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Inclusion adducts of 4,4-bis(4'-biphenylyl)cyclohexa-2,5-dienone: a clay mimic organic host

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In the lamellar architecture of the title crystal structure mediated by $C-H\cdots O$ hydrogen bonds, 1,2-dimethoxyethane and *n*-hexane are included in the hydrophobic galleries; isostructurality of these clathrates is a unique case of guest mimicry.

Host-guest inclusion compounds provide opportunities for the design of novel open architectures for diverse applications such as chemical separation, reactions and catalysis in a microcavity, and for electrooptic, nonlinear and magnetic materials.¹ Crystal engineering of 2D and 3D robust metal-organic and soft molecular open frameworks offer the promise of tailoring specific structures, functions and properties through functionalised organic molecules.² For example, 4-tritylbenzoic acid crystallises via a carboxylic acid dimer (O-H···O hydrogen bond) with wheel-axle topology, 4-halophenoxy triazines selfassemble through triangulo halogen synthons (Cl···Cl, Br···Br interaction) as hexagonal channel hosts, and ligands such as 1,3,5-benzenetricarboxylic acid, 4-aminopyridine and 4,4'bipyridine continue to be exploited in coordination polymer networks.3 We report herein the construction of a lamellar, C-H...O hydrogen bonded host lattice which includes guest species in the interlayer region, thereby expanding the family of newly emerging neutral, organic clay mimics.4

Molecule 1^{+5} (Scheme 1) was designed as a tecton⁶ with hydrogen bonding donor-acceptor groups in the quinone ring and biphenyl spacers oriented in the third dimension. It was expected that tecton 1 will self-assemble in a layer motif via C-H···O hydrogen bonded tape 2 and the biphenyl groups will constitute the pillars in the resulting 3D open framework. While implementing this molecule \rightarrow crystal synthetic strategy for a potential host, we are aware that interpenetration⁷ competes with guest inclusion during crystallisation and that the latter phenomenon (the goal of this study) occurs in only ca. 15% cases.⁸ Recrystallisation of 1 from various solvents afforded diffraction quality crystals from 1,2-dimethoxyethane (DME). The X-ray structure of $1 \cdot DME$ (2:1 stoichiometry, C2/c space group)‡ contains a C-H···O hydrogen bond chain along [001] (H···O 2.66 Å, C-H···O 160.6°; C-H distance neutronnormalised to 1.083 Å). The second C-H···O bond of the tape is long (3.05 Å, 175.6°) but at the accepted distance limit advocated by Desiraju and Steiner.9 What is significant from a crystal engineering objective is that the target synthon 2 has



2392 Chem. Commun., 2001, 2392–2393



Continuing further, 1 was recrystallised from *n*-hexane, a solvent isosteric with DME but devoid of hydrogen bonding groups. The crystal structure of $1 \cdot n$ -hexane (2:1) is iso-



Fig. 1 Crystal structure of $1 \cdot DME(2:1)$ in the *bc*-plane to show the tape synthon 2. Guest molecules are not shown for clarity. Notice that the biphenyl groups project in the third dimension.



Fig. 2 Crystal structure of $1 \cdot DME$ (2:1) down the *c*-axis. The network of host–host and host–guest C–H···O hydrogen bonds stabilise the ordered superstructure.



Fig. 3 Displacement ellipsoids at 50% probability of *n*-hexane in $1 \cdot n$ -hexane (2:1). (a) Conformation with 45% occupancy of C34, (b) conformation with 55% occupancy of C33, (c) superposition of both conformers to show the mimicry with 1,4-dimethylcyclohexane (sof of atoms).

morphous‡ with identical arrangement of host atoms in the crystal. The metrics of quinone tape C-H...O bonds are 2.67, 161.9 and 2.99 Å, 175.1°; the (Ph)C–H···O is 2.71 Å, 137.2°. In the channel, n-hexane is disordered over two orientations with 55% and 45% occupancy (Fig. 3). The slightly elongated displacement ellipsoid of the C33 atom in a low temperature crystal structure implies that there are other minor conformations that contribute to guest disorder, but it is difficult to assign their exact position because of very low electron density. Using our refinement model, the structure converges (R factor 0.0675) with site occupancy factor (sof) of 0.55 and 0.45 for C33 and C34 guest atoms. Notably, neither of the conformations of nhexane trapped in the microcavity correspond to the one in the crystal structure of pure solvent.¹² Superposition of the two conformers (Fig. 3c) suggests that host 1 may be able to separate a mixture of cis- and trans-1,4-dimethylcyclohexane.§ The guest is present in folded conformations because dimensions of the host cavity (8 \times 5 Å) force it to adopt a compact shape.¹³ The end-to-end $C \cdots C$ distance in the folded conformations of *n*hexane is 5.5 Å (5.3 Å in DME) while it is 6.4 Å in the extended zigzag conformation.12 Energy of the three conformations of nhexane (RHF-631G*)¶ is -235.2718 au (55% population), -235.2933 au (45% population) and -235.3678 au (zigzag). A survey of the Cambridge Structural Database¹⁴ (version 5.21, April 2001 update) shows that this is the first example of structural mimicry between DME and n-hexane in a host channel. The host cavity of 1, which also includes 1,4-dibromobutane, is highly selective towards these guest species. Co-solvents such as EtOAc, Et₂O, CHCl₃, CH₂Cl₂ are not included, even when present in large excess.

Finally, we note that while polymorphs of phenyl benzoquinone **3** were found to have divergent, even abstruse, crystal packing in $P\overline{1}$ (Z = 8) and $P2_1$ (Z = 2) space groups,¹⁵ pseudopolymorphs of biphenyl analogue **1** are isostructural. Therefore replacement of geminal phenyl group with biphenyl steers crystal packing towards a recurring (robust) supramolecular synthon¹⁶ and yields a novel, organic host material with clay-like properties. Metric engineering² of the lamellar–pillar molecular framework of **1** is a current goal in our studies.

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Notes and references

† **1** was synthesised from 4,4'-diphenylbenzophenone using standard reagents and reaction conditions. FT-IR: 1668, 763 cm⁻¹. ¹H NMR: δ 6.45 (d, *J* 10 Hz, 2 H), 7.20–7.50 (m, 12 H), 7.50–7.70 (m, 8 H). For synthesis of **3**, see ref. ⁵.

‡ Crystal data: (1)·(CH₃OCH₂CH₂OCH₃)_{0.5}: (C₃₀H₂₂O)·(C₄H₁₀O₂)_{0.5}, C2/ c, a = 25.464(5), b = 19.751(4), c = 9.770(2) Å, β = 97.72(3)°, Z = 8, V = 4868.9(17) Å³, 5886 unique reflections (3 < 2θ < 57°), final R = 0.0522 for 1352 observed reflections [I > 2σ(I)] for 308 parameters. Data collected on Enraf-Nonius MACH-3 diffractometer at 293(2) K using Mo-Kα X-rays (λ 0.71073 Å) in the ω scan mode. CCDC 172238. (1)·(nhexane)_{0.5}: (C₃₀H₂₂O)·(C₆H₁₄)_{0.5}, C2/c, a = 25.052(5), b = 20.185(4), c = 9.722(2) Å, β = 98.27(3)°, Z = 8, V = 4865.4(17) Å³, 4736 unique reflections (5 < 2θ < 53°), final R = 0.0675 for 2282 observed reflections [I > 2σ(I)] for 317 parameters. Data collected on a Bruker SMART diffractometer at 168(2) K using MoKα X-rays (λ 0.71073 Å) in the ω-2θ scan mode. For both structures, H-atoms were fixed and structure solution and refinement were done with SHELX-97. CCDC 172239. See http:// www.rsc.org/suppdata/cc/b1/b106598j/ for crystallographic files in .cif or other electronic format.

§ Aldrich Chemical Co. USA, mixture of isomers \$71.20 per 25g, pure cis \$227.70 per 25g.

¶ PC Spartan Pro 1.0, Wave function Inc. USA.

 $\|$ (1) $(Br(CH_2)_4Br)_{0.5}$: C2/c, a = 25.21, b = 20.21, c = 9.84 Å, $\beta = 97.8^\circ$, T = 293 K, R = 0.12. The heavy guest disorder in interlayer regions gives a high diffraction R value typical of clays.⁴ The presence of 1,4-dibromobutane in crystals was confirmed by NMR ($\delta 2.0, 3.4$).

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