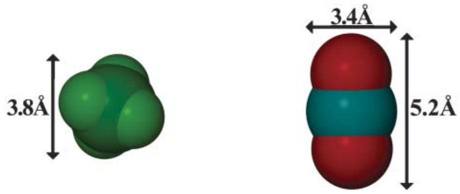

Fig. 3 Space filling models of CH_4 (green) and CO_2 (red/blue) showing approximate van der Waals dimensions.

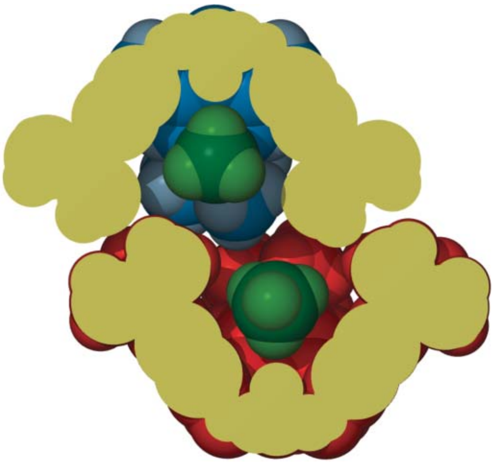

Fig. 4 A section through the dimeric capsule formed by two facing, but slightly offset calixarene molecules. For clarity, the individual calixarenes are colored blue and red with the sectioned surface shown as a yellow plane. Two idealized molecules of methane (green) have been placed inside the dimeric capsule by means of the program X-Seed[7] in order to illustrate their excellent size–shape compatibility with regard to the available space.

In recent years the search for alternative fuel technologies has intensified rapidly. The viable storage of gases for use in fuel-cells, especially for mobile applications, has been identified as a particularly pressing problem to be solved.[8] Although new materials consisting of porous metal organic frameworks have been suggested as promising gas storage substrates,[9] purely organic molecular crystals have received little attention. The paucity of data with regard to the latter is most likely due to their tendency to close-pack. Our results demonstrate that low density organic systems do indeed merit consideration as potential sorbants for volatile gases, and that such sorption process can occur under desirable conditions close to standard temperature and pressure.

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Notes and references

1 J. L. Atwood, F. Hamada, K. D. Robinson, G. W. Orr and R. L. Vincent, *Nature*, 1991, **349**, 683; G. W. Orr, L. J. Barbour and J. L. Atwood, *Science*, 1999, **285**, 1049; J. L. Atwood, L. J. Barbour, M. W. Heaven and C. L. Raston, *Angew. Chem. Int. Ed.*, 2003, **42**, 3254; J. L. Atwood, L. J. Barbour, S. J. Dalgarno, M. J. Hardie, C. L. Raston and H. R. Webb, *J. Am. Chem. Soc.*, 2004, **126**, 13170.

2 J. L. Atwood, L. J. Barbour and A. Jerga, *Science*, 2002, **296**, 2367.

3 J. L. Atwood, L. J. Barbour, A. Jerga and B. L. Schottel, *Science*, 2002, **298**, 1000.

4 J. L. Atwood, L. J. Barbour and A. Jerga, *Angew. Chem. Int. Ed.*, 2004, **43**, 2948.

5 J. L. Atwood, L. J. Barbour and A. Jerga, *Chem. Commun.*, 2002, 2952; E. B. Brouwer, G. D. Enright, K. A. Udachin, S. Lang, K. J. Ooms, P. A. Halchuk and J. A. Ripmeester, *Chem. Commun.*, 2003, 1416.

6 J. L. Atwood, L. J. Barbour, G. O. Lloyd and P. K. Thallapally, *Chem. Commun.*, 2004, 922.

7 L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189; J. L. Atwood and L. J. Barbour, *Cryst. Growth Des.*, 2003, **3**, 3.

8 R. F. Service, *Science*, 2004, **305**, 958; V. C. Menon and S. Komarneni, *J. Porous Mater.*, 1998, **5**, 43.

9 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; K. Seki, *Chem. Commun.*, 2001, 1496; S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem. Int. Ed.*, 2000, **39**, 2082.