SYNTHESIS AND SELF-ASSEMBLY OF 9,9′-SPIROBIFLUORENE-2,2′,7,7′-TETRACARBOXYLIC ACID AND ITS TETRAAMIDE. NON-CATENATED FORMATION OF ACHIRAL GRID LAYERS WITH LARGE CHIRAL PORES

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

The title tetrasubstituted spirobifluorenes **3a**, **3b** have been designed to serve as convenient achiral tectons for self-assembly of 2D layers with large chiral pores. The underlying stereochemical concept has been confirmed by the results of crystallographic analysis of tetraacid **3a**. Self-assembly of isosteric tetraamide **3b** led to markedly different results.
**Keywords**: Carboxylic acids; Spiro compounds; X-ray diffraction; Hydrogen bonds; Supramolecular chemistry; Self assembly; Crystal engineering; Organic porous materials.

Design of supramolecular compartments, grids and tubes attracts a continuing attention. A great variety of achiral as well as chiral designs have been already shown in the literature, employing metal coordination[1], π–π-stacking interactions[2] or hydrogen bonding[3] as the main driving force in self-assembly of appropriate tectons. Self-assembling properties of oligocarboxylic acids and their derivatives turned up to be a particularly versatile instrument[1,2a,3].

We are interested in chiral self-assembly of oligocarboxylic acids and their amides via hydrogen bonds. Recently, in cooperation with Professor Podlaha's laboratory, we have shown[4a–4e] that crystal self-assembly of axially twisted 1,1′-biphenyl-2,2′,6,6′-tetrasubstituted tectons **1a**, **1b** as well as their 2,2′,5,5′-tetrasubstituted isomers **2a**, **2b** opens interesting vistas in this direction. As we have found, intermolecular hydrogen bonds between the

substituents give rise to infinite 2D grids set up from chiral square-like cyclotetrameric compartments, irrespective of chirality or achirality of the starting tecton. A broader validity of this finding has been established recently employing sterically expanded 2,2′,6,6′-tetrasubstituted 1,1′-binaphthyl tectons[4f].

Going further along these lines, we have now examined self-assembling behavior of the corresponding 9,9′-spirobifluorene-2,2′,7,7′-tetrasubstituted tectons **3a** and **3b**. Model considerations led us to the expectation that the two spiro-annelated tectons might afford similar grid layers distinguished, however, by substantially larger pores.


a : X = COOH ; **b** : X = CONH$_2$
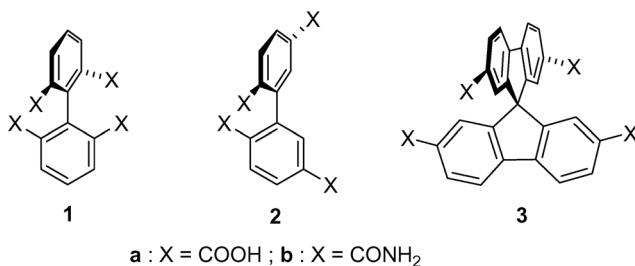
RESULTS AND DISCUSSION

Synthesis

Two high-yield routes leading to the hitherto unknown spirobifluorene tectons **3a**, **3b** are outlined in Scheme 1. The reaction of the easily accessible[5] unsubstituted spirobifluorene **4** with an excess of acetyl chloride under Friedel–Crafts conditions[6,7] (AlCl$_3$ in CS$_2$) afforded the tetraacetyl derivative **5** which on haloform reaction (Br$_2$/NaOH) gave the target tetraacid **3a**. In an alternative approach, the known[8] tetracyano derivative **7** provided the tetraacid **3a** on alkaline hydrolysis. Treatment of tetraacid **3a** with thionyl chloride and subsequently with aqueous ammonium hydroxide gave rise to the corresponding tetraamide **3b**.

Crystallographic Analysis of the Spirobifluorene Tectons 3a and 3b

Overview of molecular structures: The molecular structures of both the spirobifluorene tectons **3a** and **3b** are given in Fig. 1. The tetraacid **3a** exists in the crystal in the form of two symmetrically independent molecules
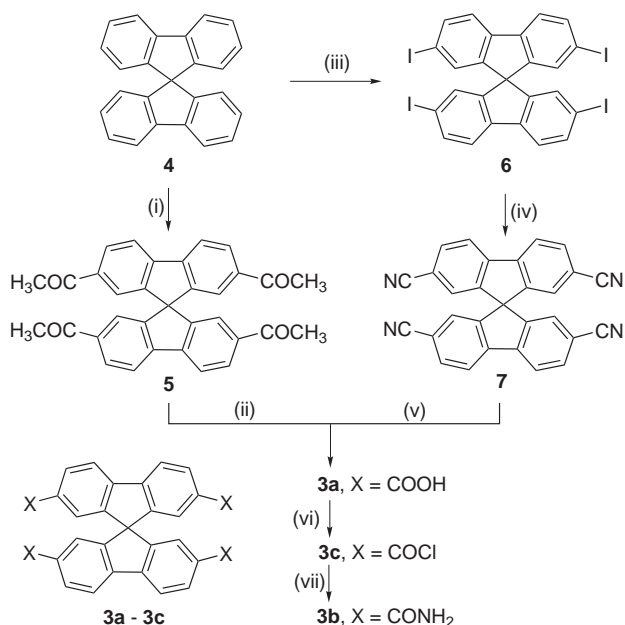
(i) CH$_3$COCl, AlCl$_3$, CS$_2$; (ii) Br$_2$/NaOH; HCl; (iii) I$_2$, HIO$_3$, CH$_3$COOH;
(iv) CuCN, DMF; (v) NaOH, aq. EtOH; HCl; (vi) SOCl$_2$; (vii) NH$_4$OH

SCHEME 1

(**A**, **B**), the molecule **A** being shown in Fig. 1a. Owing to spiro-annelation of the central cyclopentane rings, the two complementary (structurally identical) fluorene moieties are near-to-orthogonal, the dihedral angle being 89.96(5)° in **A** and 88.42(5)° in **B**. Bending of the individual fluorene arms underlies the most marked difference between the **A** and **B** molecules, accounting for unequal dihedral angles between the terminal benzene rings (4.53(2)° in **A** and 0.5(3)° in **B**). Planes of all the carboxyl substituents deviate only slightly from planes of the neighboring aromatic rings.

Also tetraamide **3b** exists in the crystal in the form of two symmetrically independent molecules (**C**, **D**), the molecule **C** being shown in Fig. 1b. As comparison of Figs 1a and 1b shows, structure features of the two investigated tectons **3a** and **3b** are similar, the main difference being a distortion of the carbamoyl substituents in **3b** out of the corresponding aromatic planes (up to 28°).

Hydrogen bonding in the crystal self-assembly of tetraacid **3a**: The individual molecules of tetraacid **3a** are linked in the crystal by intermolecular double hydrogen bonds employing all carboxyl groups in each tecton. Orthogonal arrangement of the participating substituents at the individual tectons gives rise to infinite 2D grid networks set up from the hydrogen-bonded square-like cyclotetramers (Fig. 2).
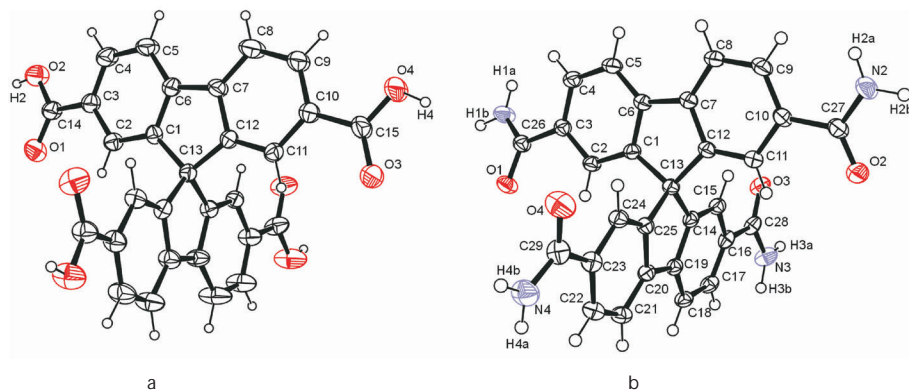

FIG. 1
Perspective view of molecule **A** of tetraacid **3a** (a), with atom numbering of a symmetrically independent half of molecule and of molecule **C** of tetraamide **3b** (b), with atom numbering. Ellipsoids for 30% (**3a**) and 50% (**3b**) probability
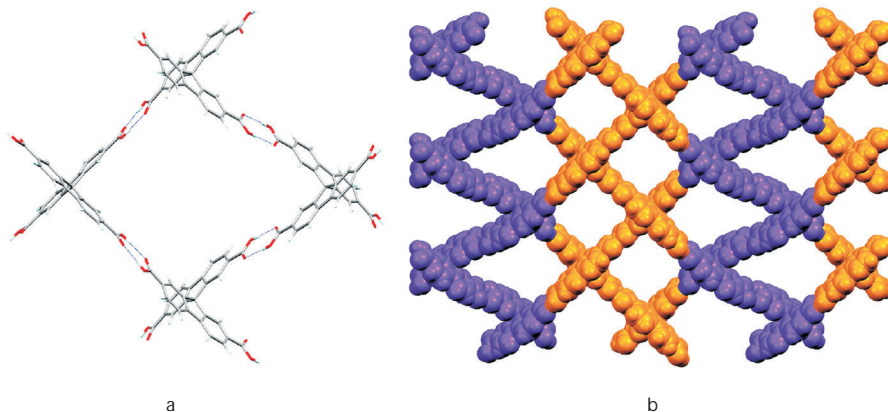

FIG. 2
The crystal self-assembly of tetraacid **3a**; a cyclotetrameric segment (drawn in sticks) (a), participation of independent molecules **A** and **B** (distinguished by color in spacefill presentation[9,10]) in the resulting grid (b). Disordered guest molecules of toluene are omitted

It has been already shown earlier that also biphenyl tectons **1a**, **1b** and **2a**, **2b** self-assemble in crystal in a square-like fashion. The geometry of cyclotetrameric compartments arising from positionally isomeric tectons **1a**, **1b** and **2a**, **2b**, respectively, has been however found to be different (Scheme 2). With **1a**, **1b**, double hydrogen bonds link alternately, in a dis-
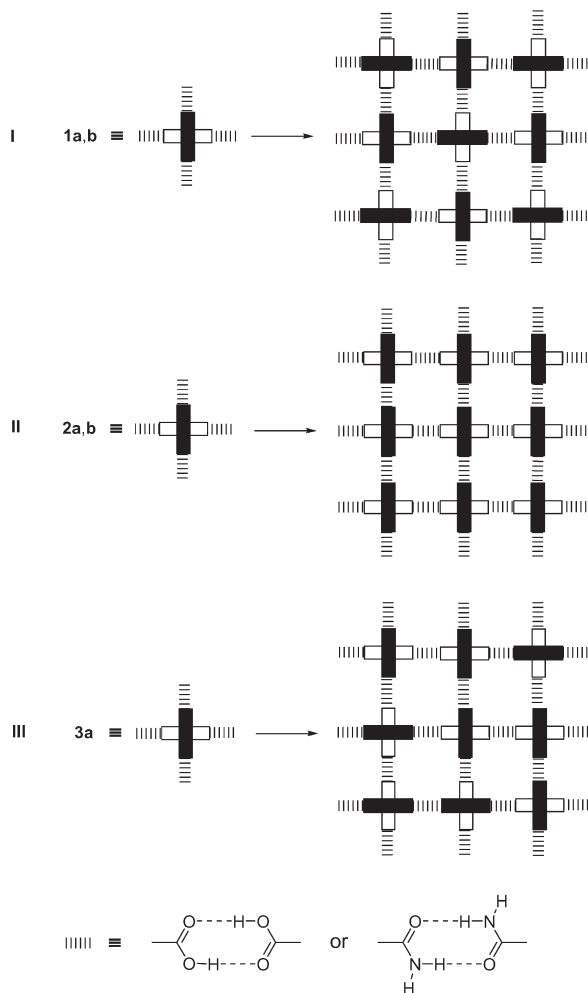
Scheme 2

Alternative stereochemical arrangements in the crystal self-assembly of tetrasubstituted biphenyl and spirobifluorene tectons **1a**, **1b**, **2a**, **2b** and **3a**. Arrangement **I** corresponds to tectons **1a**, **1b**; **II** to **2a**, **2b**, and **III** to **3a**. Black and white colors distinguish the "upper" and "lower" phenyls of the individual tectons participating in the self-assembly

sonant zigzag fashion, upper and lower phenyls of neighboring collinear tectons, in two orthogonal directions, resulting in the cyclotetrameric arrangement **I**. With **2a**, **2b**, in contrast, double hydrogen bonds link, in a consonant straight-chain fashion, upper–upper and lower–lower phenyl portions of the neighboring tectons, resulting in the cyclotetrameric arrangement **II**.

The spirobifluorene tecton **3a** employs, in the crystal self-assembly, another cyclotetrameric arrangement, **III**. Out of the four double hydrogen bonds participating in each cyclotetrameric compartment, two bonds link dissonantly upper and lower portions of the neighboring tectons. Whereas, the other two bonds link consonantly upper–upper and lower–lower moieties of the remaining tectons. In this way, arrangement **III** represents a hybrid of arrangements **I** and **II**.

Salient features of the former two arrangements, **I** and **II**, can be referred to the well-known zigzag vs straight-chain hydrogen-bonding patterns of isophthalic and terephthalic acids (Scheme 3a and 3b, respectively; R = H); these may be viewed as representing the respective parents of the corresponding biphenyl Siamese[4e] twins **1a**, **1b** and **2a**, **2b** (Scheme 3a and 3b, respectively, R = $C_6H_4(COOH)_2$). As a simple consideration of models
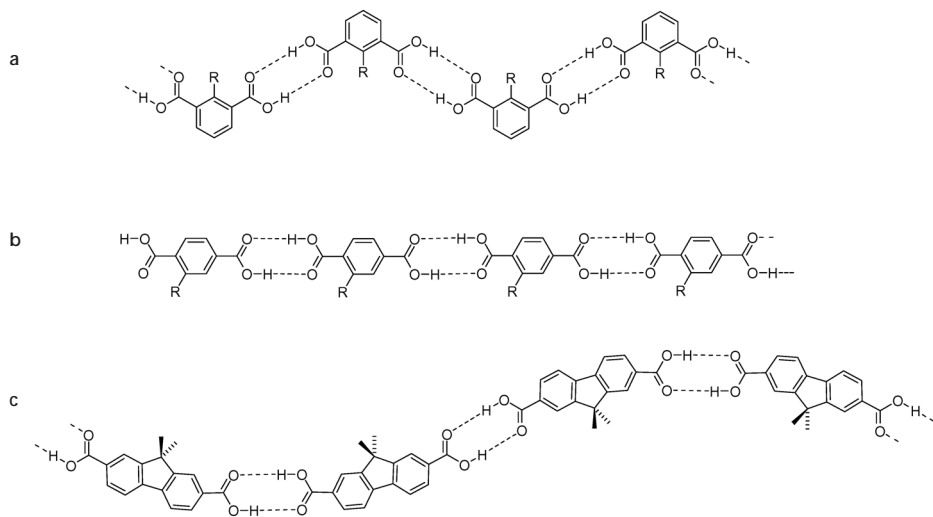
SCHEME 3

Chains of hydrogen-bonded molecules of isophthalic and terephthalic acid (R = H; **a** and **b**, respectively) compared with the corresponding chains of the corresponding Siamese twins **1a** and **2a** (R = $C_6H_4(COOH)_2$; **a** and **b**, respectively) and of the spirobifluorene tecton **3a** (**c**)

shows, the "isophthalic" (120°) and "terephthalic" (180°) orientation of the "sticking" substituents, distinguishing the Siamese twin tectons **1a**, **1b** and **2a**, **2b**, fits perfectly with the geometry of the respective arrangements **I** and **II**. In contrast, the spirobifluorene tecton **3a** with an intermediate (about 160°) orientation of the substituents (Scheme 3c) can be better accommodated within the hybrid arrangement **III**, in which "dissonant" links from **I** and "consonant" links from **II** alternate.

It is noteworthy that alternation of the dissonant vs consonant links in the self-assembly of tecton **3a** is accompanied by alternation of the independent molecules **A** and **B**, which proceeds, in both orthogonal directions, in –**A**–**A**–**B**–**B**– fashion. The dissonant links occur between the same molecules (**A**–**A** or **B**–**B**), whereas consonant links connect the opposite (**A** vs **B**) species.

A more detailed analysis of the arrangement **III** also reveals that in each hydrogen-bonded cyclotetramer only three participating tectons are collinear, whereas the fourth tecton markedly deviates (11.89(17)°), assumedly in order to minimize the residual strain. Propagation of this irregularity leads to undulation of the infinite grid. This contrasts with the arrangements **I** and **II**, in which all the participating tectons are collinear and the resulting infinite grids are accordingly planar.

Size and chirality of cyclotetrameric compartments in the self-assembly of the achiral tecton **3a**: The sides of the square-like compartments arising in the self-assembly of the spirobifluorene tecton **3a** amount to about 13 Å, which contrasts with the value of 8.6 Å established earlier[4a] for the cyclotetrameric compartments arising from the corresponding biphenyl tecton **1a**. According to the program PLATON[11], unit cell in the crystal of spirobifluorene **3a** involves 55% of a solvent-accessible void[12], contrasting with practical absence (2.7%) of free space calculated for the biphenyl analogue **1a**. The large voids existing in the **3a** crystal are filled by disordered molecules of solvent (see Experimental).

Molecules of both the compared tectons **1a** and **3a** are achiral, possessing a plane of symmetry. In contrast, the corresponding cyclotetrameric compartments in **I** and **III** (Scheme 2) possess rotational axes (D_4 and C_2, respectively) as the sole symmetry element, and exhibit accordingly local chirality. For symmetry reasons, compartments of opposite chirality, differing from each other by clockwise or anticlockwise arrangement of the downwards- and upwards-directed hydrogen bonds), are distributed regularly within the resulting infinite grids. However, the pattern of chirality distribution in the two grids compared is different (Scheme 4a and 4b, respectively).
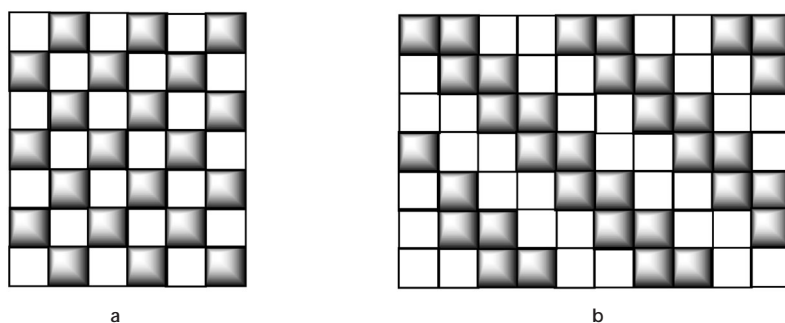
Distribution of cyclotetramers of opposite chirality (gray vs white squares) in the hydrogen-bonded grid of the crystal of **a** biphenyl tecton **1a** and **b** spirobifluorene tecton **3a**

Hydrogen bonding in the crystal self-assembly of tetraamide tecton **3b**: In contrast to the tetraacid tectons **3a**, which are linked via double hydrogen bonds, the corresponding tetraamide tectons **3b** exploit single hydrogen bonds in the crystal self-assembly. Although the orthogonal arrangement of the carbamoyl substituents also promotes formation of square-like compartments via hydrogen bonds (Fig. 3), two fundamental differences in the self-assembly of the two isosteric tectons **3a** and **3b** become apparent. The
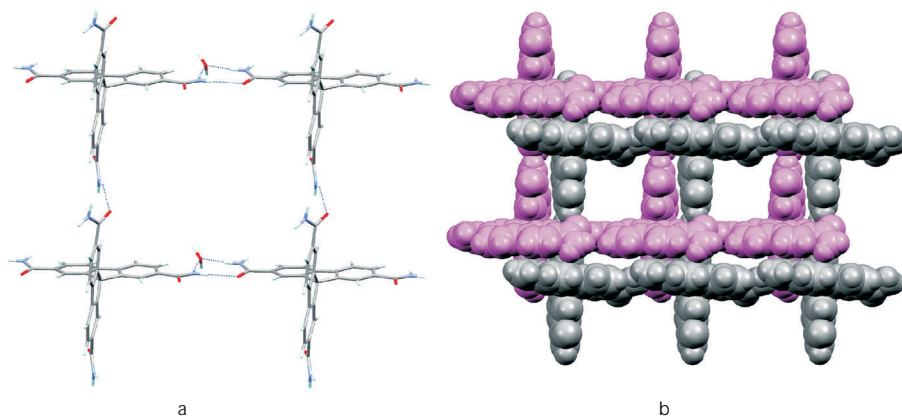
FIG. 3
The crystal self-assembly of tetraamide **3b**; cyclotetrameric segment set-up from molecules **D** (drawn in sticks) via single amide–amide hydrogen bonds (two bonds being reinforced via insertion of a hydrogen-bonded molecule of water) (a), intertwinning of two cyclotetrameric compartments set up separately from molecules **C** and **D** (distinguished by color in spacefill presentation[9,10]) (b); molecules of solvents are omitted

first difference concerns the vacant space inside the individual cyclotetrameric compartments. In contrast to the very large free space inside tetraacid **3a** compartments, the corresponding vacancies in the crystal of tetraamide **3b** are greatly diminished by formation of interpenetrating double layers (cf. Fig. 3b), the residual space being fully occupied by hydrogen-bonded solvent molecules.

Another difference concerns the inner architecture of the cyclotetrameric compartments. In contrast to the arrangement **III** (Scheme 2), which is preferred by the tetraacid tecton **3a**, the arrangement of the type **II** prevails in the self-assembly of the tetraamide analogue **3b**. The resulting arrangement **II** is achiral, in contradiction with the alternative arrangements **I** and **III** which both are intrinsically chiral.

Crystal self-assembly of other 2,2′,7,7′-tetrasubstituted spirobifluorene tectons. Comments on a recent report in the literature: Wuest[8], in a concurrent study aimed at enhancing crystal porosity investigated several other tetrasubstituted spirobifluorene tectons. The crystal self-assembly of two of the Wuest tectons, **3d** and **3e**, allows a direct comparison with the results of our study.
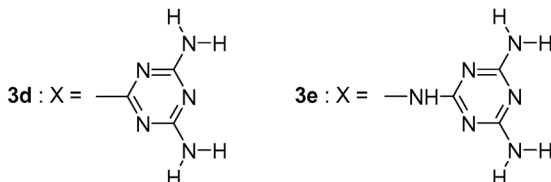
Both the tectons **3d**, **3e** self-associate via hydrogen bonding of the di(tri)aminotriazine groups (Scheme 5). In contrast to our tecton **3a**, participating via eight hydrogen bonds with four neighbors in the formation of simple 2D cyclotetrameric grids, both the Wuest tectons **3d** and **3e** participate via sixteen hydrogen bonds with six neighbors resulting in complex 3D networks. In the self-assembly of **3d**, two of the six neighbors form hydrogen bonds with the central tecton according to the motif **a** defining in this way a 2D square grid. The remaining four neighbors form hydrogen bonds with the central tecton according to the motifs **b** and **c**, defining together a 3D diamond network with two-fold interpenetration.

Similar combination of the hydrogen-bonding motifs **a**–**c** occurs also in the self-assembly of the tecton **3e**, resulting in a four-fold diamond-like network interpenetrated by a square 2D grid.
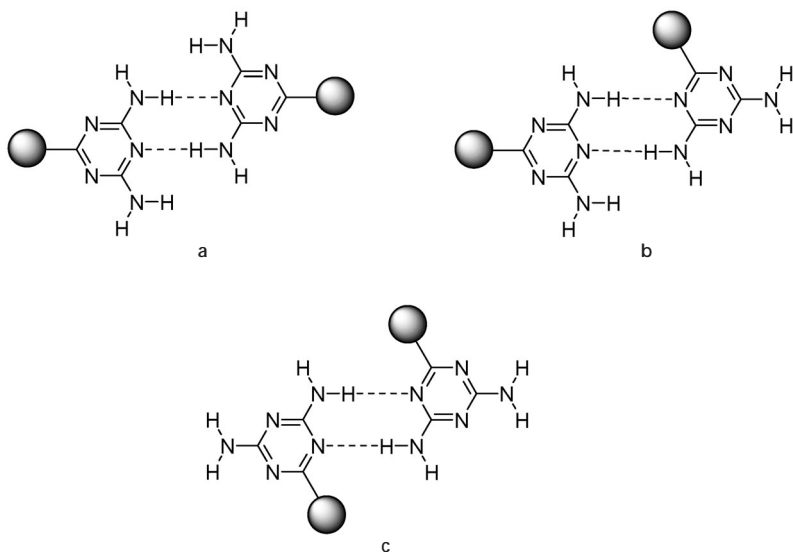
Hydrogen bonding motifs (**a**, **b**, **c**) in the self-assembly of the Wuest[8] tectons **3d** and **3e**; spheres represent the aromatic core of the tectons

Noteworthy is stereochemistry of the 2D square network participating in the complex self-assembly. As a closer inspection of the Wuest's results reveals, stereochemistry of the cyclotetrameric compartments in the square grid corresponds with the arrangement **I** (Scheme 2), which we earlier established[4a–4c] in the self-assembly of the tectons **1a** and **1b**.

EXPERIMENTAL

General

Melting points were determined on a Kofler apparatus and are uncorrected. NMR spectra were measured on a Bruker Avance 400 (^{1}H at 400 MHz) spectrometer in CDCl$_3$ or in DMSO-d_6. Chemical shifts (δ in ppm) are referenced either to TMS (^{1}H in CDCl$_3$) or residual solvent signal (δ_H(DMSO) 2.50), coupling constants (J) are given in Hz. Mass spectra were recorded on a ZAB-EQ (VG-Analytical) instrument (EI 70 eV).

Synthesis

2,2′,7,7′-Tetraacetyl-9,9′-spirobifluorene (**5**). Anhydrous AlCl$_3$ (9.00 g, 67.5 mmol) was gradually added to a stirred solution of 9,9′-spirobifluorene[5] (1.00 g, 3.16 mmol) in CS$_2$ (30 ml). After cooling to 0 °C, acetyl chloride (1.58 g, 20.13 mmol) in CS$_2$ (5 ml) was dropped into the stirred reaction mixture. Stirring was continued at room temperature overnight, then the

reaction was quenched with concentrated hydrochloric acid (10 ml) in crushed ice (100 g). Organic portion was extracted with ethyl acetate (3 × 60 ml), combined extracts were washed with water (50 ml) and dried with anhydrous $MgSO_4$. Solvents were removed in vacuo and the crude product (1.49 g) was dissolved in hot dioxane and crystallized on dilution with *n*-hexane. The suspension was filtered off, the crystalline product was washed with *n*-hexane and dried in vacuo. Yield 1.28 g (84%), m.p. 349–352 °C. For $C_{33}H_{24}O_4$ (484.5) calculated: 81.80% C, 4.99% H; found: 81.56% C, 4.94% H. ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 dd, 4 H, [3]J = 8.0, [4]J = 1.5 (H-3,3′,6,6′); 8.02 dd, 4 H, [3]J = 8.0, [5]J = 0.7 (H-4,4′,5,5′); 7.29 dd, 4 H, [4]J = 1.5, [5]J = 0.7 (H-1,1′,8,8′); 2.49 s, 12 H (4 × CH_3CO). MS-EI, *m/z* (rel.%): 484 (M[+], 75), 469 (80), 311 (40), 227 (33), 97 (43), 83 (46), 57 (100).

9,9′-Spirobifluorene-2,2′,7,7′-tetracarbonitrile (**7**). Prepared by modification of the reported[8] procedure (replacement of 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene with the corresponding tetraiodo derivative[13]). A mixture of tetraiodide **6** (1.20 g, 1.44 mmol) and CuCN (0.58 g, 3.22 mmol) in DMF (10 ml) was heated under argon to 145 °C for 4 h. After cooling, the reaction mixture was diluted with 0.2 M HCl (100 ml) and extracted with ethyl acetate (3 × 80 ml). Combined extracts were washed with water (2 × 50 ml) and dried with anhydrous $MgSO_4$. Solvents were removed in vacuo and the crude product was crystallized from a dioxane/petroleum ether mixture and recrystallized from an ethyl acetate/ethanol mixture. Yield 451 mg (74%), m.p. > 360 °C, ref.[8] m.p. > 300 °C, spectral data in an accordance with ref.[8]

9,9′-Spirobifluorene-2,2′,7,7′-tetracarboxylic acid (**3a**). For the preparation two methods were used

A. From 2,2′,7,7′-tetraacetyl-9,9′-spirobifluorene (**5**). Bromine (3.60 g, 22.5 mmol) was dropped into a stirred solution of NaOH (3.00 g, 75 mmol) in water (15 ml) at 0 °C, then tetraacetyl derivative **5** (603 mg, 1.24 mmol) dissolved in 30 ml dioxane was added dropwise during 0.5 h. The mixture was heated to 50 °C under stirring for 4 h. After addition of an aqueous solution of $Na_2S_2O_5$ (5.0 g), the mixture was acidified with 2 M HCl to pH 1. The resulting suspension was concentrated in vacuo to 40 ml, the crude tetraacid was filtered off, washed with water and crystallized from aqueous ethanol. The tetraacid retained solvents even after drying in vacuo (20 h, 20 Pa, room temperature). Yield 544 mg (76%), m.p. > 360 °C. Single crystals of tetraacid **3a** for X-ray measurement were grown from an acetone/toluene solution by slow evaporation. For $C_{29}H_{16}O_8$ (492.5)·$2H_2O$·C_2H_5OH calculated: 64.81% C, 4.83% H; found: 64.88% C, 4.73% H. ^{1}H NMR (400 MHz, DMSO-d_6): 13.08 br s, 4 H (4 × COOH); 8.32 dd, 4 H, [3]J = 8.0, [5]J = 0.5 (H-4,4′,5,5′); 8.11 dd, 4 H, [3]J = 8.0, [4]J = 1.5 (H-3,3′,6,6′); 7.16 dd, 4 H, [4]J = 1.5, [5]J = 0.5 (H-1,1′,8,8′). MS-EI, *m/z* (rel.%): 492 (M[+], 55), 479 (53), 416 (68), 360 (50), 340 (55), 311 (45), 277 (43), 253 (40), 129 (45), 111 (4), 97 (80), 83 (77), 71(87), 57 (100).

B. From 9,9′-spirobifluorene-2,2′,7,7′-tetracarbonitrile (**7**). A mixture of tetracarbonitrile **7** (250 mg, 0.60 mmol), a solution of NaOH (1.2 g, 30 mmol) in water (5 ml) and ethanol (10 ml) was heated under stirring to reflux for 3 h. The solution was diluted with water (30 ml) and acidified with 2 M HCl to pH 1. The resulting suspension was heated for easier filtration, the tetraacid was filtered off, washed with water and crystallized from aqueous ethanol. Yield 286 mg (83%), the product being in all respects identical with that obtained by procedure *A*.

9,9′-Spirobifluorene-2,2′,7,7′-tetrakis(carbonyl chloride) (**3c**). A mixture of tetraacid **3a** (300 mg, 0.609 mmol), thionyl chloride (30 ml) and a drop of DMF was heated to reflux for 3 h. Volatiles were removed in vacuo, toluene (20 ml) was added to the yellow residue and

the mixture was again evaporated. The crude tetrachloride was dissolved in dry dioxane and insoluble side-products were removed by filtration. The soluble tetrachloride **3c** crystallized from a dioxane solution after addition of *n*-hexane; crystals were filtered off, washed with *n*-hexane and dried in vacuo. Yield 304 mg (88%). The sample decomposed above 340 °C. For $C_{29}H_{12}Cl_4O_4$ (566.2) calculated: 61.52% C, 2.14% H, 25.05% Cl; found: 61.40% C, 2.21% H, 24.93% Cl. ^{1}H NMR (400 MHz, CDCl$_3$): 8.34 dd, 4 H, ^3J = 8.2, ^4J = 1.7 (H-3,3′,6,6′); 8.15 dd, 4H, ^3J = 8.2, ^5J = 0.5 (H-4,4′,5,5′); 7.41 dd, 4 H, ^4J = 1.7, ^5J = 0.5, 4 H (H-1,1′,8,8′). MS-EI, *m/z* (rel.%): 568 (M$^+$, 8), 566 (M$^+$, 16), 564 (M$^+$, 14), 533 (100), 531 (99), 466 (16), 311 (40), 247 (18), 215 (15), 155 (37).

9,9′-Spirobifluorene-2,2′,7,7′-tetracarboxamide (**3b**). A solution of tetrachloride **3c** (190 mg, 0.335 mmol) in dry dioxane (10 ml) was dropped under stirring into a concentrated aqueous ammonium hydroxide (25%, 10 ml) at 0 °C. After 20 min stirring the reaction mixture was evaporated to dryness and the solid residue was crystallized from hot water. Yield 145 mg (88%) of white crystals, m.p. > 360 °C. For $C_{29}H_{20}N_4O_4$ (488.5)·H$_2$O calculated: 68.77% C, 4.38% H, 11.06% N; found: 68.95% C, 4.25% H, 10.88% N. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): 8.22 d, 4 H, ^3J = 8.0 (H-4,4′,5,5′); 8.03 dd, 4 H, ^3J = 8.0, ^4J = 1.5 (H-3,3′,6,6′); 7.94 br s, 4 H (4 × CONH); 7.30 br s, 4 H (4 × CONH); 7.16 d, ^4J = 1.5, 4 H (H-1,1′,8,8′). MS-EI, *m/z* (rel.%): 488 (M$^+$, 3), 470 (4), 416 (9), 340 (11), 310 (11), 277 (10), 261 (14), 185 (10), 129 (27), 111 (22), 95 (53), 91 (100), 57 (73), 55(73). Tetraamide **3b** afforded X-ray quality crystals from solution in aqueous ethanol by slow evaporation.

Single Crystal X-ray Analysis

Crystals of compounds **3a** and **3b** were mounted on glass capillaries with epoxy cement. Diffraction data were collected on a Nonius KappaCCD diffractometer using MoKα radiation (λ = 0.71073 Å, graphite monochromator). The structures were solved by direct methods (SIR92 [14]) and refined by full-matrix least squares on F^2 (SHELXL97 [15]). Relevant crystallographic data are given in Table I.

The structure determination of **3a** was difficult. The crystals decayed rapidly still in the mother liquor leaving for selection of single crystal only a very limited time; moreover, most of the crystals were twins. In order to avoid loss of the solvent, the crystal has to be measured at low temperature; however, it cracks by cooling and under 200 K splits into small blocks probably due to inhomogeneity in distribution of solvent. The vast disorder of the solvent is further witnessed by a diffuse scattering and a steep decrease in diffraction power at high diffraction angle. The diffraction experiment therefore allows to elucidate only the framework of tetraacid **3a** whereas the information concerning the solvent molecules is lost due to their disorder and crystal defects. Only one disordered molecule of toluene could be identified in the asymmetric unit leaving 44% accessible for other molecules of solvent. In order to simplify the situation, all solvent molecules were excluded from the further refinement via the SQUEEZE-procedure (from PLATON[11]). The volume available for solvents was found to be 4638 Å and the number of electrons per unit excluded (by SQUEEZE) were 332.

The framework is built-up by two symmetrically independent molecules (**A** and **B**) of the tetraacid, both being placed in special position so that one of the two fluorene moieties is generated by operation of two-fold axis of space group *C*2/*c* passing through C13 and C13′ atoms. All non-hydrogen atoms of the tetraacid were refined anisotropically. The atoms of two carboxyl moieties of molecule **B** acquire large displacement parameters in the direction

TABLE I
Crystallographic data

Parameter	3a	3b
Formula	$C_{29}H_{16}O_8{}^a$	$C_{29}H_{20}N_4O_4 \cdot 1.6H_2O \cdot 0.4C_2H_6O$
M_r	492.42^a	535.64
Crystal system	monoclinic	triclinic
Space group	$C2/c$ (No. 15)	$P\text{-}1$ (No. 2)
a, Å	15.9820(6)	12.7430(1)
b, Å	38.4860(17)	14.1690(2)
c, Å	14.2450(7)	14.9190(1)
α, °		95.1700(7)
β, °	105.418(2)	101.7130(6)
γ, °		91.4670(5)
Z	8	4
V, Å^3	8446.5(6)	2624.22(5)
Temperature, K	200(2)	150(2)
D_c, g cm^{-3}	0.774^a	1.356
Crystal dimensions, mm	$0.6 \times 0.26 \times 0.075$	$0.5 \times 0.3 \times 0.28$
Appearance	colorless prism	colorless prism
μ, mm^{-1}	0.057^a	0.096
h range	–17, 17	–16, 16
k range	–42, 42	–18, 18
l range	–15, 15	–19, 19
Reflections measured	38856	89069
– independent (R_{int})	5862(0.055)	12070(0.031)
– observed [$I > 2\sigma(I)$]	4331	10122
Parameters refined	336^a	721
S	1.062^a	1.037
$R[F^2 > 2\sigma(F^2)]$	0.086^a	0.0453
$wR^2(F^2)$	0.282^a	0.1291
$\Delta\rho_{max}$; $\Delta\rho_{min}$, e Å^{-3}	0.389^a; -0.404^a	0.671; –0.293

[a] The values were calculated without contribution of solvent, see Experimental.

Parameters of hydrogen bonds in the investigated crystals

Compd	Specification D–H⋯A	Distance, Å			Bond angle, ° D H A
		D–H	H⋯A	D⋯A	
3a	O2–H2⋯O1′[ai]	0.82[a]	1.79	2.603(7)	170.6
	O2′–H2′⋯O1[ai]	0.82[a]	1.81	2.627(7)	173.5
	O4–H4⋯O3[aii]	0.82[a]	1.79	2.599(7)	170.3
	O4′–H4′⋯O3′[aiii]	0.82[a]	1.81	2.611(9)	166.8
3b	N1–H1A⋯O2[bi]	0.89	2.00	2.7307(18)	138.6
	N1–H1B⋯O4′[bii]	0.93	2.00	2.9195(16)	169.6
	N2–H2A⋯O3′[biii]	0.90	2.03	2.8978(19)	161.9
	N2–H2B⋯O4[biv]	0.93	2.56	3.3643(19)	145.6
	N3–H3A⋯O2w[bv]	0.96	1.98	2.9282(19)	171.8
	N3–H3B⋯O5	0.97	2.07	3.0276(19)	168.6
	N4–H4B⋯O1′[bvi]	0.98	2.26	3.2076(19)	162.2
	N1′–H1A′⋯O3w[bvii]	0.88	1.93	2.8074(19)	174.3
	N1′–H1B′⋯O6[bvii]	0.90	2.25	3.002(9)	140.3
	N2′–H2B′⋯O3′[bii]	0.93	1.91	2.8227(18)	165.6
	N2′–H2A′⋯O1′[bi]	0.89	2.15	2.8353(17)	133.9
	N3′–H3A′⋯O4′[bviii]	0.84	2.10	2.8908(15)	156.2
	N3′–H3B′⋯O1w	0.94	2.14	3.0609(17)	164.5
	N4′–H4A′⋯O1[bix]	0.92	2.09	2.9937(17)	170.2
	N4′–H4B′⋯O1w[bix]	0.92	2.00	2.8506(15)	152.9
	O1w–H11⋯O2′[bii]	0.90	1.82	2.7101(15)	172.7

[a] Idealized position.
Symmetry codes: (ai) 2 – x, –y, 1 – z; (aii) 7/2 – x, 1/2 – y, 2 – z; (aiii) 5/2 – x, 1/2 – y, 2 – z; (bi) x – 1, y, z; (bii) –x, 1 – y, 1 – z; (biii) 1 + x, y, 1 + z; (biv) 2 – x, –y, 2 – z; (bv) 1 – x, 1 – y, 1 – z; (bvi) 1 – x, –y, 1 – z; (bvii) 1 – x, 1 – y, –z; (bviii) x, y – 1, z; (bix) x, 1 + y, z; (bx) x, 1 + y, z.

perpendicular to the carboxyl plane as a consequence of their disorder. The hydrogen atoms on carbons were fixed into idealized positions (riding model) and assigned displacement parameter $H_{iso}(H) = 1.2 U_{eq}$(pivot atom). Also hydrogen atoms of the OH groups were calculated in idealized positions to form the "best" hydrogen bond to adjacent oxygen and assigned displacement parameter $H_{iso}(H) = 1.2 U_{eq}$(pivot atom). This solution of hydrogen bond network can be regarded as unambiguous because of very short intermolecular O⋯O distances (Table II).

Even if the precision of structure determination is poor, it is sufficient to provide key information concerning the self-assembly of tetraacid **3a**.

The structure determination of tetraamide **3b** was unexceptional, hampered only by occupational disorder of one molecule of solvent; ethanol molecule is not fully present and in 20% of the crystals is substituted by water (oxygen O6). All non-hydrogen atoms (except O6) were refined anisotropically. The hydrogen atoms on carbons were fixed in idealized positions (riding model) and assigned displacement parameter $H_{iso}(H) = 1.2 U_{eq}$(pivot atom). The hydrogens on O and N were found on a difference Fourier map and refined with constraints (riding model) with assigned displacement parameter $H_{iso}(H) = 1.2 U_{eq}$(pivot atom). The position of hydrogen atoms on O6 could not be resolved because their contribution to overall electron density is very low. CCDC 284565 (for **3a**) and 284566 (for **3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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