aqueous ammonia solution (40 mL). After the mixture was stirred for 24 h at room temperature, it was poured into 10% aqueous hydrochloric acid (200 mL). The resulting precipitate was removed by filtration and washed with diethyl ether (4 × 20 mL). The residue was dissolved in 20% aqueous sodium hydroxide solution (200 mL), and the desired product was extracted with diethyl ether (3 × 50 mL). After the solution was dried over $MgSO_4$, the solvent was removed under reduced pressure and pure **1d** (1.8 g, 66%) was obtained as an orange solid (m.p. 97 °C).

Enantioselective allylation of **2b** to **4b** (Table 1, entry 2): The ligand **1d** (70 mg, 0.2 mmol) and $CuBr \cdot Me_2S$ (3 mg, 0.02 mmol) were dissolved in THF (5 mL). After the clear solution was cooled to $-90\,^{\circ}C$, **3a** (0.3 mL, 2.4 mmol) and **2b** (440 mg, 2.0 mmol) were added successively. The reaction mixture was stirred for 18 h at $-90\,^{\circ}C$ and then worked up as usual. The crude residue obtained after evaporation of the solvents was purified by flash chromatography (diethyl ether/pentane 1/50) to provide the desired product **4b** (370 mg, 72% yield; S_N2':S_N2 ratio = 97:3). The enantiomerical excess of the chiral product was determined by gas chromatography (Chiraldex capillary column) to be 87%.

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Self-Assembly of 1,1′-Biphenyl-2,2′,6,6′-tetracarboxylic Acid: Formation of an Achiral Grid with Chiral Compartments**

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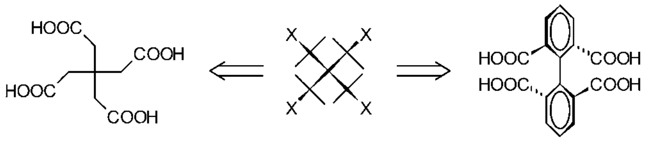
Supramolecular self-assembly is the spontaneous association of molecular subunits (tectons) into structurally well-defined aggregates, which are organized by noncovalent interactions (synthons).[1, 2] The most versatile synthons for the self-assembly of organic tectons are intermolecular hydrogen bonds. Tetrafunctional molecules with tetrahedrally arranged substituents have been investigated in this context and have shown to be endowed with the fascinating faculty of building diamond-like networks,[3] with methanetetraacetic acid **1** being a prototypal example.[4] We are interested in the hydrogen bond driven self-assembly of 2,2′,6,6′-tetrasubstituted biaryls[5, 6] that are topologically related to the tetrasubstituted methanes. For example, if we stretch the D_{2d} symmetry conformer of the tecton **1** along its axis a framework of 1,1′-biphenyl-2,2′,6,6′-tetracarboxylic acid (**2**) gradually (on further elaboration) emerges (Scheme 1).



1 **2**

Scheme 1. Stereochemical correlation of tectons **1** and **2.**

Consideration of models that use a double hydrogen bond as the synthon suggests that the self-assembling properties of the two topologically related tectons **1** and **2** should be entirely different. In contrast to the intrinsic propensity of the tetrahedral tecton **1** to form chairlike distorted cyclohexamers that underlie the three-dimensional diamondoid network,[3, 4] the biaryl tecton **2** should prefer to undergo cyclotetramerization and result ultimately in a unilayered "square" grid (Figure 1).

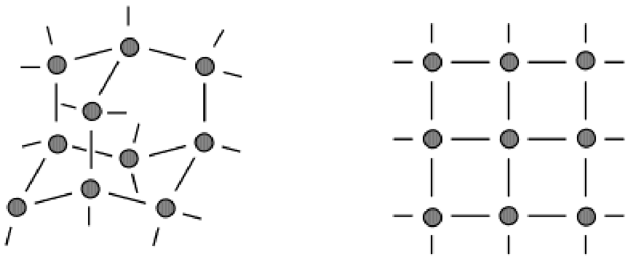


Figure 1. Schematic representation of diamondoid and square grids.

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In accord with this a priori analysis a crystal structure determination[7] of the tetraacid **2** confirmed an approximately perpendicular[10] orientation of the aromatic rings in the individual tectons (Figure 2), and demonstrated their self-assembly by double hydrogen bonds.[11] All four carboxyl groups participate in the intermolecular hydrogen bonding to give rise to a quasi-planar network set up from the hydrogen-bonded cyclotetramers (Figure 3). In contrast to the individual tectons **2**, which possess D_{2d} symmetry and are accordingly achiral, the self-assembled cyclotetramers possess (in an ideal arrangement) a unique[12, 13] D_4 symmetry and are therefore, individually chiral. Homochiral cyclotetramers are arranged diagonally, whereas alternation of chirality occurs in the horizontal and vertical rows of the network (Figure 4). In contrast to the chirality of the tetrameric compartments, the infinite unilayered grid is achiral as a consequence of crystal symmetry. The neighboring grids are stacked in a staggered (non-concatenated) manner[14] (Figure 3).

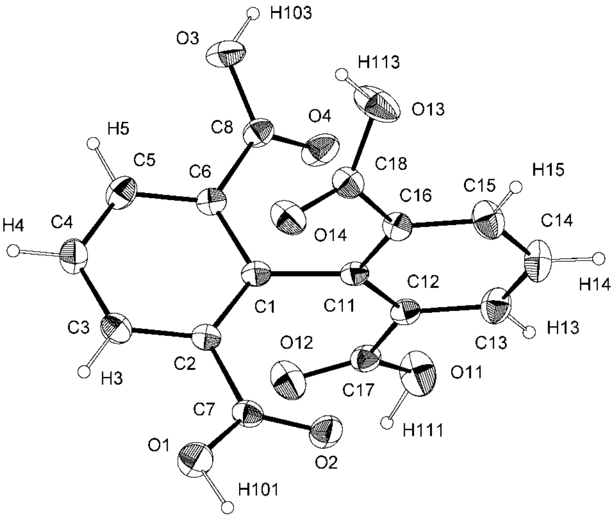

Figure 2. An ORTEP diagram of the molecular structure of **2** with the crystallographic numbering scheme.

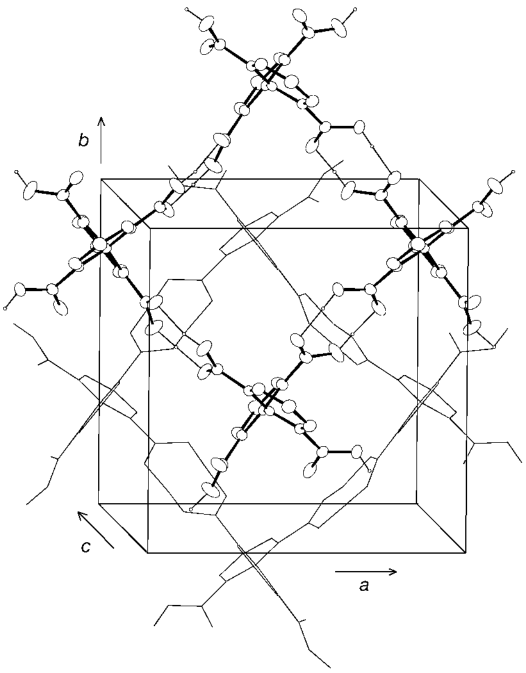

Figure 3. Self-assembly of **2** into unilayered hydrogen-bonded networks and stacking of the neighboring layers in the crystal (the molecules in the second layer are distinguished by thinner lines).

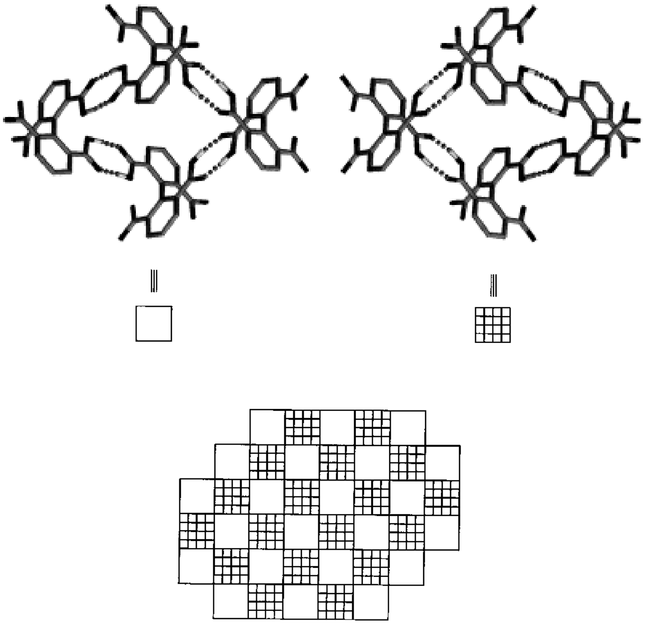

Figure 4. Schematic representation of the distribution of cyclotetramers of opposite chirality (indicated by empty and shaded squares) in the unilayered hydrogen-bonded network in the crystal of **2**.

In this way, self-assembly of the biaryl tecton **2** represents a novel type of supramolecular architecture, which allows a further tuning in three important directions. Firstly, the effective size of the individual compartments may be varied extensively by using, for example, the principle[15, 16] of vinylogy and phenylogy (namely the introduction of vinyl and phenyl spacers). Secondly, chirality of the individual macrocyclic compartments may be extended to the overall network[17] by the use of chiral biaryl tectons. Thirdly, the stacking of the individual layers may be controlled[18, 19] by introduction of appropriate substituents into the 4,4′-positions of the biaryl tecton. If successful, the proposed tuning of the structure might provide a novel access to the design of chiral porous solids.[20]

Experimental Section

2: Potassium permanganate (8.69 g, 55 mmol) was gradually added (0.5 h) to a stirred suspension of 1,1′-biphenyl-2,2′,6,6′-tetracarboxaldehyde[21] (5.32 g, 20 mmol) in aqueous 0.3 M KOH solution (100 mL) at 80°C. After additional (1 h) heating, the excess of the oxidant was destroyed by several drops of a 37 % aqueous solution of formaldehyde. The precipitated manganese dioxide was filtered off and washed with hot water (100 mL). The combined aqueous solutions were reduced to 100 mL, acidified with concentrated hydrochloric acid to pH 1, and cooled in a refrigerator. The separated tetraacid **2** was collected, washed with water, and dried. Yield 5.41 g (82 %), m.p. >370 °C (>350 °C,[22a] >300 °C[22b]). Single crystals were grown from hot water by slow cooling.

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[11] There are two crystallographically independent double hydrogen bonds, both nearly planar and with asymmetrically disposed hydrogen atoms, one links O1 and O2 with O12′and O11′ whereas the other links O3 and O4 with O14″ and O13″.

[12] According to Eliel,[13] no organic molecules of D_4 symmetry have yet been synthesized. Also, to the best of our knowledge, no hydrogen bond organized substructure of D_4 symmetry has been found in any previously known crystal structure.

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[17] Viability of this concept has been already demonstrated in our recent crystallographic study[5] of the chiral 2,2′-bipyridine-3,3′-dicarboxylic acid-1,1′-dioxide (C_2 symmetry), which revealed a self-assembly into a chiral "square" grid that was organized by the hydrogen bonding (−N−O ··· H−O−CO−) synthon.

[18] While generation of polar layers is relatively straightforward, their eclipsed stacking remains generally a great challenge for crystal engineering. The eclipsed stacking may be induced in the present case, for example, by introduction of the 4,4′-carboxyl groups into the tecton **2**, to allow the formation of an additional (orthogonal) network of intermolecular hydrogen bonds. A successful application of such a hydrogen-bond network in cross-linking supramolecular tapes has recently been reported.[19]

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High-Yielding Rotaxane Synthesis with an Anion Template**

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Molecules such as rotaxanes and catenanes that are non-covalently interlocked by mechanical bonds between two or more molecular components are of current interest. Their synthesis is usually based on some kind of template assistence such as the preorganization of building blocks by metal coordination, hydrophobic and donor-acceptor interactions, or hydrogen bonding.[1] Here we report on a new synthesis of rotaxanes based on the action of a supramolecular nucleophile, which is formed from the molecular recognition of an anionic stopper by a tetralactam wheel.

Some examples of recognition of anions by neutral organic ligands have been reported, and mostly feature several amide, sulfonamide, or urea groups as the hydrogen bond donors.[2] Macrocyclic lactams such as **1**, which have often been used in rotaxane and catenane syntheses,[1d] contain several aromatic

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