Pergamon

Tetrahedron 56 (2000) 6675–6681

TETRAHEDRON

The Idiosyncrasies of Tetrabenzo[24]crown-8 in the Solid State

Stuart J. Cantrill,[a] Jon A. Preece,[b] J. Fraser Stoddart,[a,*] Zhen-He Wang,[a] Andrew J. P. White[c] and David J. Williams[c]

[a]Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, CA 90095, USA
[b]School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
[c]Department of Chemistry, Imperial College, South Kensington, London SW7 2AY, UK

Received 20 January 2000; accepted 6 March 2000

Abstract—In the solid state, the macrocyclic polyether, tetrabenzo[24]crown-8 (TB24C8), is an interesting molecule. When crystallized from MeCN solution, a bis-MeCN clathrate is formed, in which the TB24C8 macroring—by adopting a conformation with approximate tennis-ball-seam symmetry (D_{2d})—forms C–H···π-linked supramolecular chains. However, when crystallized from $CHCl_3$/Et_2O solution, the TB24C8 crystallizes alone—adopting a self-filling 'flattened-out' conformation with C_i symmetry—forming C–H···π-linked sheets which stack upon one another by virtue of—yet again (!)—C–H···π hydrogen bonds. By contrast, the solid-state superstructure of the [2]pseudorotaxane formed between TB24C8 and dibenzylammonium hexafluorophosphate (DBA·PF_6), contains no C–H···π interactions. However, a multitude of more enthalpically favorable C–H···F hydrogen bonds—to a highly-ordered matrix of PF_6^- anions—stabilizes the formation of the [2]pseudorotaxane array. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The concept of hard and soft acids and bases can be extended[1] to the analysis of hydrogen bonding.[2] Classically, the X–H···Y interaction, where X and Y are heteroatoms, can be considered[3] as a hard acid/hard base combination, which leads to relatively large binding enthalpies ($-\Delta H$) in the range 3–7 kcal mol^{-1}. The structural integrities and functional aspects of living systems have been ascribed in part[4] to those interactions. However, in recent times, weaker and more subtle hydrogen bonding forces have been identified as important stabilizing interactions in biological systems.[5] These interactions take the form of: (i) weak acid/hard base[6] combinations (C–H···X); as well as (ii) hard acid/weak base[7] ones (X–H···π). Both are associated with $-\Delta H$ values of the order of 2–4 kcal mol^{-1}. Finally, a soft acid/soft base[1,8–11] combination (C–H···π) has been estimated to be associated with $-\Delta H$ values of around 1 kcal mol^{-1}. There is still considerable debate as to the exact nature of these weaker hydrogen bonds,[12] e.g. are they electrostatic or dispersive in nature? Whatever interpretation is put upon them, the interactions are attractive. In particular, the C–H···π interaction has received a great deal of attention[1,8] recently in an attempt to establish its overall importance. Some of these investigations have been conducted for compounds in solution using ingenious approaches,[13–15] such as the molecular torsion balance[14] and chemical double mutant cycles.[7e,15] Moreover, attempts have also been made to investigate the nature of C–H···π interactions in the solid state[16,17] by studying structurally related polynuclear compounds[16] and designing molecular scaffolds[17] which favor or disfavor edge-to-face T-type geometries. It has been found[18] that, although these C–H···π interactions are weak, they can play a significant role in the assembly of crystalline organic compounds when they operate in a cooperative manner.[19] At this time, it is becoming clear that the C–H···π interaction—perhaps the weakest and most subtle of hydrogen bonding interactions—is being recognized as a significant phenomenon in the fields of coordination chemistry,[20] stereochemistry,[21] biochemistry,[5,22] molecular recognition[8c,23] and self-assembly.[24]

A recent quantitative investigation[25] of the aromatic crown ether/dialkylammonium ion recognition motif[26] prompted us to explore[27] the effect, upon this system, of varying the number and positioning of benzo rings fused to the macrocyclic polyether skeleton. One of the compounds chosen for this study was tetrabenzo[24]crown-8 (TB24C8).[28] Although initially our goal was to explore this crown ether's ability to bind[27a] $R_2NH_2^+$ ions, as we proceeded with our investigations, it became apparent that TB24C8 was an intriguing compound in its own right. Here, we report[29] the solid state superstructures of solvated (MeCN)[30] and free TB24C8. Although both superstructures exhibit cooperative C–H···π interactions, in the latter, the superstructure is dominated totally by these interactions involving both faces of all the benzo rings in such a manner that the resulting three-dimensional superstructure is held together by an

---

Keywords: C–H···π interactions; crown ethers; hydrogen bonding; pseudorotaxanes; supramolecular chemistry.

* Corresponding authors. Tel.: +1-310-206-7078; fax: +1-310-206-1843; e-mail: stoddart@chem.ucla.edu

PII: S0040-4020(00)00475-0

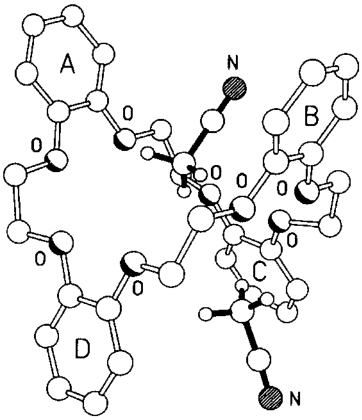

Figure 1. The solid-state superstructure of TB24C8·2MeCN.

array of Ar-H···π···H–CHO motifs. Additionally, we describe the solid-state superstructure[31] of a [2]pseudorotaxane[32] array-formed during co-crystallization of TB24C8 with dibenzylammonium hexafluorophosphate ($DBA{\cdot}PF_6$)[26b] that is stabilized by a highly ordered matrix of PF_6^- anions, which participate in numerous C–H···F interactions.[33,34] In this case, it appears that the weaker C–H···π interactions are superseded by more enthalpically favorable N^+–H···O,[3] C–H···O,[6] and C–H···F[33] hydrogen bonding interactions, which take over and dominate the solid-state superstructure.

Results and Discussion

Crystals of TB24C8·2MeCN were grown by vapor diffusion of Et_2O into an MeCN solution of TB24C8. The X-ray analysis (Fig. 1) of these crystals showed them to be an acetonitrile solvate in which the crown ether has a tennis ball seam-like conformation with approximate D_{2d} symmetry. Rings **A** and **B**, and **C** and **D** have centroid···centroid separations of 8.05 and 7.30 Å, respectively, and associated inter-ring cleft angles of 41 (**A/B**) and 36° (**C/D**). Within these clefts are inserted the two MeCN solvent molecules, each of which are held in place by weak C–H···O hydrogen bonds between one of their methyl hydrogen atoms and a proximal catechol oxygen atom on the TB24C8 rings; the C–H···O hydrogen bond geometries are C···O, H···O (Å), C–H···O (°), 3.35, 2.45, 153 and 3.56, 2.58, 177, respectively. There are no π–π interactions involving the cyano groups. Although the presence of the included MeCN molecules inhibits intercomplex π–π stacking interactions, notably there are intercomplex C–H···π interactions. In one instance, one of the polyether methylene hydrogen atoms in one molecule interacts with the π-system of ring **A** in another (H···π 2.91 Å, C–H···π 140°), and there is also an aromatic–aromatic edge-to-face interaction between ring **B** in one molecule and ring **C** in another (centroid···centroid separation 5.09 Å, with an associated C–H···π geometry of H···π 2.86 Å and C–H···π 157°). Perhaps the most elegant intermolecular interactions are associated with the insertion of ring **C** of one molecule into the cleft formed between rings **A** and **B** of another (the **A**···**C** and **B**···**C** centroid···centroid separations are 5.12 and 4.99 Å, respectively) to form a supramolecular chain (Fig. 2), which is stabilized by pairs of cooperative C–H···π interactions (**a**: H···π 3.16 Å, C–H···π 136° and **b**: H···π 2.93 Å, C–H···π 142°).

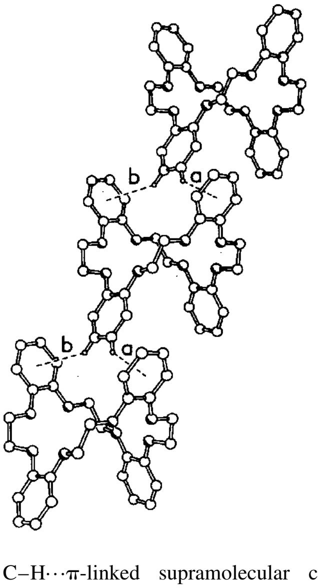

Figure 2. The C–H···π-linked supramolecular chain formed by TB24C8·2MeCN in the solid state.

Crystals of TB24C8 grown by vapor diffusion of Et_2O into a $CHCl_3$ solution of TB24C8 produced crystals free of included solvent. Here, the crown ether adopts a conformation (Fig. 3) that is totally different from that present in TB24C8·2MeCN, the molecule having a distinctly 'flattened-out' and self-filling conformation with crystallographic C_i symmetry in which rings **A** and **B** are inclined by 59° to each other. This dramatic change in conformation—in comparison with that observed in the acetonitrile solvate—represents a departure from the conventional planar geometry[35] that extends from the catechol units to include the two adjacent *O*-methylene groups in each OCH_2CH_2O linkage in TB24C8·2MeCN to one in which there is an approximately orthogonal relationship between the planes of the catechol rings and one or both of the associated O–CH_2 bonds in each of the four OCH_2CH_2O linkages in the unsolvated TB24C8. The absence of solvent, coupled with the change in conformation, gives rise to a crystal packing that is totally dominated/controlled by cooperative C–H···π interactions that involve all four catechol rings. These interactions fall into two distinct categories: (i) those utilizing aryl-methine hydrogen atoms *meta* to the catechol oxygen atoms to link (Fig. 4a) the

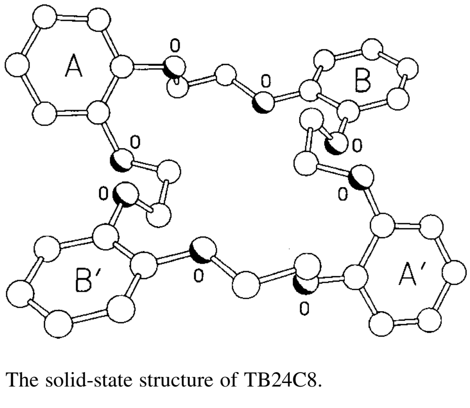

Figure 3. The solid-state structure of TB24C8.

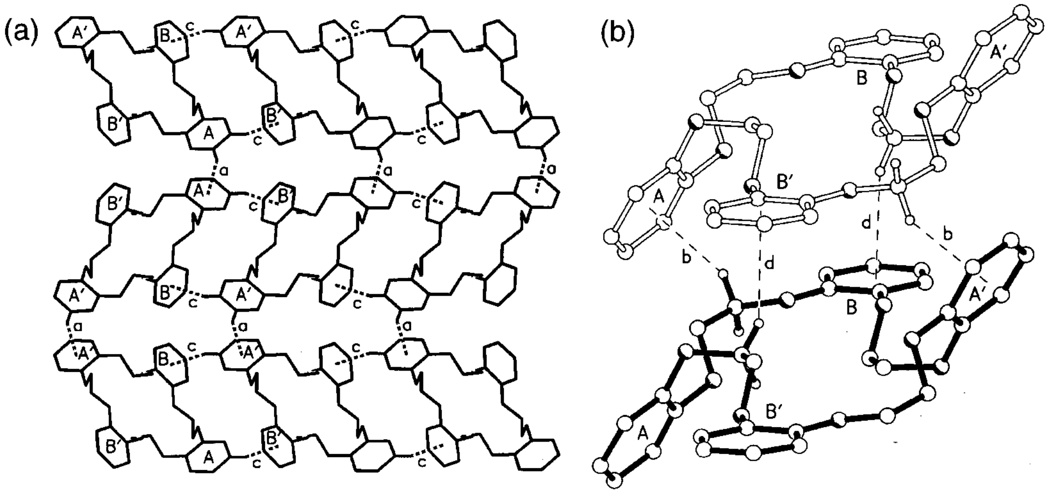

Figure 4. (a) Part of one of the $\mathrm{C{-}H}\cdots\pi$ (aryl-methine) linked sheets of molecules present in the solid-state superstructure of TB24C8. (b) The linking of the adjacent sheets by means of $\mathrm{C{-}H}\cdots\pi$ (*O*-methylene) interactions.

molecules to form sheets; and (ii) those involving methylene hydrogen atoms to link adjacent sheets (Fig. 4b). Another key feature of this $\mathrm{C{-}H}\cdots\pi$-linked superstructure is that all four catechol rings have $\mathrm{H}\cdots\pi$ approaches to both of their faces. In each instance, there is (Fig. 5) an aryl-methine proton approaching one face of a catechol ring, and an *O*-methylene proton approaching the other ($\mathrm{C{-}H}\cdots\pi$ geometries $\{\mathrm{H}\cdots\pi, \mathrm{C{-}H}\cdots\pi\}$: **a** 2.83 Å, 156°; **b** 2.84 Å, 152°; **c** 2.76 Å, 154°; **d** 2.82 Å 145°). In the case of all four catechol rings, the pairs of $\mathrm{H}\cdots\pi$ vectors (**a**:**b** 171° and **c**:**d** 174°) are almost co-linear. It is perhaps surprising that, for a molecule possessing four aryl ring systems, there are no face-to-face π–π interactions.[36]

It is now of interest to compare and contrast the two solid-state superstructures described above with that of the [2]pseudorotaxane formed between TB24C8 and dibenzylammonium hexafluorophosphate (DBA·$\mathrm{PF_6}$). Although TB24C8 has been shown[27a] to have a negligible affinity for the $\mathrm{DBA^+}$ cation in solution, the kinetically-controlled crystallization of these two components affords[31] a [2]pseudorotaxane array in the solid state. Single crystals of [TB24C8/DBA][$\mathrm{PF_6}$] were obtained upon slow evaporation of a $\mathrm{CHCl_3/MeCN}/n\text{-}\mathrm{C_6H_{14}}$ (7:3:3) solution containing a 1:1 mixture of the 'rod' and 'wheel' components. The X-ray crystallographic analysis reveals that the asymmetric unit contains *four* independent 1:1 complexes, each possessing (Fig. 6) a very similar co-conformation,[37] with the only significant difference being in the relative orientation of one of the benzyl groups with respect to the plane of the $\mathrm{C_{Ph}CH_2NH_2^+CH_2C_{Ph}}$ backbone. The approximate tennis ball

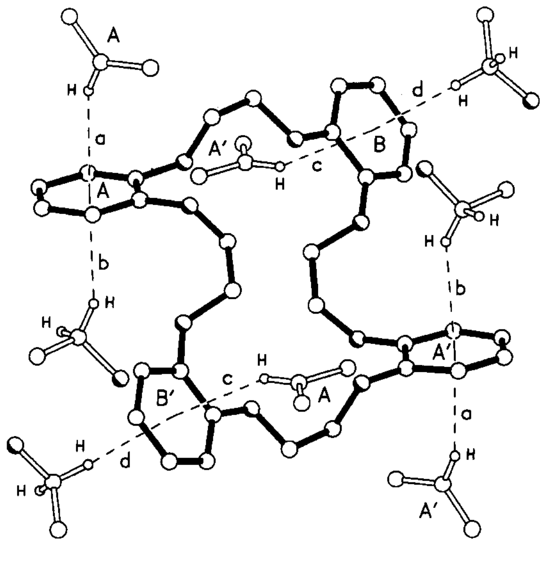

Figure 5. The systematic approaches of the aryl-methine and *O*-methylene protons to the opposite faces of all four catechol rings (**A**, **A'**, **B** and **B'**) in the solid-state superstructure of TB24C8.

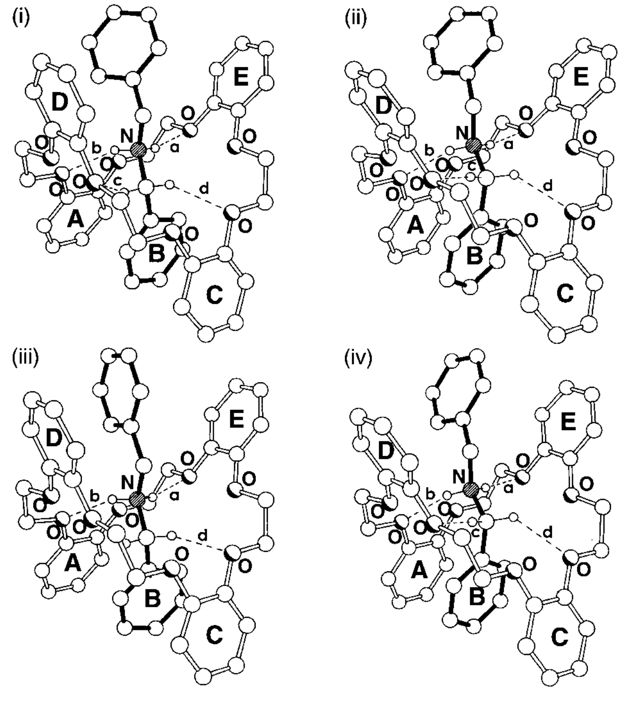

Figure 6. Ball-and-stick representations of the four crystallographically independent [2]pseudorotaxanes present in the crystals of [TB24C8/DBA][$\mathrm{PF_6}$] showing the $[\mathrm{N^+{-}H}\cdots\mathrm{O}]$ and $[\mathrm{C{-}H}\cdots\mathrm{O}]$ hydrogen bonding. The hydrogen bonding geometries and inter-ring separations are given in Table 1.

Table 1. [N$^+$–H···O] and [C–H···O] hydrogen bonding parameters a–d and centroid···centroid separations (Å) for pairs of aromatic rings in the four independent [TB24C8/DBA][PF$_6$] supermolecules (Fig. 6) that exist in the solid state

Interaction (*H-Bonding*)	Supermolecule			
	(i)	(ii)	(iii)	(iv)
a				
[N$^+$···O] (Å)	2.91	2.96	2.98	2.92
[H···O] (Å)	2.03	2.08	2.11	2.03
[N$^+$–H···O] (°)	165	167	163	169
b				
[N$^+$···O] (Å)	3.05	3.04	2.99	3.00
[H···O] (Å)	2.20	2.16	2.13	2.13
[N$^+$–H···O] (°)	158	164	159	164
c				
[C···O] (Å)	3.34	3.29	–	3.27
[H···O] (Å)	2.51	2.33	–	2.31
[C–H···O] (°)	144	175	–	178
d				
[C···O] (Å)	3.16	3.14	3.12	3.19
[H···O] (Å)	2.32	2.33	2.18	2.43
[C–H···O] (°)	146	141	160	136
[cat···cat]				
[A···C]	7.67	7.93	7.90	7.66
[D···E]	7.96	8.64	7.86	8.09
[cat···Ph]				
[A···B]	3.86	3.71	3.86	3.55
[B···C]	3.96	4.23	4.22	4.12

Table 2. Hydrogen bond lengths (Å) for the interactions between the F atoms of the PF$_6^-$ anions and the H atoms located on either the DBA$^+$ cation or the TB24C8 ring in the four independent [TB24C8/DBA][PF$_6$] supermolecules that exist in the solid state

Interaction	Supermolecule			
	(i)	(ii)	(iii)	(iv)
[F···H(*m*-Ph)]	2.60	2.45	2.47	2.55
[F···H(*m*-Ph)]	2.55	2.60	2.55	–
	2.55	–	–	–
[F···H(*o*-cat)]	2.56	2.34	2.52	2.43
[F···H(polyether)]	2.55	2.45	2.47	2.35
	2.59	2.54	2.55	2.57
	2.49	–	2.57	2.59
	–	–	2.55	2.58

seam symmetry (D_{2d}) adopted by the TB24C8 macrocycle is similar to that observed in TB24C8·2MeCN. Stabilization of the individual 1:1 complexes is achieved (Table 1) via the usual[26c] combination of [N$^+$–H···O] (**a** and **b**) and [C–H···O] (**c** and **d**) hydrogen bonding interactions, which are supplemented by face-to-face π–π stacking interactions whereby benzo rings **A** and **C** of the crown ether sandwich phenyl ring **B** of the DBA$^+$ cation. These supermolecules are in turn stabilized by a wealth of C–H···F hydrogen bonding[33] interactions (Table 2) originating from a highly ordered matrix formed by the associated PF$_6^-$ anions. The unusual lack of disorder observed for the PF$_6^-$ anions is perhaps indicative of their participation[38] in directing the formation of the overall three-dimensional lattice. The PF$_6^-$ anions are embedded (Fig. 7) into layers of the 1:1 complexes, occupying clefts (Fig. 8) formed between each group of four supermolecules. Adjacent layers-related by C_2 symmetry-are almost in register, thereby encapsulating the PF$_6^-$ anions. Each anion participates in at least five [C–H···F] interactions, involving no fewer than four of its F atoms to H-bond donors located in (i) the benzo rings or (ii) the ethyleneoxy linkages of TB24C8 or (iii) the phenyl rings of the DBA$^+$ cation.

Conclusions

In summary, it is noteworthy that in the solid-state superstructures of both TB24C8 and TB24C8·2MeCN, although both the *O*-methylene and Ar-H protons have the option (which they avoid) of forming hydrogen bonds to oxygen atoms—which represent better hydrogen bond acceptors than π-systems[39]—and the benzo rings have the opportunity to interact in a face-to-face π–π stacking manner, the three-dimensional superstructure is dominated solely by C–H···π interactions. The exclusive use of this motif could result for a number of reasons, including (i) the phenolic nature of *all* of the oxygen atoms in the TB24C8 macroring which reduces their propensity to act as effective hydrogen bond acceptors;[27a] (ii) edge-to-face geometries that are favored over their face-to-face alternatives because the small surface area of the catechol rings enhances the electrostatic interactions in preference to dispersive ones;[36,40] and finally (iii) the C–H···π networks that extend throughout each solid-state superstructure and are thus associated with extensive positive cooperativity.[18,19] Although perhaps the weakest of hydrogen bonds, the role played by C–H···π interactions in molecular recognition events is undoubtedly an important one, and is highlighted in the first two solid-state superstructures reported in this Paper. If there is a take-home message from our investigations of the idiosyncrasies of TB24C8 in the solid state, it is that the weak C–H···π hydrogen bond should not be overlooked

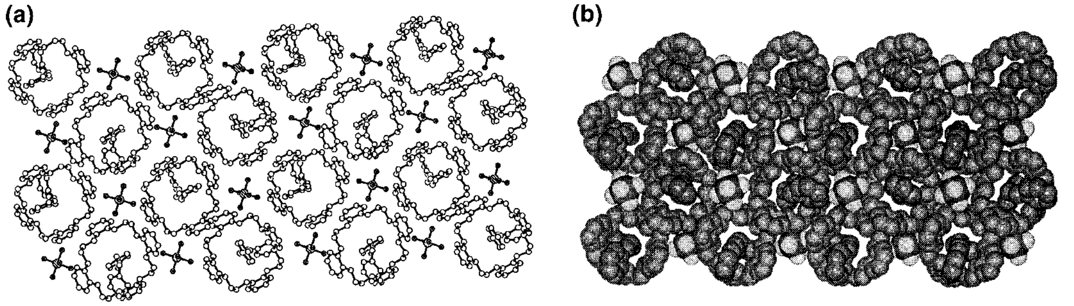

Figure 7. (a) Ball-and-stick; and (b) space-filling representations (hydrogen atoms omitted for clarity) showing the layer structure of [TB24C8/DBA][PF$_6$].

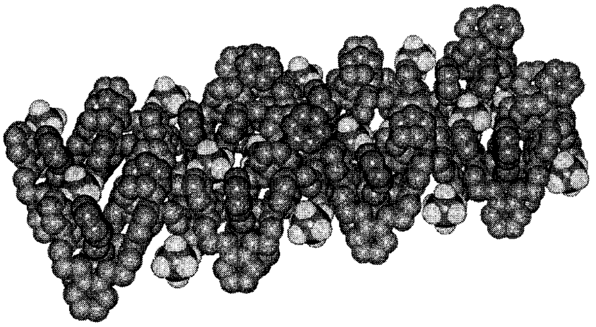

Figure 8. A space-filling representation (hydrogen atoms omitted for clarity) of [TB24C8/DBA][PF_6] showing the embedding of the PF_6^- anions into the egg-box-like clefts formed in the layer structure of [2]pseudorotaxane supermolecules.

when considering noncovalent bonding interactions, as it may be present more often than we think. As Nishio has commented,[5d] a considerable portion of what in the past may have been imprecisely defined as 'hydrophobic interactions' could well be as a consequence of the C–H···π interaction. However, as demonstrated in the case of [TB24C8/DBA][PF_6], this weak noncovalent interaction can be usurped easily by other—more enthalpically favorable—interactions. This solid-state superstructure appears to be determined by a plethora of stabilizing C–H···F hydrogen bonding interactions to highly ordered, interstitially located, PF_6^- anions at the expense of an extended C–H···π network.

Experimental

Crystal data for TB24C8·2MeCN

Crystals of TB24C8·2MeCN were grown by vapor diffusion of Et_2O into MeCN solution of TB24C8. $C_{32}H_{32}O_8$·2MeCN, M=626.7, monoclinic, $P2_1/c$ (no. 14), a=16.018(1), b=10.200(2), c=21.394(2) Å, β=108.24(1)°, V=3319.7(7) Å^3, Z=4, ρ_c=1.254 g cm^{-3}, μ(CuKα)=7.28 cm^{-1}, F(000)=1328, T=173 K; clear plates, 0.93×0.47×0.10 mm, Siemens P4 rotating anode diffractometer, ω-scans, 5198 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give R_1=0.063, wR_2=0.150 for 3570 independent observed reflections [$|F_o|>4\sigma(|F_o|)$, $2\theta\leq124°$] and 416 parameters. CCDC 132743.[41]

Crystal data for TB24C8

Crystals of TB24C8 were grown by vapor diffusion of Et_2O into $CHCl_3$ solution of TB24C8. $C_{32}H_{32}O_8$, M=544.6, monoclinic, $P2_1/c$ (no. 14), a=9.585(2), b=18.931(2), c=7.297(1) Å, β=94.29(1)°, V=1320.3(3) Å^3, Z=2 (the molecule has crystallographic C_i symmetry), ρ_c=1.370 g cm^{-3}, μ(CuKα)=8.07 cm^{-1}, F(000)=576, T=293 K; clear plates, 0.50×0.47×0.13 mm, Siemens P4/PC diffractometer, ω-scans, 2077 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give R_1=0.049, wR_2=0.134 for 1713 independent observed reflections [$|F_o|>4\sigma(|F_o|)$, $2\theta\leq124°$] and 182 parameters. CCDC 132744.[41]

Crystal data for [TB24C8/DBA][PF_6]

Crystals of [TB24C8/DBA][PF_6] were grown by slow evaporation of a $CHCl_3$/MeCN/n-C_6H_{14} solution (7:3:3) containing an equimolar mixture of TB24C8 and DBA·PF_6. [$C_{46}H_{48}NO_8$][PF_6]·0.5MeCN·0.125CH_2Cl_2, M=919.0, triclinic, space group $P\bar{1}$ (no. 2), a=14.182(1), b=23.357(2), c=28.107(2) Å, α=91.51(1), β=90.51(1), γ=104.37(1)°, V=9015(1) Å^3, Z=8 (there are four crystallographically independent 1:1 complexes in the asymmetric unit), ρ_c=1.354 g cm^{-3}, μ(CuKα)=13.7 cm^{-1}, F(000)=3842, T=183 K; clear platy prisms, 0.43×0.20×0.07 mm, Siemens P4 rotating anode diffractometer, graphite-monochromated CuKα radiation, ω-scans, 24143 independent reflections. The structure was solved by direct methods and all the full occupancy non-hydrogen atoms were refined anisotropically. Disorder was found in the thread component of one of the four crystallographically independent [2]pseudorotaxanes and in one of the included acetonitrile solvent molecules; in each case two partial occupancy orientations were identified with only the non-hydrogen atoms of the major occupancy orientations being refined anisotropically (the rest being refined isotropically). Refinements were by blocked full matrix least-squares based on F^2 to give R_1=0.089, wR_2=0.216 for 12765 independent observed reflections [$|F_o|>4\sigma(|F_o|)$, $2\theta\leq115°$] and 2264 parameters. CCDC 132801.[41]

References

1. Nishio, M.; Umezawa, Y.; Hirota, M. *The CH/π Interaction. Evidence, Nature and Consequences*, Wiley-VCH: New York, 1998.

2. Jeffrey, G. A. *An Introduction to Hydrogen Bonding*, Oxford University: New York, 1997.

3. For literature on X–H···Y hydrogen bonds, see: (a) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, 1960. (b) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin: New York, 1968. (c) MacGillivray, L. R.; Atwood, J. L. *Nature* **1997**, *389*, 469–472. (d) Rose, K. N.; Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Chem. Commun.* **1998**, 407–408. (e) Dewa, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1998**, *120*, 8933–8940. (f) Madsen, G. K. H.; Iversen, B. B.; Larsen, F. K.; Kapon, M.; Reisner, G. M.; Herbstein, F. H. *J. Am. Chem. Soc.* **1998**, *120*, 10040–10045.

4. (a) Watson, J. D.; Crick, F. H. C. *Nature* **1953**, *171*, 737–738. (b) Watson, J. D. *The Double Helix: A Personal Account of the Discovery of the Structure of DNA*; Atheneum: New York, 1968. (c) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer: Berlin, 1991. (d) Rose, G. D.; Wolfenden, R. *Annu. Rev. Biophys. Biomol.* **1993**, *22*, 381–415. (e) Draper, D. E. *Trends Biochem. Sci.* **1996**, *21*, 145–149. Although hydrogen bonding is undoubtedly a crucial factor in terms of both DNA structure and function, the relative importance of specific Watson–Crick hydrogen bonding interactions has recently been called into question. See: (f) Moran, S.; Ren, R. X.-F.; Rumney IV, S.; Kool, E. T. *J. Am. Chem. Soc.* **1997**, *119*, 2056–2057. (g) Evans, T. A.; Seddon, K. R. *Chem. Commun.* **1997**, 2023–

2024. (h) Morales, J. C.; Kool, E. T. *J. Am. Chem. Soc.* **1999**, *121*, 2323–2324.

5. (a) Chakrabarti, P.; Samanta, U. *J. Mol. Biol.* **1995**, *251*, 9–14. (b) Maeda, I.; Shimohigashi, Y.; Ikesue, K.; Nose, T.; Ide, Y.; Kawano, K.; Ohno, M. *J. Biochem.* **1996**, *119*, 870–877. (c) Umezawa, Y.; Nishio, M. *Bioorg. Med. Chem.* **1998**, *6*, 493–504. (d) Umezawa, Y.; Nishio, M. *Bioorg. Med. Chem.* **1998**, *6*, 2507–2515. (e) Glusker, J. P. *Top. Curr. Chem.* **1998**, *198*, 1–56. (f) Umezawa, Y.; Tsuboyama, S.; Takahashi, H.; Uzawa, J.; Nishio, M. *Bioorg. Med. Chem.* **1999**, *7*, 2021–2026.

6. For literature on C–H$\cdots$X hydrogen bonds, see: (a) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070. (b) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290–296. (c) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441–449. (d) Steiner, T. *Chem. Commun.* **1997**, 727–734. (e) Berger, I.; Egli, M. *Chem. Eur. J.* **1997**, *3*, 1400–1404. (f) Mascal, M. *Chem. Commun.* **1998**, 303–304. (g) Jeffrey, G. A. *J. Mol. Struct.* **1999**, *486*, 293–298.

7. For literature on X–H$\cdots\pi$ hydrogen bonds, see: (a) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641–5653. (b) Drew, M. G. B.; Willey, G. R. *J. Chem. Soc., Perkin Trans. 2* **1986**, 215–220. (c) Rzepa, H. S.; Webb, M. L.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 765–768. (d) Rodham, D. A.; Suzuki, S.; Suenram, R. D.; Lovas, F. J.; Dasgupta, D.; Blake, G. A. *Nature* **1993**, *362*, 735–737. (e) Adams, H.; Harris, K. D. M.; Hembury, G. A.; Hunter, C. A.; Livingston, D.; McCabe, J. M. *Chem. Commun.* **1996**, 2351–2352. (f) Bisson, A. P.; Lynch, V. M.; Monahan, M. K. C.; Anslyn, E. V. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2340–2342. (g) Malone, J. F.; Murray, C. M.; Charlton, M. H.; Docherty, R.; Lavery, A. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3429–3436. (h) Rozas, I.; Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **1997**, *101*, 9457–9463. (i) Braga, D.; Grepioni, F.; Tedesco, E. *Organometallics* **1998**, *17*, 2669–2672.

8. For a general consideration of the C–H$\cdots\pi$ interaction, see: (a) Nishio, M.; Hirota, M. *Tetrahedron* **1989**, *45*, 7201–7245. (b) Hunter, C. A. *Chem. Soc. Rev.* **1994**, 101–109. (c) Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, *51*, 8665–8701. (d) Laxmi Madhavi, N. N.; Katz, A. K.; Carrell, H. L.; Nangia, A.; Desiraju, G. R. *Chem. Commun.* **1997**, 1953–1954. (e) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University: Oxford, 1999. (f) Umezawa, Y.; Tsuboyama, S.; Takahashi, H.; Uzawa, J.; Nishio, M. *Tetrahedron* **1999**, *55*, 10047–10056. Additionally, for a comprehensive list of references on almost every aspect of the C–H$\cdots\pi$ interaction, consult the homepage of Professor Motohiro Nishio on the Internet at http://www.tim.hi-ho.ne.jp.dionisio.

9. For literature on C–H$\cdots\pi$(aryl) hydrogen bonds, see: (a) Desiraju, G. R.; Gavezzotti, A. *J. Chem. Soc., Chem. Commun.* **1989**, 621–623. (b) Oki, M. *Acc. Chem. Res.* **1990**, *23*, 351–356. (c) Etter, M. C. *J. Phys. Chem.* **1991**, *95*, 4601–4610. (d) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, *23*, 283–288. (e) Ashton, P. R.; Preece, J. A.; Stoddart, J. F.; Tolley, M. S.; White, A. J. P.; Williams, D. J. *Synthesis* **1994**, 1344–1352. (f) Boyd, D. R.; Evans, T. A.; Jennings, W. B.; Malone, J. F.; O'Sullivan, W.; Smith, A. *Chem. Commun.* **1996**, 2269–2270. (g) Ashton, P. R.; Hörner, B.; Kocian, O.; Menzer, S.; White, A. J. P.; Stoddart, J. F.; Williams, D. J. *Synthesis* **1996**, 930–940.

10. For literature on C–H$\cdots\pi$(alkynyl) hydrogen bonds, see: (a) Steiner, T. *Chem. Commun.* **1995**, 95–96. (b) Steiner, T.; Starikov, E. B.; Amado, A. M.; Teixeira-Dias, J. J. C. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1321–1326. (c) Steiner, T.; Tamm, M.; Grzegorzewski, A.; Schulte, N.; Veldman, N.; Schreurs, A. M. M.; Kanters, J. A.; Kroon, J.; van der Maas, J.; Lutz, B. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2441–2446. (d) Robinson, J. M. A.; Kariuki, B. M.; Gough, R. J.; Harris, K. D. M.; Philp, D. *J. Solid State Chem.* **1997**, *134*, 203–206. (e) Weiss, H.-C.; Bläser, D.; Boese, R.; Doughan, B. M.; Haley, M. M. *Chem. Commun.* **1997**, 1703–1704. (f) Philp, D.; Robinson, J. M. A. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1643–1650. (g) Robinson, J. M. A.; Kariuki, B. M.; Harris, K. D. M.; Philp, D. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2459–2469.

11. For a report of a C–H$\cdots\pi$(alkenyl) hydrogen bond, see: Müller, T. E.; Mingos, D. M. P.; Williams, D. J.*J. Chem. Soc., Chem. Commun.* **1994**, 1787–1788.

12. (a) Steiner, T.; Desiraju, G. R. *Chem. Commun.* **1998**, 891–892. (b) Harder, S. *Chem. Eur. J.* **1999**, *5*, 1852–1861.

13. Ehama, R.; Tsushima, M.; Yuzuri, T.; Suezawa, H.; Sakakibara, K.; Hirota, M. *Bull. Chem. Soc. Jpn* **1993**, *66*, 814–818.

14. (a) Paliwal, S.; Gieb, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 4497–4498. (b) Kim, E.; Paliwal, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 11192–11193. (c) Nakamura, K.; Houk, K. N. *Org. Lett.* **1999**, *13*, 2049–2051.

15. (a) Bisson, A. P.; Carver, F. J.; Hunter, C. A.; Waltho, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 10292–10293. (b) Adams, H.; Carver, F. J.; Hunter, C. A.; Morales, J. C.; Seward, E. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1542–1544. (c) Carver, F. J.; Hunter, C. A.; Seward, E. M. *Chem. Commun.* **1998**, 775–776.

16. Desiraju, G. R.; Gavezzotti, A. *Acta Crystallogr.* **1989**, *B45*, 473–482.

17. L'Esprance, R. P.; Engem, D. V.; Dayal, D.; Pascal, R. A. *J. Org. Chem.* **1991**, *56*, 688–694.

18. Umezawa, Y.; Tsuboyama, S.; Honda, K.; Uzawa, J.; Nishio, M. *Bull. Chem. Soc. Jpn* **1998**, *71*, 1207–1213.

19. In a positively cooperative process, the small but favorable equilibrium of nucleation is overcome by the numerous favorable associations of the subsequent growth. Thus, additional interactions become a thermodynamically favored process wherein they are distinct from isodemic processes in which they have the same probability of forming as previous and subsequent interactions. For a full discussion, see: Lindsey, J. S. *New J. Chem.* **1991**, *15*, 153–180.

20. (a) Karpishin, T. B.; Stack, T. D. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 6115–6125. (b) Yamanari, K.; Nozaki, T.; Fuyuhiro, A.; Kushi, Y.; Kaizaki, S. *J. Chem. Soc., Dalton Trans.* **1996**, 2851–2856. (c) Mizutani, M.; Tomosue, S.; Kinoshita, H.; Jitsukawa, K.; Masuda, H.; Einaga, H. *Bull. Chem. Soc. Jpn* **1999**, *72*, 981–988.

21. (a) Araki, S.; Sakakibara, K.; Hirota, M.; Nishio, M.; Tsuzuki, S.; Tanabe, K. *Tetrahedron Lett.* **1991**, *32*, 6587–6590. (b) Araki, S.; Seki, T.; Sakakibara, K.; Hirota, M.; Kodama, Y.; Nishio, M. *Tetrahedron: Asymmetry* **1992**, *4*, 555–574. (c) Quan, R. W.; Li, Z.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996**, *118*, 8156–8157.

22. (a) Matouschek, A.; Kellis, J. T.; Serrano, L.; Fersht, A. R. *Nature* **1989**, *340*, 122–126. (b) Burley, S. K.; Petsko, G. A. *Trends Biotechnol.* **1989**, *7*, 354–359. (c) Serrano, L.; Bycroft, M.; Fersht, A. R. *J. Mol. Biol.* **1991**, *218*, 465–475. (d) Kennan, A. J.; Whitlock, H. W. *J. Am. Chem. Soc.* **1996**, *118*, 3027–3028. (e) Jitsukawa, K.; Iwai, K.; Masuda, H.; Ogoshi, H.; Einaga, H. *J. Chem. Soc., Dalton Trans.* **1997**, 3691–3698. (f) Wedemayer, G. J.; Patten, P. A.; Wang, L. H.; Schultz, P. G.; Stevens, R. C. *Science* **1997**, *276*, 1665–1669. (g) Shimohigashi, Y.; Nose, T.; Yamauchi, Y.; Maeda, I. *Biopolymers* **1999**, *51*, 9–17.

23. (a) Cochran, J. E.; Parrott, T. J.; Whitlock, B. J.; Whitlock, H. W. *J. Am. Chem. Soc.* **1992**, *114*, 2269–2270. (b) Kobayashi, K.; Asakawa, Y.; Kikuchi, Y.; Toi, H.; Aoyama, Y. *J. Am. Chem.*

Soc. **1993**, *115*, 2648–2654. (c) Yanagihara, R.; Aoyama, Y. *Tetrahedron Lett.* **1994**, *35*, 9725–9728. (d) Vincenti, M.; Dalcanale, E. *J. Chem. Soc., Perkin Trans 2* **1995**, 1069–1076. (e) Schladetzky, K. D.; Haque, T. S.; Gellman, S. H. *J. Org. Chem.* **1995**, *60*, 4108–4113. (f) Kikuchi, Y.; Aoyama, Y. *Bull. Chem. Soc. Jpn* **1996**, *69*, 217–220. (g) Timmerman, P.; Verboom, W.; Reinhoudt, D. N. *Tetrahedron* **1996**, *52*, 2663–2704. (h) Davis, A. P.; Wareham, R. S. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2270–2273. (i) Cloninger, M. J.; Whitlock, H. W. *J. Org. Chem.* **1998**, *63*, 6153–6159. (j) Kusukawa, T.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 1397–1398.

24. (a) Claessens, C. G.; Stoddart, J. F. *J. Phys. Org. Chem.* **1997**, *10*, 254–272. (b) Lindeman, S. V.; Kosynkin, D.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 13268–13269. (c) Hancock, K. S. B.; Steed, J. W. *Chem. Commun.* **1998**, 1409–1410. (d) Hadjikakou, S. K.; Demertzis, M. A.; Miller, J. R.; Kovala-Demertzi, D. *J. Chem. Soc., Dalton Trans.* **1999**, 663–666.

25. Ashton, P. R.; Fyfe, M. C. T.; Hickingbottom, S. K.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2117–2128.

26. (a) Kolchinski, A. G.; Busch, D. H.; Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1995**, 1289–1291. (b) Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1865–1869. (c) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 709–728. (d) Fyfe, M. C. T.; Stoddart, J. F. *Adv. Supramol. Chem.* **1999**, *5*, 1–53.

27. (a) Ashton, P. R.; Bartsch, R. A.; Cantrill, S. J.; Hanes, Jr., R. E.; Hickingbottom, S. K.; Lowe, J. N.; Preece, J. A.; Stoddart, J. F.; Talanov, V. S.; Wang, Z.-H. *Tetrahedron Lett.* **1999**, *40*, 3661–3664. (b) Cantrill, S. J.; Fyfe, M. C. T.; Heiss, A. M.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Org. Lett.* **2000**, *2*, 61–64.

28. For the synthesis of TB24C8, see: Brown, G.R.; Foubister, A. J. *J. Med. Chem.* **1983**, *26*, 590–592.

29. After our own X-ray crystallographic investigations had been completed, reports of the solid-state structures of TB24C8 (see: Bryan, J. C.; Bunick, G. J.; Sachleben, R. A. *Acta Crystallogr.* **1999**, *C55*, 250–252) and TB24C8·2MeCN (see: Bryan, J. C.; Sachleben, R. A.; Hay, B. P. *Inorg. Chim. Acta* **1999**, *290*, 86–94) appeared in the literature. In the case of the free TB24C8 structure, the authors comment that: '*Despite the large number of arene rings in this compound, no π stacking is observed. However, close C–H···π contacts, some of which may represent hydrogen bonds are clearly present. These weak hydrogen bonds may also play a role in determining the observed crown conformation.*' We wish to present our analyses of these two solid-state superstructures in the context of these extensive C–H···π networks that permeate throughout the crystalline lattices, highlighting, in particular, the dominant role that these weak intermolecular forces play in engineering the overall three-dimensional superstructures.

30. For other solid-state examples of crown ether/acetonitrile complexes. see: (a) Allwood, B. L.; Fuller, S. E.; Ning, P. C. Y. K.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1356–1360. (b) Rogers, R. D.; Richards, P. D.; Voss, E. J. *J. Incl. Phenom.* **1988**, *6*, 65–71. (c) Garrell, R. L.; Smyth, J. C.; Fronczek, F. R.; Gandour, R. D. *J. Incl. Phenom.* **1988**, *6*, 73–78. (d) Rogers, R. D. *J. Incl. Phenom.* **1988**, *6*, 629–645. (e) Thuéry, P.; Nierlich, M.; Bryan, J. C.; Lamare, V.; Dozol, J.-F.; Asfari, Z.; Vicens, J. *J. Chem. Soc., Dalton Trans.* **1997**, 4191–4202.

31. Ashton, P. R.; Cantrill, S. J.; Preece, J. A.; Stoddart, J. F.; Wang, Z. -H.; White, A. J. P.; Williams, D. J. *Org. Lett.* **1999**, *1*, 1917–1920.

32. A [2.]pseudorotaxane is a binary complex in which a linear rod-like component is threaded through the cavity of a wheel-shaped component. See: Ashton, P. R.; Philp, D.; Spencer, N.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1991**, 1677–1679.

33. For reports of C–H···F hydrogen bonding interactions, see: (a) Teff, D. J.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1997**, *36*, 4372–4380. (b) Thalladi, V. R.; Weiss, H.-C.; Bläser, D.; Boese, R.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 8702–8710. (c) Steiner, T. *Acta Crystallogr.* **1998**, *B54*, 456–463. (d) Grepioni, F.; Cojazzi, G.; Draper, S. M.; Scully, N.; Braga, D. *Organometallics* **1998**, *17*, 296–307. (e) Dai, C.; Nguyen, P.; Marder, T. B.; Scott, A. J.; Clegg, W.; Viney, C. *Chem. Commun.* **1999**, 2493–2494. (f) Renak, M. L.; Bartholomew, G. P.; Wang, S.; Ricatto, P. J.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 7787–7799.

34. It is perhaps worthy of note that an example of a C–F···π interaction has been reported recently. See: Hayashi, N.; Mori, T.; Matsumoto, K. *Chem. Commun.* **1998**, 1905–1906.

35. Makriyannis, A.; Fesik, S. *J. Am. Chem. Soc.* **1982**, *104*, 6462–6463.

36. Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.

37. Whereas the term 'conformation' refers to the spatial arrangement of atoms in a single molecule—resulting from torsions about single or partial double bonds—the term 'co-conformation' describes the relative three-dimensional dispositions of: (a) the constituent parts (e.g. host and guest) in supramolecular systems; and of (b) the components of interlocked molecular compounds, such as catenanes and rotaxanes. See: Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2068–2070.

38. In the realm of crown ether/dialkylammonium ion binding, we have observed previously the PF_6^- anion-assisted formation—in the solid state—of *discrete supermolecules* with pseudorotaxane geometries, which are also stabilized by complementary C–H···F hydrogen bonding interactions. See: (a) Ashton, P. R.; Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 12514–12524. (b) Ashton, P. R.; Fyfe, M. C. T.; Hickingbottom, S. K.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1998**, *4*, 577–589. (c) Ashton, P. R.; Fyfe, M. C. T.; Martínez-Díaz, M.-V.; Menzer, S.; Schiavo, C.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1998**, *4*, 1523–1534. (d) Fyfe, M. C. T.; Stoddart, J. F.; Williams, D. J. *Struct. Chem.* **1999**, *10*, 243–259.

39. Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120–131.

40. Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768–4774.

41. Copies of the crystallographic data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB12 1EZ, UK (Fax: (+44) 1223-336033; e-mail: teched@ccdc.cam.ac.uk).