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A new pseudopolymorph of hexakis(4-cyanophenyl)benzene

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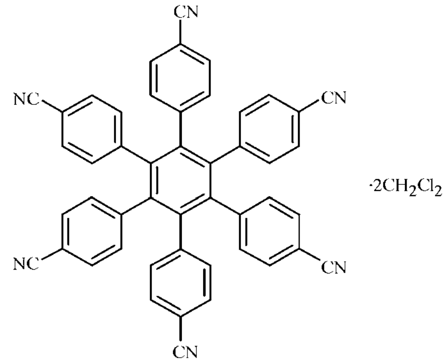
The title compound (systematic name: benzene-4,4′,4″,4‴,-4⁗,4′′′′′-hexaylhexabenzonitrile dichloromethane disolvate), $C_{48}H_{24}N_6 \cdot 2CH_2Cl_2$, crystallizes as an inclusion compound during the slow diffusion of methanol into a solution of hexakis(4-cyanophenyl)benzene in CH_2Cl_2. The hexakis(4-cyanophenyl)benzene molecule lies on an axis of twofold rotation in the space group *Pbcn*. Weak C H···N interactions between hexakis(4-cyanophenyl)benzene molecules define an open network with space for including guests. The resulting structure is a new pseudopolymorph of hexakis-(4-cyanophenyl)benzene. The eight known pseudopolymorphs have few shared architectural features, in part because none of the intermolecular interactions that are present plays a dominant role or forces neighboring molecules to assume particular relative orientations.

Comment

Networks of hydrogen bonds continue to be used extensively by crystal engineers to help maintain the integrity of crystals and to position their constituent molecules predictably (Wuest, 2005). Hydrogen bonds offer the advantages of strength and directionality, leading to the formation of robust networks that frequently define cavities or channels for the inclusion of guests. Crystal engineers have also explored the potential of weaker intermolecular interactions, which can exhibit some of the geometric, structural and spectroscopic characteristics of hydrogen bonds (Desiraju, 2002). For example, we recently reported a study of structures maintained in part by weak C H···N interactions involving the nitrile groups of hexakis(4-cyanophenyl)benzene, (I) (Maly *et al.*, 2006). Despite having a well defined molecular geometry imposed by the hexaphenylbenzene core, compound (I) crystallized under seven different sets of conditions to give inclusion compounds with widely different structures. Although networks maintained by C H···N interactions were observed in all of these pseudopolymorphs, the particular geometries of the interactions varied widely and the overall structures proved to depend critically on the choice of solvent. These observations underscore the difficulty of using C H···N interactions to engineer crystals with predictable structural features.



(II)

This conclusion has now been reinforced by the analysis of the structure of a new pseudopolymorph obtained by crystallizing compound (I) from CH_3OH CH_2Cl_2 as the dichloromethane disolvate, (II). In this structure, the molecule of (I) lies on an axis of twofold rotation directed through atoms C1 and C4 in the plane of the inner benzene ring composed of atoms C1 C4/C3^{i}/C2^{i} [symmetry code: (i) $-x$, y,

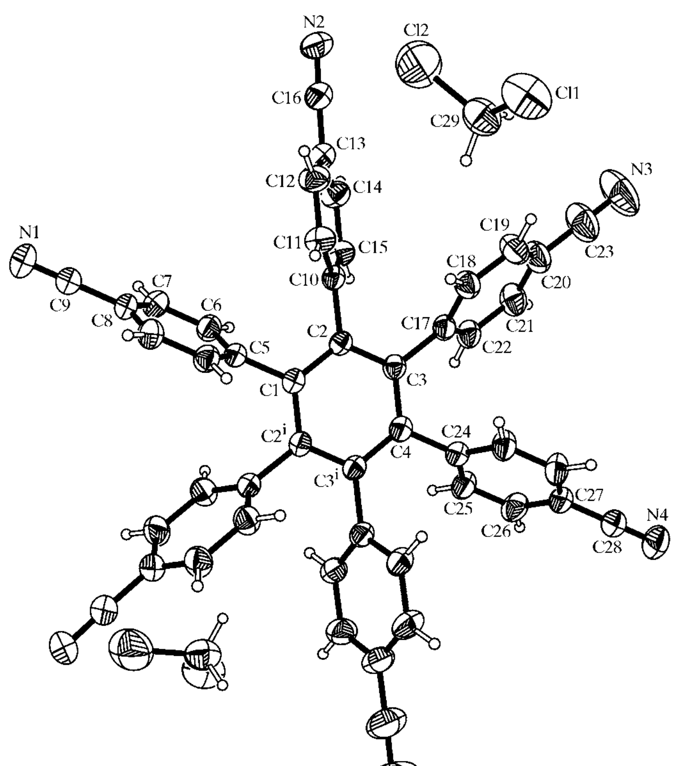


Figure 1
A view of the structure of (II), showing the atom numbering scheme of the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level. Only one part of the disordered solvent molecules is shown. The unlabeled parts of the molecules are related by the symmetry operation (x, y, $z + \frac{1}{2}$).

$-z + \frac{1}{2}$]. The hexaphenylbenzene core of compound (II) has a chiral propeller conformation, with torsion angles in the range 61.97 (4) 73.37 (4)° (Fig. 1). Similar conformations have been noted in other pseudopolymorphs of compound (I) (Maly *et al.*, 2006).

The observed structure contains equal numbers of each enantiomer. The disc-like shape of hexaphenylbenzene and its derivatives normally favors structures in which the molecules lie parallel and define distinct layers. For example, hexaphenylbenzene itself (Bart, 1968), its inclusion compound with anisole (Larson *et al.*, 1990), and its derivatives substituted in the *para* position by 4-(carboxyphenyl)ethynyl (Kobayashi *et al.*, 2005), iodo (Kobayashi *et al.*, 2005), carboxy (Kobayashi *et al.*, 2000), trifluorovinyloxy (Spraul *et al.*, 2004), hydroxy (Kobayashi *et al.*, 1999), ethynyl (Constable *et al.*, 2000), $CONH_2$ (Kobayashi *et al.*, 2003) and CN (Maly *et al.*, 2006) all have crystal structures in which the molecules are roughly coplanar. In contrast, the new polymorph of (I) reported here crystallizes to form a structure in which the molecules occupy two sets of planes, which intersect along the *b* axis at an angle of 68.29 (3)°. The only previously reported non-coplanar architecture was obtained when hexakis(4-carbamoylphenyl)benzene was crystallized under hydrothermal conditions (Kobayashi *et al.*, 2003).

In the structure of (II), each molecule of (I) is surrounded by 14 neighbors, with ten neighbors linked to the central molecule by a total of 12 C H···N interactions involving H···N distances less than 2.80 Å and C H···N angles greater than 90° (Fig. 2 and Table 1). Four additional neighbors have C H···N interactions that are only slightly longer [H···N distances of 2.85 (1) Å] (Fig. 2). The resulting network defines spaces for including partially disordered dichloromethane molecules, which engage in van der Waals interactions and C H···N interactions with nearby molecules of (I). Specifically, atom Cl1 is in close contact [3.324 (8) Å] with the centroid (*Cg*1) of the inner benzene ring of the molecule at ($x + 1$, y, z), with a C29 Cl1···*Cg*1 angle of 163.6 (3)°. Approximately 21% of the volume of the crystal is accessible to guests, as measured by standard methods (Spek, 2003). This value falls within the wide range of percentages (15 58%) found in the other seven known pseudopolymorphs of (I). It is interesting to note that compound (I) crystallizes from pure methanol as an inclusion compound of composition (I)·$2CH_3OH$ (Maly *et al.*, 2006), whereas crystallization from CH_3OH CH_2Cl_2 produces an inclusion compound containing only CH_2Cl_2, which is presumably a preferred guest.

Together, these observations confirm that nitrile groups tend to engage in C H···N interactions and can help direct the construction of open molecular networks. However, the use of these interactions in crystal engineering is limited by their weakness and lack of clear directional preferences, which lead, in the case of (I), to crystallization as multiple pseudopolymorphs with very diverse structures.

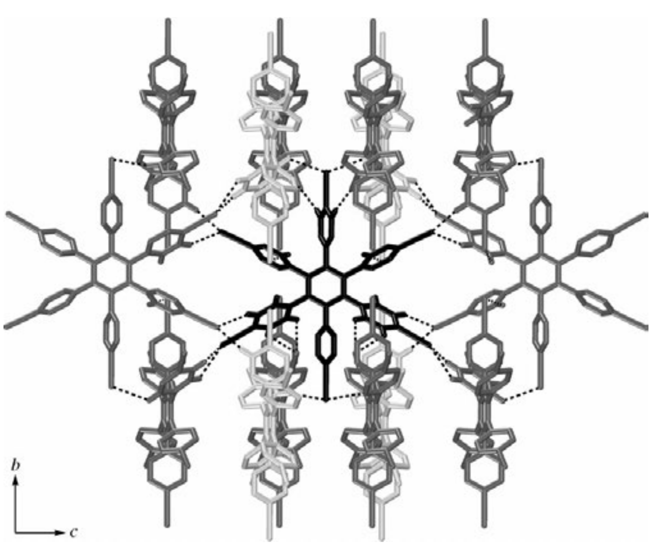


Figure 2
View of a molecule of (I) (black) in compound (II), showing the neighboring molecules that are linked to it by C H···N interactions (broken lines), with H···N distances of less than 2.80 Å (dark gray) and H···N distances of 2.85 (1) Å (light gray). H atoms not involved in hydrogen bonding have been omitted for clarity.

Experimental

Hexakis(4 cyanophenyl)benzene, (I), was synthesized according to the reported method of Maly *et al.* (2006). Crystals were grown by placing a solution of compound (I) in CH_2Cl_2 (0.1 *M*, 2 ml) at the bottom of a test tube, then carefully covering it with successive layers composed of pure CH_2Cl_2 (1 ml), a 1:1 mixture of CH_2Cl_2 and CH_3OH (1 ml), and finally pure CH_3OH (2 ml). The test tube was sealed tightly and left undisturbed. Crystals of (II) appeared after several days.

Crystal data

$C_{48}H_{24}N_6 \cdot 2CH_2Cl_2$	$Z = 4$
$M_r = 854.58$	$D_x = 1.311$ Mg m ^{3}
Orthorhombic, *Pbcn*	Cu $K\alpha$ radiation
$a = 11.0921$ (3) Å	$\mu = 2.82$ mm ^{1}
$b = 19.3442$ (3) Å	$T = 150$ (2) K
$c = 20.1742$ (4) Å	Block, colorless
$V = 4328.73$ (16) Å^3	0.15 × 0.08 × 0.07 mm

Data collection

Bruker SMART 6000 diffractometer	57445 measured reflections
ω scans	3865 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	3494 reflections with $I > 2\sigma(I)$
$T_{min} = 0.700$, $T_{max} = 0.850$	$R_{int} = 0.051$
	$\theta_{max} = 68.2°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.119P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.138$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.27$ e Å ^{3}
3865 reflections	$\Delta\rho_{min} =$ 0.28 e Å ^{3}
286 parameters	

H atoms were placed in idealized positions, with C H distances in the range 0.95 0.99 Å, and refined using a riding model, with U_{iso}(H) $1.2U_{eq}$(C).

The dichloromethane solvent molecule was found to be disordered over two sites. The first molecule (C29, Cl1 and Cl2) was refined with restraints on the C Cl distances and atomic displacement para meters by the use of SADI and DELU instructions in *SHELXL97*

Table 1
Hydrogen bond geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{C19-H19}\cdots\mathrm{N2}^{\mathrm{i}}$	0.95	2.65	3.5076 (17)	151
$\mathrm{C7-H7}\cdots\mathrm{N2}^{\mathrm{ii}}$	0.95	2.61	3.5355 (16)	165
$\mathrm{C21-H21}\cdots\mathrm{N3}^{\mathrm{iii}}$	0.95	2.69	3.320 (2)	124
$\mathrm{C29-H29}B\cdots\mathrm{N4}^{\mathrm{iv}}$	0.99	2.59	3.288 (9)	127

Symmetry codes: (i) $x+1, \; y+1, \; z$; (ii) $x \; \frac{1}{2}, \; y+\frac{3}{2}, \; z$; (iii) $x \; \frac{1}{2}, \; y+\frac{1}{2}, \; z$; (iv) $x+\frac{1}{2}, y+\frac{1}{2}, \; z+\frac{1}{2}$.

(Sheldrick, 1997). The second part of the disordered dichloro methane molecule (C30, Cl3 and Cl4) was refined to be similar to the first part by the use of SAME and EADP instructions in *SHELXL97*. With these restraints, the occupancy factors converged to 0.5312 (11) and 0.4688 (11).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2006).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3032). Services for accessing these data are described at the back of the journal.

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