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Supporting Information

Engineering Hydrogen-Bonded Molecular Crystals Built from Derivatives of Hexaphenylbenzene and Related Compounds

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Contents

General X-Ray Crystallographic Information

Each crystal was taken from a pool of Fluorolube/Paratone oil, mounted on a nylon loop fiber, and immediately placed under a cold stream of N_2 on a Bruker AXS diffractometer. The radiation used was Cu Kα radiation (λ = 1.54178 Å) produced from a FR591 rotating anode generator equipped with MONTEL 200 or HELIOS optics. The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination and data collection were carried out using SMART Version 5.630 software.[1] Data reduction was performed using SAINT Version 7.01 software.[2] The structure refinement was performed using SHELXL.[3] The data were corrected for absorption using the SADABS program within the SHELXTL 6.14 software package.[4,5]

Each structure was solved using direct methods. This procedure yielded the heavy atoms, along with a number of the C, N, and O atoms. Subsequent Fourier synthesis yielded the remaining atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined within the SHELXL software.[3] These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic *U* of the atoms to which they were bonded. The final refinement of each compound usually included anisotropic thermal parameters on all non-hydrogen atoms. All CIF files were checked for errors using the free on-line Checkcif service provided by the International Union of Crystallography (http://www.iucr.org/acs/checkcif.html).

In the case of crystals of tecton **4** grown from DMSO/THF, a problem of low data completeness was encountered. This is due to the fact that in the current geometry of the Proteum diffractometer used for data collection, the detector is partly masked by the video microscope, and a sample-changing robot limits access to the detector at high positive θ. Under these conditions, data sets can be fully collected only up to θ = 67 degrees (sinθ/λ = 0.598). As a result, data completeness can be rather low, especially when the crystal system is triclinic. The reported completeness and 2θ values have been maximized by using a special data-collection strategy employing two different crystal-to-detector distances and the collection of all accessible data.

For some weakly diffracting samples, useful data were collected only up to 50-55° in 2θ because diffraction at higher angles was not visible, a feature mainly explained by the large disordered solvent content in these systems. This explains also the observed high values for R1 and wR2 in certain cases. Any high shift-to-error ratios encountered were lowered by performing further cycles of refinement. Any other problematic aspects of the structural solutions are discussed in the following sections.

Crystal Structure of Tecton 4 Grown from DMSO/THF

The structure was solved with direct methods in the triclinic space group P-1. Some disordered solvent molecules were refined using a combination of restraints on distances while keeping the disordered parts similar (use of the SAME and SADI instructions[3]). Some residual peaks from unresolved disordered solvent were not included in the final refinement, and the contribution of the remaining solvent was treated using the SQUEEZE option in PLATON.[6] Hydrogen atoms of the water molecules could not be located, but the final structure was reported with a chemical formula that includes these hydrogen atoms.

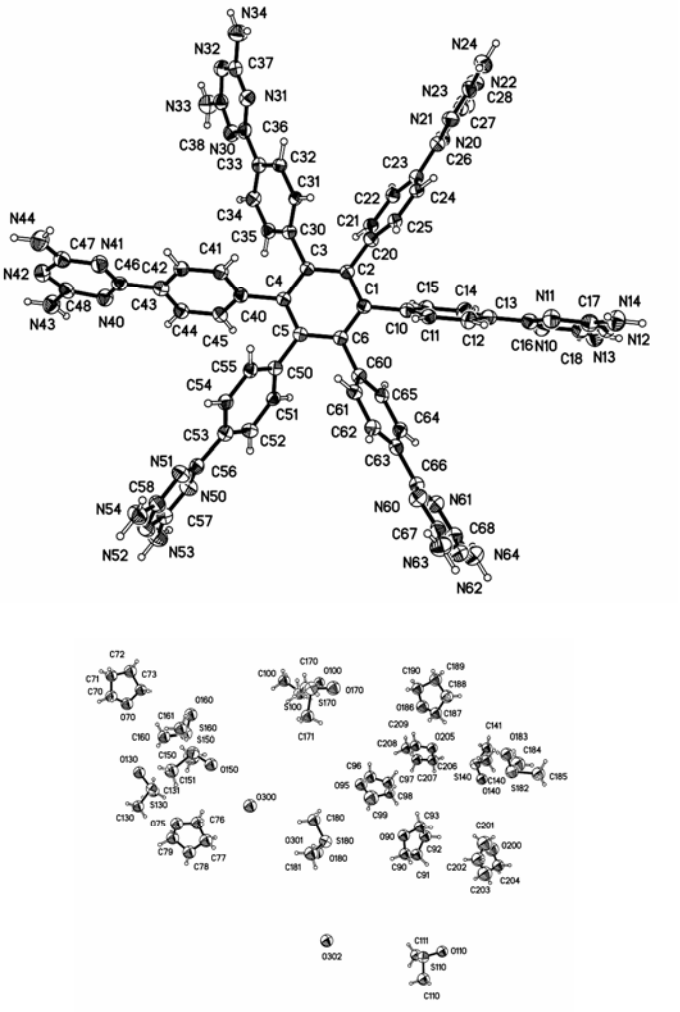


Figure S1. ORTEP view of the structure of crystals of tecton **4** grown from DMSO/THF, with the numbering scheme adopted for the asymmetric unit. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are represented by a sphere of arbitrary size. Only one part of the disordered molecule and solvent is shown.

Table S1. Bond lengths [Å] and angles [°] related to the hydrogen bonding observed in crystals of tecton **4** grown from DMSO/THF.

D-H	..A	d(D-H)	d(H..A)	d(D..A)	<DHA
N(13)-H(13B)	O(140)	0.88	2.11	2.976(9)	167
N(13)-H(13A)	O(160)#1	0.88	2.18	3.030(8)	162
N(14)-H(14A)	O(160)#2	0.88	2.10	2.814(9)	137.8
N(14)-H(14B)	N(12)#3	0.88	2.10	2.972(6)	169.5
N(23)-H(23A)	N(52)#4	0.88	2.14	3.012(6)	169.4
N(23)-H(23B)	O(150)#5	0.88	2.19	2.845(9)	131.3
N(24)-H(24A)	O(302)#4	0.88	2.07	2.929(9)	165.4
N(24)-H(24B)	O(183)	0.88	2.07	2.943(8)	171.7
N(33)-H(33A)	O(100)	0.88	2.21	2.874(6)	131.4
N(33)-H(33B)	N(32)#6	0.88	2.13	3.003(5)	172.6
N(34)-H(34A)	O(100)#6	0.88	2.10	2.966(5)	167.3
N(34)-H(34B)	N(61)#7	0.88	2.42	3.181(7)	144.8
N(43)-H(43A)	N(42)#8	0.88	2.09	2.965(6)	178.8
N(43)-H(43B)	O(300)#8	0.88	2.35	2.993(14)	130.4
N(44)-H(44B)	O(300)	0.88	2.29	3.098(13)	152.5
N(53)-H(53A)	O(150)#9	0.88	2.10	2.966(8)	166
N(53)-H(53B)	O(301)	0.88	2.21	3.075(8)	169.2
N(54)-H(54A)	N(22)#10	0.88	2.09	2.965(6)	175.9
N(54)-H(54B)	O(302)	0.88	2.25	2.90(1)	131
N(63)-H(63A)	O(110)	0.88	2.24	2.921(7)	134.5
N(63)-H(63B)	N(62)#11	0.88	2.12	2.986(5)	169.5
N(64)-H(64A)	O(110)#11	0.88	2.14	2.963(5)	156.2
N(64)-H(64B)	N(31)#9	0.88	2.47	3.229(6)	144.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2 #2 x,y+1,z+1 #3 -x+1,-y+2,-z+3
#4 x+1,y,z+1 #5 x,y,z+1 #6 -x+2,-y+1,-z+2
#7 x+1,y,z #8 -x+1,-y+1,-z+1 #9 x-1,y,z
#10 x-1,y,z-1 #11 -x,-y+2,-z+2

Crystal Structure of Tecton 4 Grown from DMSO/Toluene

The selected crystal diffracted weakly (only 47% of observed reflections), and useful data were collected up to θ = 53° only. The structure was solved with direct methods in the triclinic space group P-1. Only DMSO and water molecules were found in the cavities. These solvent molecules were refined using similarity and distance restraints. Hydrogen atoms of the water molecules could not be located, but the final structure was reported with a chemical formula that includes these hydrogen atoms.

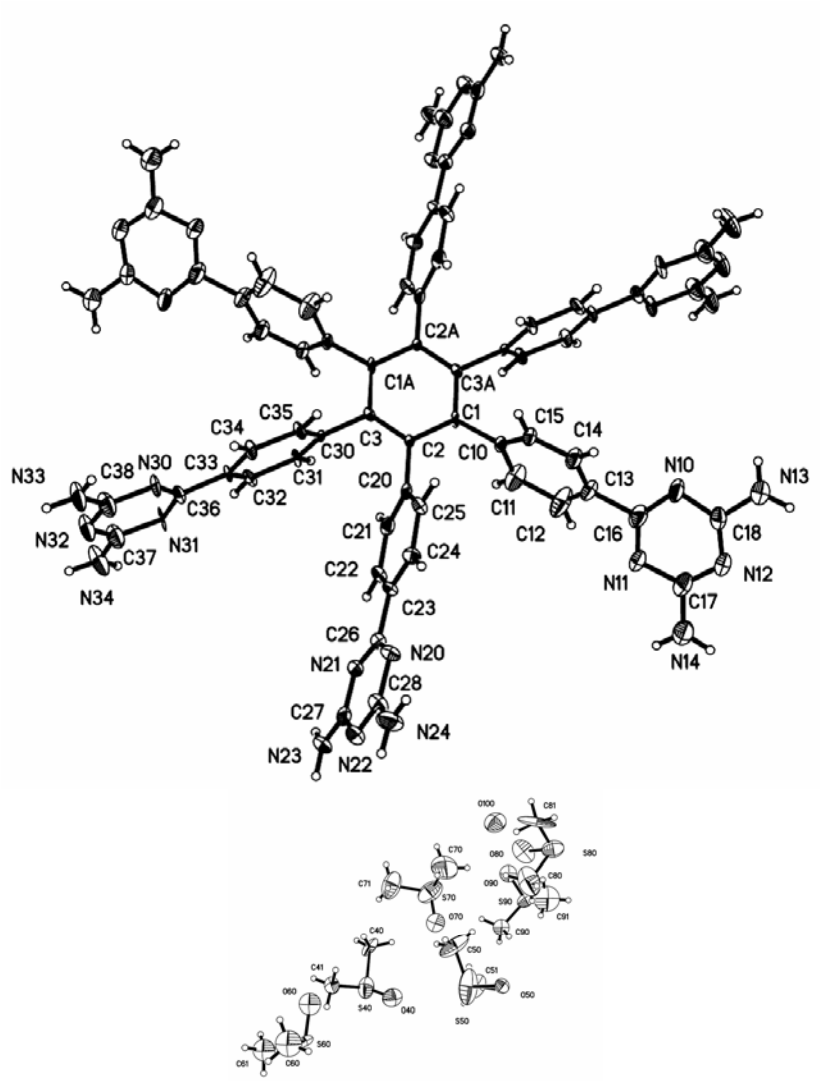


Figure S2. ORTEP view of the structure of crystals of tecton **4** grown from DMSO/toluene, with the numbering scheme adopted for the asymmetric unit. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are represented by a sphere of arbitrary size. Only one part of the disordered solvent molecules is shown.

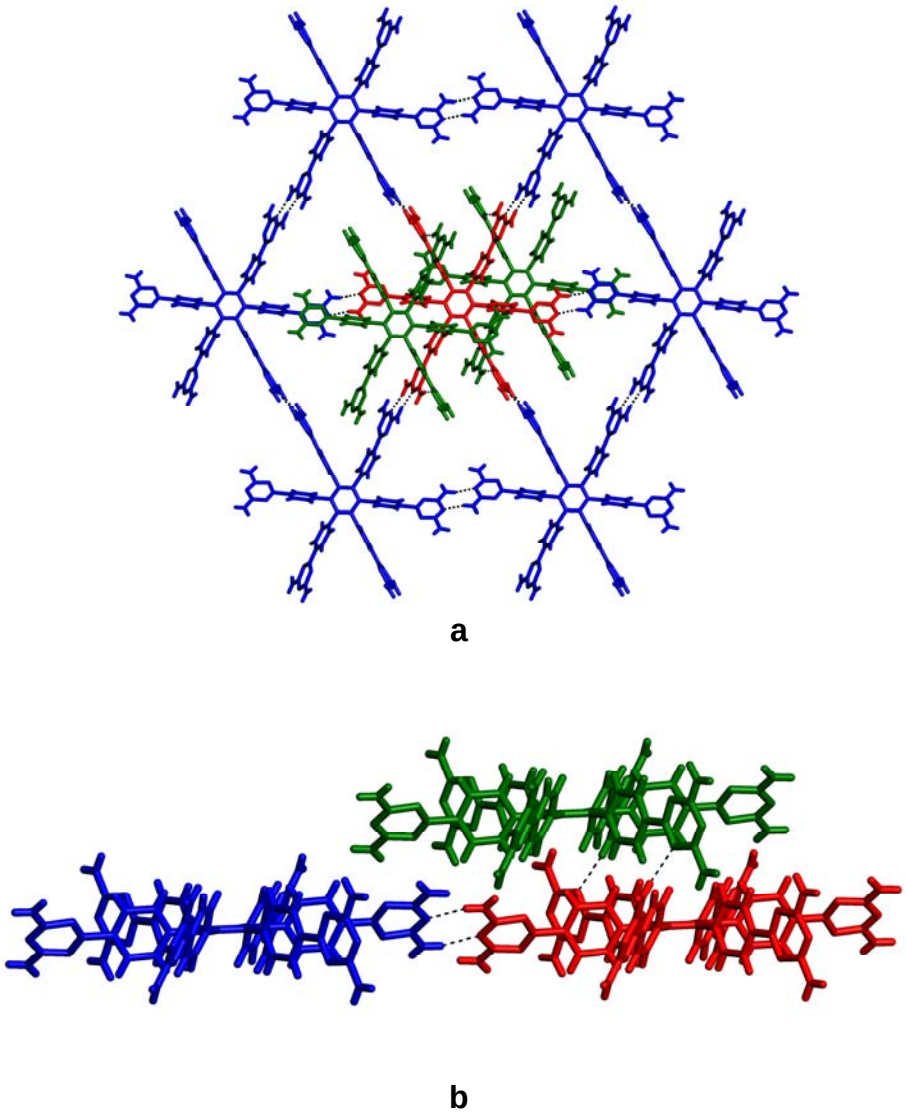


Figure S3. (a) View of the structure of crystals of tecton **4** grown from DMSO/toluene, showing a central tecton (red) and its eight hydrogen-bonded neighbors (blue and green). Six of the neighbors (blue) interact according to motif **I** and lie approximately in the plane of the central molecule, and the other two (green) lie above and below the plane. (b) Side view showing the central molecule (red), one of the coplanar neighbors (blue), and one of the neighbors in an adjacent sheet (green). In both views, guests are omitted for clarity, and hydrogen bonds are represented by broken lines.

Table S2. Bond lengths [Å] and angles [°] related to the hydrogen bonding observed in crystals of tecton **4** grown from DMSO/toluene.

D-H	..A	d(D-H)	d(H..A)	d(D..A)	<DHA
N13-H13A	O100#2	0.88	2.17	2.997(11)	155.9
N13-H13B	O70#3	0.88	2.16	2.997(11)	160.2
N14-H14A	N12#2	0.88	2.20	3.052(11)	161.6
N14-H14B	O90	0.88	2.30	3.088(11)	148.0
N23-H23A	O50#4	0.88	2.07	2.934(11)	167.2
N23-H23B	N30#5	0.88	2.19	3.035(11)	160.8
N24-H241	N22#4	0.88	2.16	3.029(11)	170.8
N24-H242	O50	0.88	2.15	2.791(11)	129.0
N33-H33A	N32#6	0.88	2.07	2.936(11)	170.3
N34-H34B	O40#7	0.88	2.38	3.198(11)	155.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z #2 -x,-y+1,-z #3 -x+1,-y+1,-z
#4 -x+1,-y+2,-z+1 #5 x-1,y,z #6 -x+3,-y+3,-z+1
#7 x,y+1,z

Crystal Structure of Tecton 4 Grown from DMSO/Benzene

The structure was solved in the trigonal space group *R-3* using direct methods. The selected crystal diffracted weakly. The arm of the molecule is statistically disordered between two positions. Only one DMSO molecule (linked by hydrogen bonding to compound **4**) and one benzene molecule were located. The contribution of the remaining solvent was treated using the SQUEEZE option in PLATON.[6]

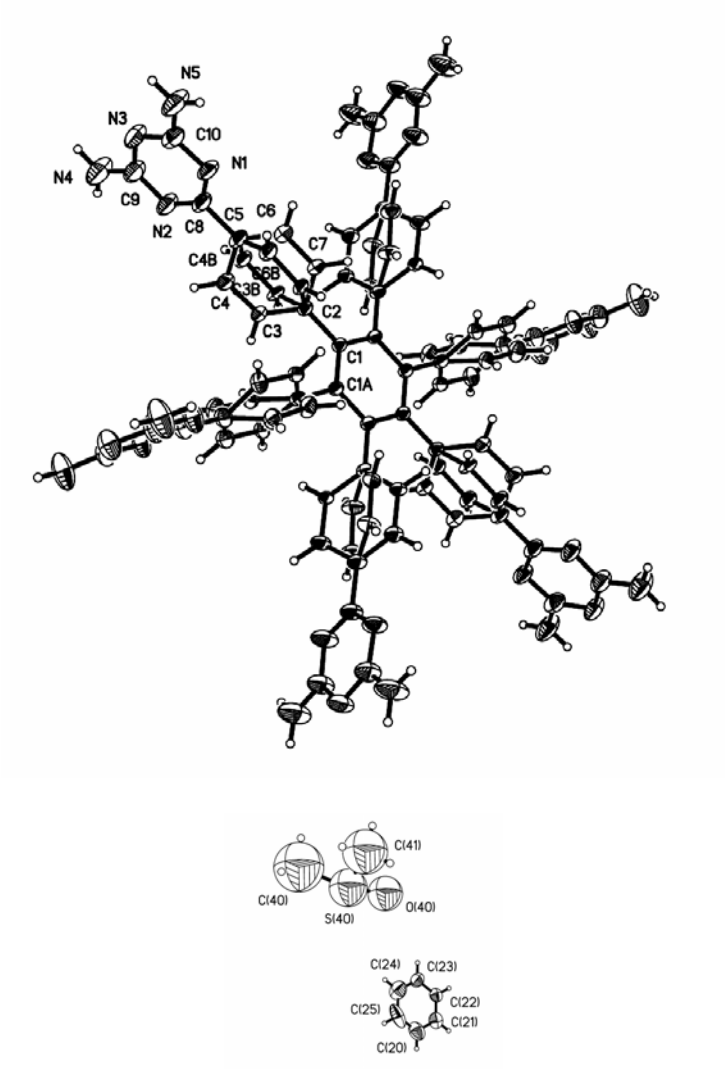


Figure S4. ORTEP view of the structure of crystals of tecton **4** grown from DMSO/benzene, with the numbering scheme adopted for the asymmetric unit. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are represented by a sphere of arbitrary size. Only one part of the disordered solvent molecules is shown.

Table S3. Bond lengths [Å] and angles [°] related to the hydrogen bonding observed in crystals of tecton **4** grown from DMSO/benzene.

D-H	..A	d(D-H)	d(H..A)	d(D..A)	<DHA
N(4)-H(4A)	N(3)#3	0.88	2.02	2.8990(19)	173.3
N(4)-H(4C)	O(40)	0.88	2.22	2.908(3)	135.3
N(5)-H(5A)	O(40)#4	0.88	2.14	2.944(3)	150.8
N(5)-H(5B)	O(40)#3	0.88	2.37	3.193(3)	155

Symmetry transformations used to generate equivalent atoms:

#1 y+1,-x+y+1,-z+1 #2 x-y,x-1,-z+1
#3 -x+5/3,-y+1/3,-z+4/3 #4 x,y,z-1

Crystal Structure of Tecton 4 Grown from Formic Acid/Methanol

The structure was solved in the trigonal space group *R-3* using direct methods. The crystal examined was found to be twinned. In addition, it diffracted weakly, and useful data could be collected only up to θ = 53.34°. The solvent molecules were not clearly located and identified. There were modeled using the PLATON/SQUEEZE program,[6] which located a large void with a total potential volume of 4345 Å^3 and electron count of 963.

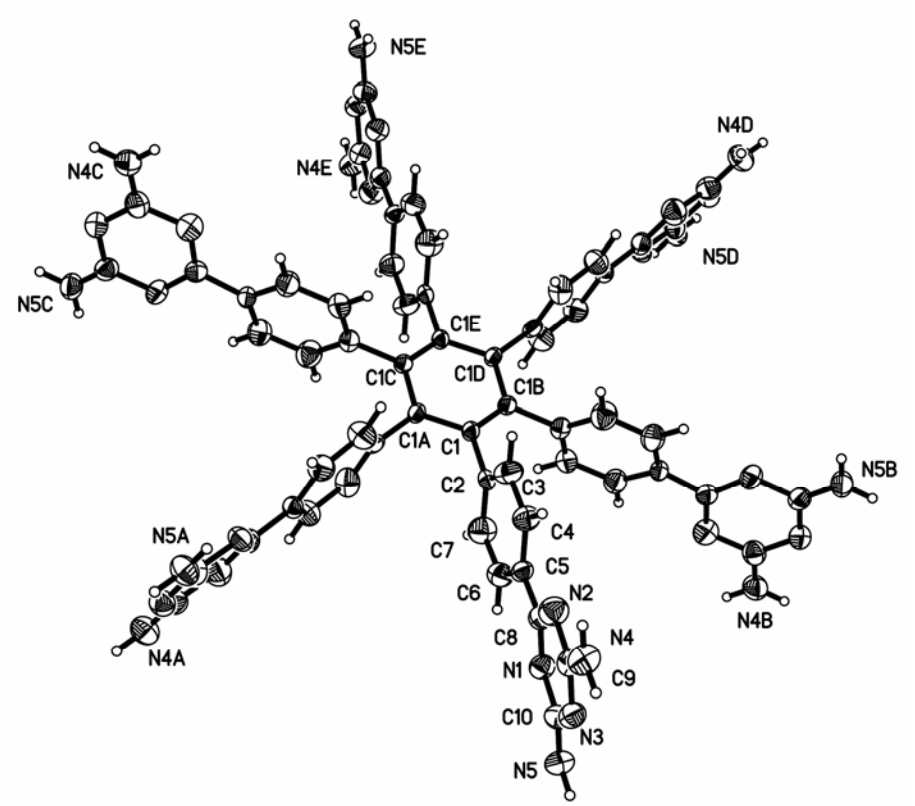
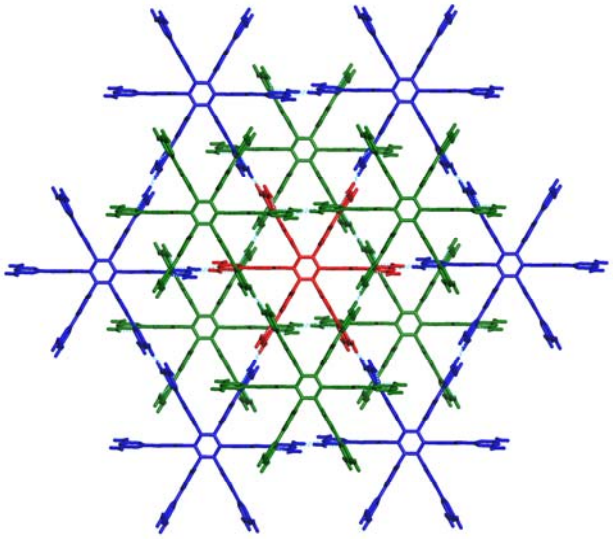
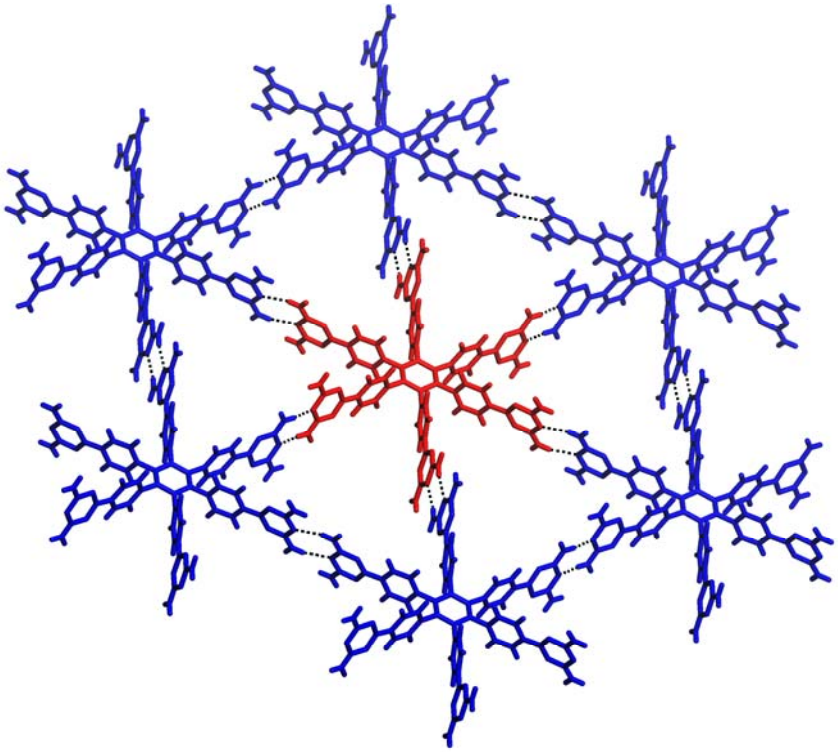


Figure S5. ORTEP view of the structure of crystals of tecton **4** grown from formic acid/methanol, with the numbering scheme adopted for the asymmetric unit. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are represented by a sphere of arbitrary size.



a



b

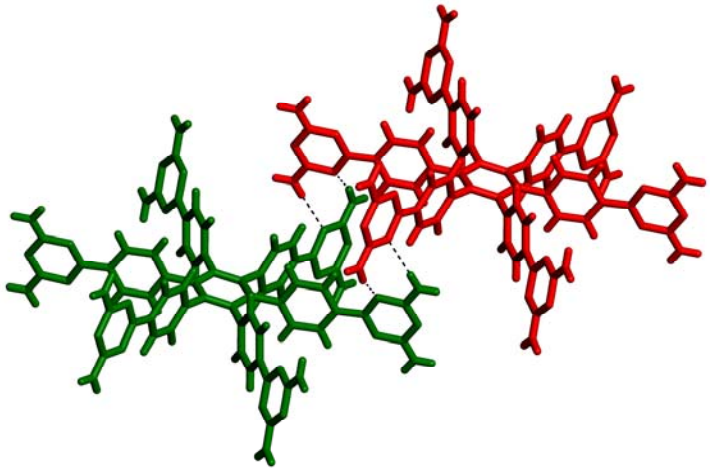


Figure S6. (a) View of the structure of crystals of tecton **4** grown from formic acid/methanol, showing a central molecule (red) and its twelve hydrogen-bonded neighbors (blue and green). Six of the neighbors (blue) lie approximately in the plane of the central molecule (red) and form hydrogen bonds to it via motif **I**, thereby defining a sheet. Of the other six neighbors (green), half lie above the sheet, half lie below, and all form hydrogen bonds of type **III** to the central molecule (red). Guests are omitted for clarity, and hydrogen bonds are represented by broken lines. (b) Detailed view of the central tecton (red) and its six coplanar hydrogen-bonded neighbors (blue). (c) Detailed view of hydrogen bonding between the central molecule (red) and one of the six neighbors in adjacent sheets (green).

Table S4. Bond lengths [Å] and angles [°] related to the hydrogen bonding observed in crystals of tecton **4** grown from formic acid/methanol.

D-H	..A	d(D-H)	d(H..A)	d(D..A)	<DHA
N(4)-H(4B)	N(1)#1	0.88	2.14	2.975(4)	157.1
N(5)-H(5B)	N(3)#2	0.88	2.21	3.079(3)	167.2
N(5)-H(5A)	N(2)#3	0.88	2.37	3.197(4)	157.4

Symmetry transformations used to generate equivalent atoms:

#1 -x+y-1/3,-x-2/3,z+1/3 #2 -x-1,-y-1,-z #3 -y-2/3,x-y-1/3,z-1/3

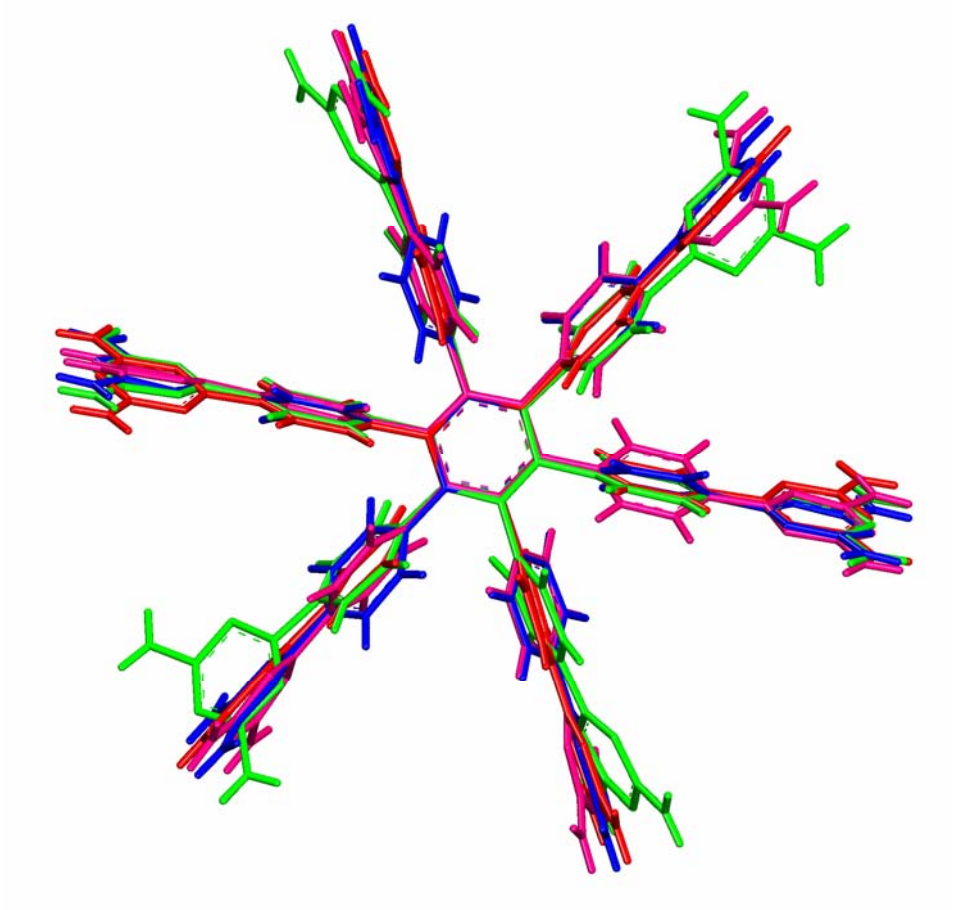


Figure S7. Overlay of the different conformers of compound **4** as observed in the structures of crystals grown from formic acid/methanol (red), DMSO/benzene (blue), DMSO/toluene (green), and DMSO/THF (pink). The molecular structures were aligned using the "Superpose Structures Tool" of MS Modeling 4.0.[7] The molecules were aligned using the RMS atom-fitting algorithm. In this procedure, the molecules are kept rigid, translated, and rotated to match in a way that minimizes the root-mean-square (RMS) distances between the equivalent atoms in the structures. RMS values are reported below:

Solvent of crystallization	**Color**	**RMS (Å^2)**
HCOOH/methanol	Red	1.408
DMSO/benzene	Blue	1.223
DMSO/toluene	Green	1.437
DMSO/THF	Pink	1.215

Crystal Structure of Tecton 6 Grown from DMSO/Acetone

The structure was solved by direct methods in the monoclinic space group C2/c. Only four DMSO solvent molecules were located, and they were refined using restraints on distances and angles. The contribution of the other solvent molecules was accounted for by using the PLATON/SQUEEZE procedure.[6] PLATON found 445 electrons compatible with approximately 16 acetone molecules in the unit cell (2 acetone molecules per asymmetric unit).

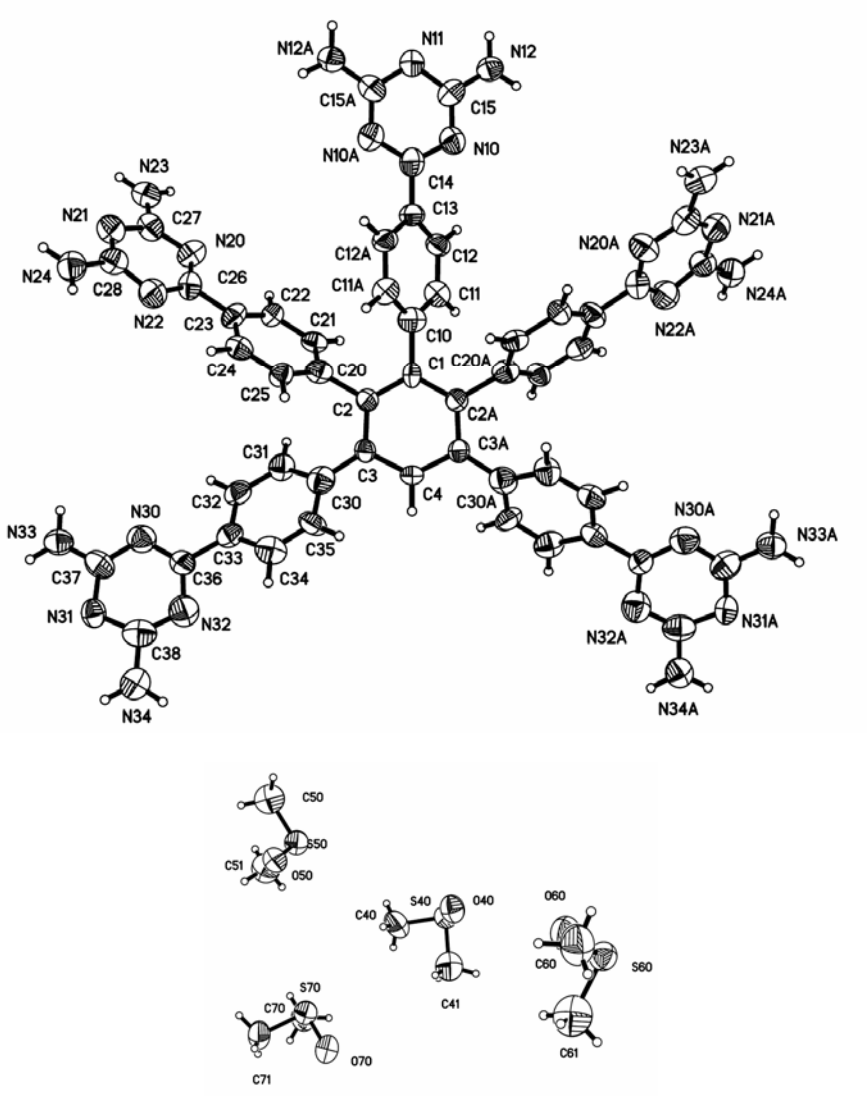


Figure S8. ORTEP view of the structure of crystals of tecton **6** grown from DMSO/acetone, with the numbering scheme adopted. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are represented by a sphere of arbitrary size.

Table S5. Bond lengths [Å] and angles [°] related to the hydrogen bonding observed in crystals of tecton **6** grown from DMSO/acetone.

D-H	..A	d(D-H)	d(H..A)	d(D..A)	<DHA
N(12)-H(12A)	O(40)#1	0.88	2.27	3.151(6)	174.4
N(23)-H(23A)	O(60)#2	0.88	2.20	3.043(6)	160.4
N(23)-H(23B)	O(50)#3	0.88	1.98	2.849(6)	170.9
N(24)-H(24B)	O(60)#4	0.88	2.16	2.870(6)	136.8
N(24)-H(24A)	N(21)#5	0.88	2.08	2.844(7)	144.4
N(33)-H(33B)	O(60)#6	0.88	2.43	3.263(6)	159.4
N(34)-H(34A)	O(60)#7	0.88	2.06	2.820(6)	144.0
N(34)-H(34B)	N(31)#8	0.88	2.19	3.052(7)	164.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1	#2 -x+3/2,-y+3/2,-z+1
#2 x+1,-y+1,z-1/2	#4 x+1,y,z
#5 -x+5/2,-y+3/2,-z+1	#6 x+1,-y+2,z-1/2
#7 -x+3/2,y+1/2,-z+3/2	#8 -x+5/2,-y+5/2,-z+1

Crystal Structure of Tecton 5 Grown from DMSO/Acetonitrile

The selected crystal diffracted weakly, and useful data could be collected only up to θ = 58.35°. The structure was solved with direct methods in the monoclinic space group C2/c with the asymmetric unit containing one half of molecule of compound **5**. Some solvent molecules were found disordered and were refined with a combination of restraints on distances and angle while keeping the disordered parts similar (use of the SAME and SADI instructions[3]).

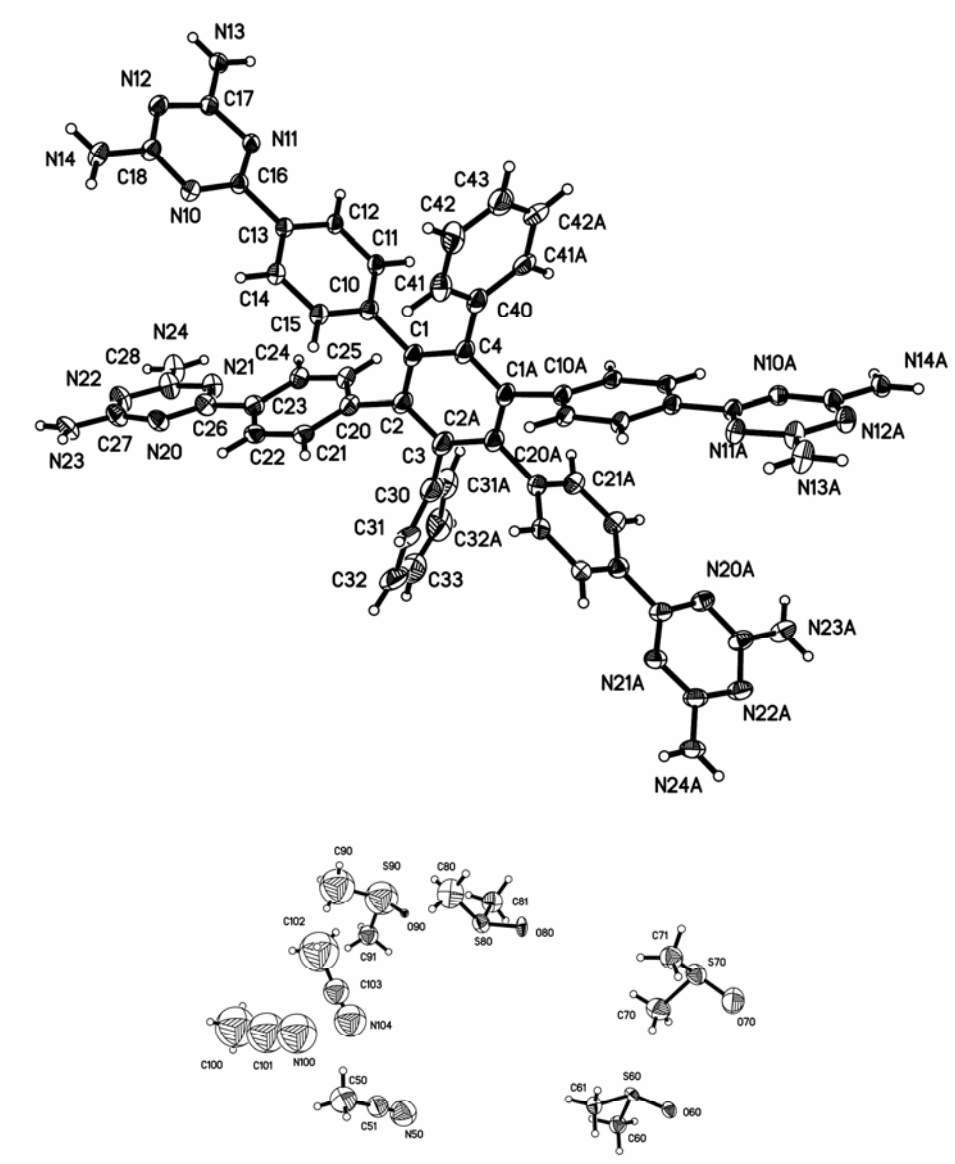


Figure S9. ORTEP view of the structure of crystals of tecton **5** grown from DMSO/acetonitrile, with the numbering scheme adopted. Ellipsoids are drawn at the 30% probability level. Only one part of the disordered solvent molecules is shown. Hydrogen atoms are represented by a sphere of arbitrary size.

Crystal Structure of Tecton 7 Grown from DMSO/Methanol

The selected crystal diffracted weakly, and useful data could be collected only up to θ = 58.9°. The structure was solved with direct methods in the monoclinic space group $P2_1/c$ with the asymmetric unit containing one whole molecule of compound **7** in general position. One arm of the molecule was found to be disordered over two positions.

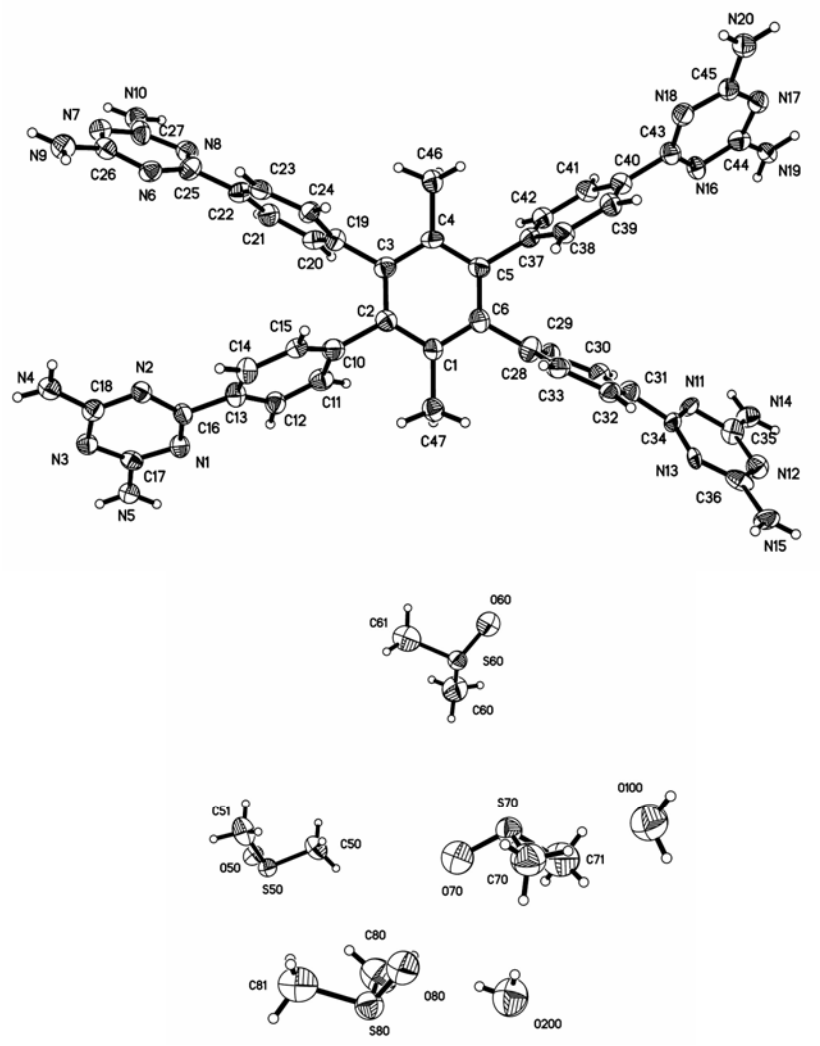


Figure S10. ORTEP view of the structure of crystals of tecton **7** grown from DMSO/methanol, with the numbering scheme adopted. Ellipsoids are drawn at the 30% probability level. Only one part of the disordered arm and the solvent molecules is shown. Hydrogen atoms are represented by a sphere of arbitrary size.

Table S7. Bond lengths [Å] and angles [°] related to the hydrogen bonding observed in crystals of tecton **7** grown from DMSO/methanol.

D-H	..A	d(D-H)	d(H..A)	d(D..A)	<DHA
N9-H9A	N7#1	0.88	2.61	3.30(9)	136.5
N9-H9B	N3#2	0.88	2.30	3.15(9)	163.5
N10-H10A	O60#3	0.88	2.08	2.91(9)	156.3
N10-H10B	O50#4	0.88	2.07	2.95(14)	171.0
N10-H10B	O51#4	0.88	1.89	2.7(3)	160.0
N14-H14B	N17#5	0.88	2.30	3.13(15)	155.5
N15-H15B	O80#6	0.88	2.00	2.67(12)	132.0
N14-H14A	O80#7	0.88	2.78	3.41(16)	129.5
N14-H14B	N17#5	0.88	2.30	3.13(15)	155.5
N15B-H15C	N12B#8	0.88	2.49	3.24(15)	144.9
N15B-H15D	O80#6	0.88	2.45	2.93(12)	114.7
N4-H4A	O60#9	0.88	2.04	2.91(9)	170.8
N4-H4B	N5#2	0.88	2.98	3.68(9)	137.0
N5-H5A	N2#10	0.88	2.40	3.25(9)	164.1
N5-H5B	N6#10	0.88	2.23	3.07(9)	158.4
N19-H19A	N18#5	0.88	2.08	2.95(9)	168.7
N19-H19B	O70#11	0.88	2.57	3.18(9)	127.4
N20-H20A	N11B#12	0.88	2.62	3.29(10)	134.3
N20-H20B	N16#12	0.88	2.30	3.16(10)	166.0
O100-H101	O80#6	0.95	2.28	3.01(11)	131.0
O100-H102	O200#6	0.95	2.61	3.50(6)	158.0
O200-H202	N15B#13	0.95	2.83	3.54(13)	132.0

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y+1,-z+3 #2 x,-y+1/2,z+1/2 #3 -x,y-1/2,-z+3/2
#4 -x, -y+1,-z+1 #5 x,-y+5/2,z-1/2 #6 -x+1,y+1/2,-z+3/2
#7 x, -y+3/2,z-1/2 #8 -x+1,-y+2,-z+1 #9 x,y-1,z+1
#10 x, -y+1/2,z-1/2 #11 x,y+1,z #12 x,-y+5/2,z+1/2
#13 -x+1, y-1/2,-z+3/2

Crystal Structure of Tecton 7 Grown from DMSO/Dioxane

The structure was solved with direct methods in the monoclinic space group C2/m with an asymmetric unit including one-half molecule of compound **7** on a mirror site. The selected crystal was found to be twinned. In addition, it diffracted weakly, and useful data could be collected only up to $\theta = 56.3°$. Five DMSO molecules could be located, and a sixth DMSO molecule was found to be disordered over a mirror site and was modeled by using the PLATON/SQUEEZE procedure.[6]

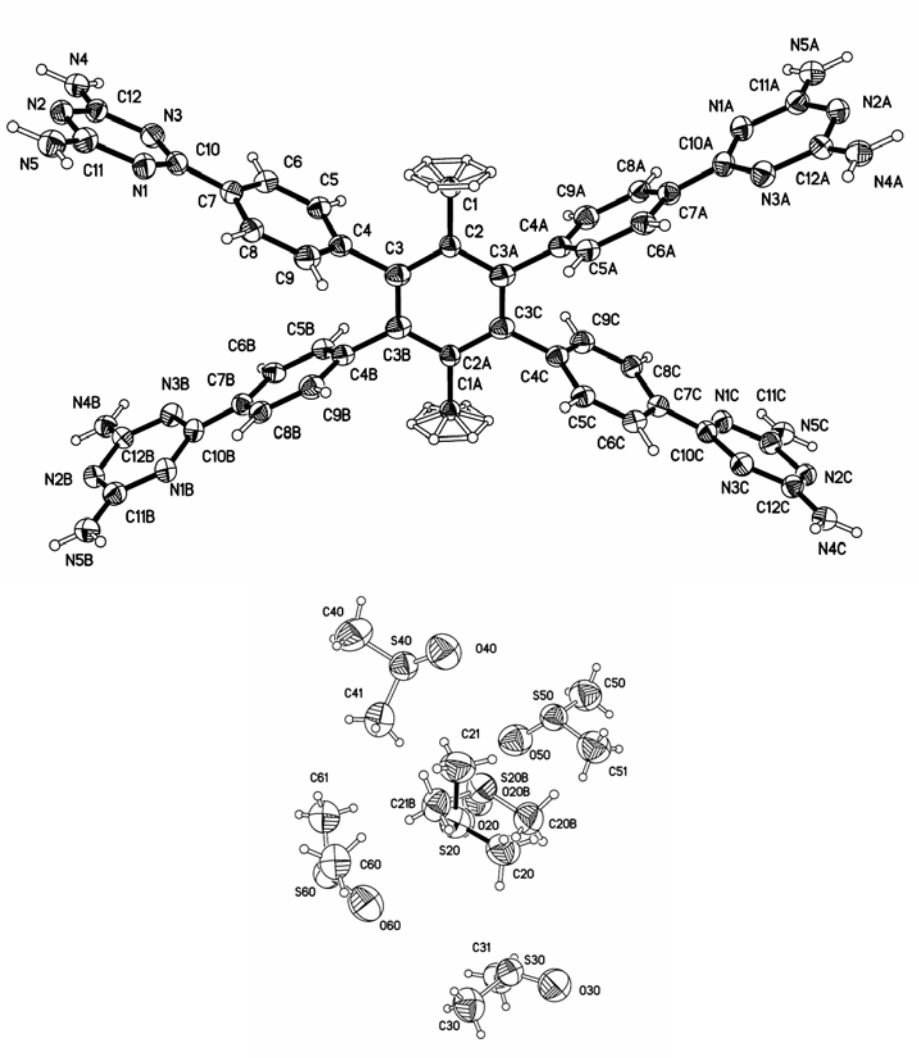


Figure S11. ORTEP view of the structure of crystals of tecton **7** grown from DMSO/dioxane, with the numbering scheme adopted. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are represented by a sphere of arbitrary size.

Crystal Structure of Tecton 8 Grown from DMSO/Acetone

The structure was solved with direct methods in the monoclinic space group $P2_1/c$ with an asymmetric unit including one-half molecule of compound **8**. Most of the included DMSO molecules are disordered and were refined using a combination of restraints on distances while keeping the disordered parts similar (use of the SAME and SADI instructions[3]). Hydrogen atoms were positioned geometrically with no attempt to optimize their positions (some hydrogen atom locations result in short contacts between different disordered parts).

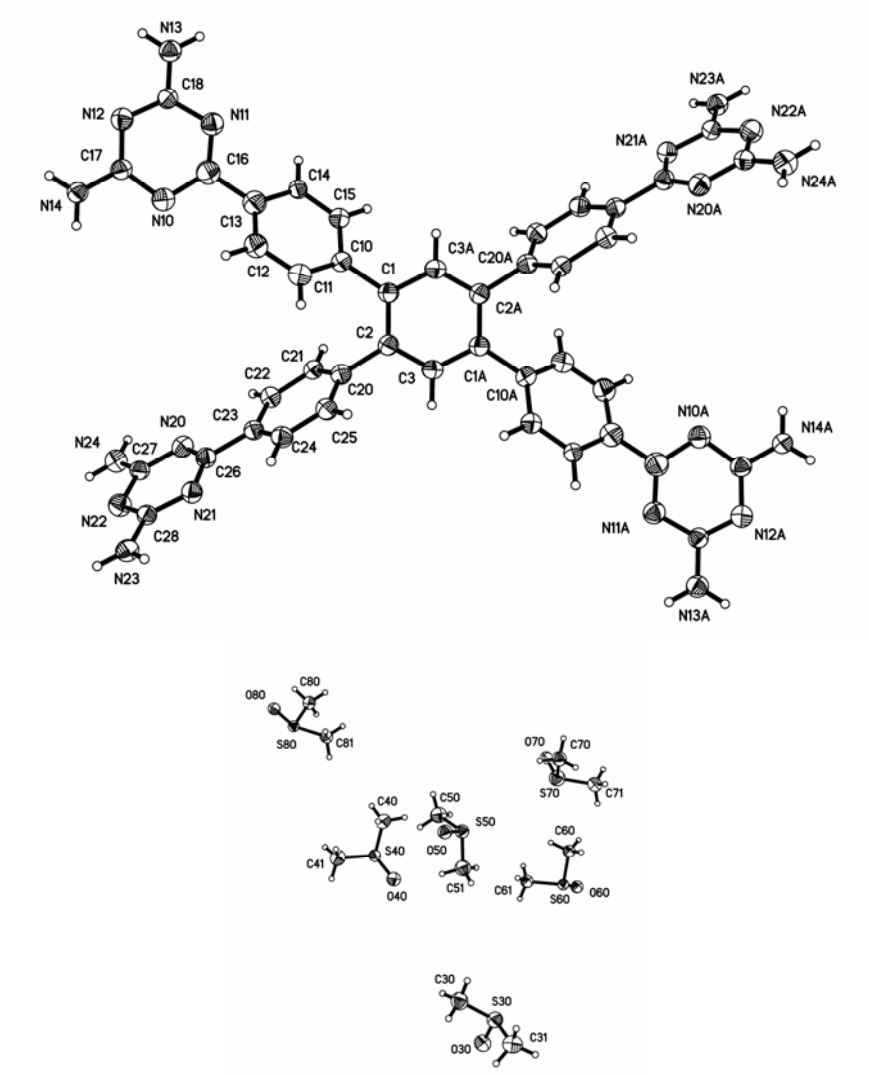


Figure S12. ORTEP view of the structure of crystals of tecton **8** grown from DMSO/acetone, with the numbering scheme adopted. Ellipsoids are drawn at the 30% probability level. Only one part of the disordered DMSO solvent molecules is shown. Hydrogen atoms are represented by a sphere of arbitrary size.

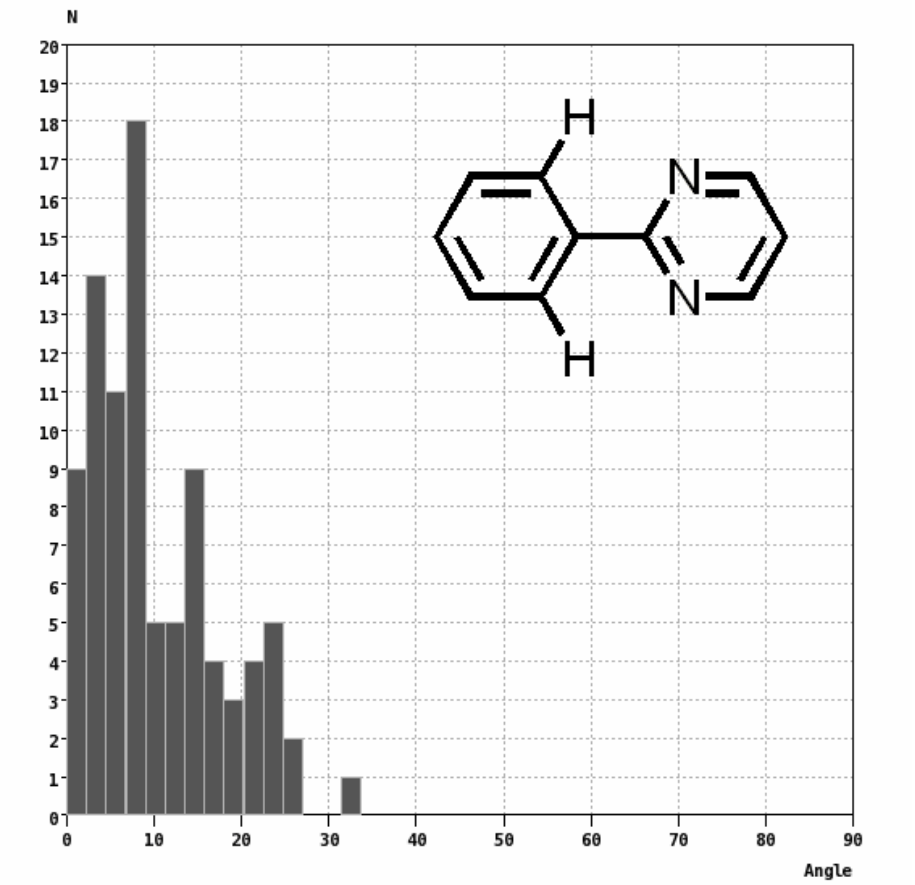


Figure S13. Histogram showing the frequency of torsional angles between the average planes of the aromatic rings in 2-phenylpyrimidines, as observed in crystal structures compiled in the Cambridge Structural Database (Version 5.27). Structures containing metals or with atoms other than hydrogen at the indicated positions were not included in the analysis to avoid torsional effects arising from coordination or from ortho substitution. In addition, phenylpyrimidines in which the atoms of nitrogen were protonated or otherwise substituted were removed individually from the set of data.

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