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Self-assembly of chiral hydrogen-bonded grid layers from terephthalic Siamese twins

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Abstract—2,2′,5,5′-Tetracarboxy- and 2,2′,5,5′-tetracarbamoyl-substituted biphenyls and also the 2,2′,3,3′,6,6′-hexacarboxy-substituted analogue behave as Siamese twins of terephthalic tectons in the single crystal self-assembly, giving rise to chiral 2D grid layers. A comparison has been made with the corresponding 2,2′,6,6′-tetrasubstituted biphenyls which mimic isophthalic twins in their self-assembly. © 2003 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Supramolecular chemistry inspires the design of microporous layers employing self-assembly of molecular subunits (tectons) as the synthetic tool.[1–3] We are interested in the design of supramolecular layers displaying chiral micropores. Recently, we have shown[4–7] that 2,2′,6,6′-tetracarboxy- and 2,2′,6,6′-tetracarbamoyl-substituted biphenyl tectons **1** and **2** open interesting vistas in this direction.

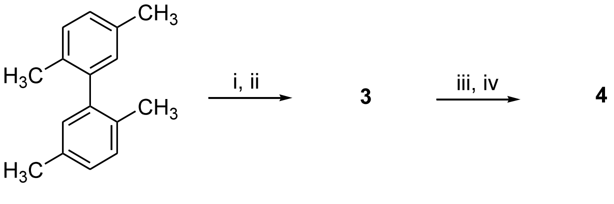
Now we have examined the self-assembly behavior of the corresponding 2,2′,5,5′-tetrasubstituted positional isomers. Herein, we report crystallographic results obtained employing 1,1′-biphenyl-2,2′,5,5′-tetracarboxylic acid **3** and 1,1′-biphenyl-2,2′,5,5′-tetracarboxamide **4** as the prototypal tectons. At the same time, we report the results obtained with 1,1′-biphenyl-2,2′,3,3′,6,6′-hexacarboxylic acid **5** possessing the self-assembling potential of both the novel 2,2′,5,5′- as well as the earlier investigated 2,2′,6,6′-tetrasubstituted biphenyls.

2. Results and discussion

2.1. Synthesis

Oxidation of the known[8] 2,2′,5,5′-tetramethylbiphenyl **6** with potassium permanganate in pyridine afforded the target tetracarboxylic acid **3** in nearly quantitative yield. A successive treatment of the tetraacid **3** with thionyl chloride and ammonium hydroxide yielded the corresponding tetracarboxamide **4** (Scheme 1).

The hexacarboxylic acid (*S*)-**5** was prepared analogously from the tetramethyldicarboxylic acid (*S*)-**7**, which in turn was prepared by resolution[9] of the corresponding racemate (*RS*)-**7**. This was obtained according to Gronowitz and Hansen,[10] however, it melted without decomposition at 243.5–245.5°C, instead of at 290–306°C (dec.) as given by these authors. The mp of the acid did not change after conversion into the dimethyl ester derivative, its purification by chromatography and subsequent saponification. In contrast, the mp and specific rotation of the resolved diacid agree with the



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Scheme 1. *Reagents*: (i) $KMnO_4$, pyridine; (ii) conc. aq. HCl; (iii) $SOCl_2$; (iv) aq. NH_4OH/dioxane.

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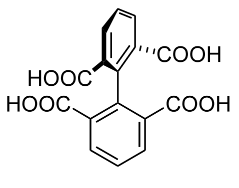

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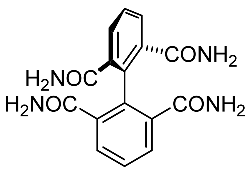

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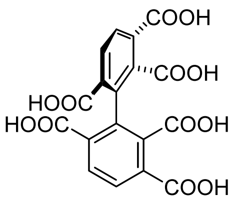

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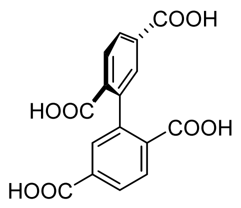

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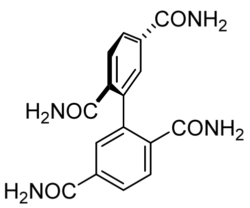

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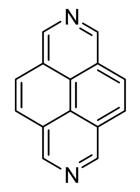

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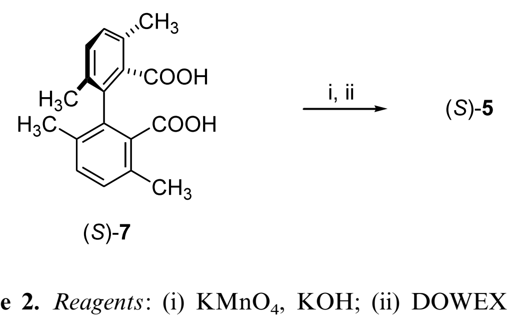
published values.[9,11] The hexacarboxylic acid (*S*)-**5** was configurationally stable for 4 h at 85°C in 0.1 M NaOH, thus proving that no racemization is likely during the preparation (Scheme 2).

2.2. X-Ray crystallographic analysis

2.2.1. An overview of the molecular structures of 3–5. The molecular structures of **3**–**5** are displayed in Section 4.2. For all of the novel tectons, the intramolecular bond angles and distances are unexceptional. The aromatic rings are invariably almost planar, the deviation of the individual carbon atoms from the main plane being less than 0.02 Å. The biphenyl axis is bent at the C1–C1′ junction in all the investigated tectons, but the individual displacements are markedly different. The observed values are −0.131(2) Å at C1′ and 0.590(4) Å at C4′ in the tetraamide **4**, on comparison with the corresponding values of −0.418(2) Å at C11′, 1.445(4) Å at C14′, −0.403(2) Å at C21′, and 1.422(4) Å at C24′ established for two independent molecules of the hexaacid **5**. Less pronounced are the observed displacements of the pivot atoms of the substituents from the parent aromatic planes (0.070(3) and 0.180(2) Å for the tetraamide **4**; from −0.038(2) to 0.154(2) Å for the hexaacid **5**).

The values for the dihedral angles between the planes of the individual phenyl rings are noteworthy because they are markedly different in the investigated tectons, being 56.23(6)° for the tetraacid **3** (in the molecular complex), 46.75(3)° for the tetraamide **4** and 82.00(4)° (or 83.94(3)°) for the hexaacid **5** (cf. Section 4.2). Different repulsion between the proximal substituents is assumed to be the factor responsible for this behavior.



Scheme 2. *Reagents*: (i) $KMnO_4$, KOH; (ii) DOWEX 50X8 (H^+).

Aditionally, the planes of the carboxyl or carbamoyl substituents are turned out from the parent ring planes and the individual distortions are different. Thus, in the tetraamide **4**, one carbamoyl group is nearly coplanar with the parent phenyl ring, whereas the other is tilted away (dihedral angles 11.2(2) and 43.4(1)°, respectively). In both of the two independent molecules of the hexaacid **5**, the planes of the carboxyl substituents are tilted away from the parent phenyls slightly in 3,3′-positions (11.15(27) and 11.29(27)°) and in 6,6′-positions (12.29(26) and 11.39(27)°), but substantially in 2,2′-positions (89.90(6) and 89.62(6)°).

2.2.2. Self-assembly of 1,1′-biphenyl-2,2′,5,5′-tetracarboxamide, 4. The individual molecules of the tetracarboxamide **4** in the crystal are linked by intermolecular amide–amide (asymmetric) double hydrogen bonds. All four carboxamide groups in each molecule participate in the hydrogen-bonded network. Upper phenyls in the neighboring tectons are chained, in one direction, via the hydrogen-bonded carboxamide groups placed alternately in the positions 2 and 5, whereas the corresponding 2′,5′-substituents at the lower phenyls create a separate chain proceeding in another direction. Combination of the two divergent chains leads to an infinite rhombic grid set up from hydrogen-bonded cyclotetrameric compartments (Fig. 1). Lengths of the participating (N)H···O double hydrogen bonds correspond to 1.96 and 2.05 Å.

The 2D grid layers in the crystal are arranged in a staggered manner, which allows the phenyl groups of the residing tectons to protrude from one layer into the others. This effective packing is supported by formation of intermolecular single amide–amide hydrogen bonds among the stacked layers (lengths of the (N)H···O

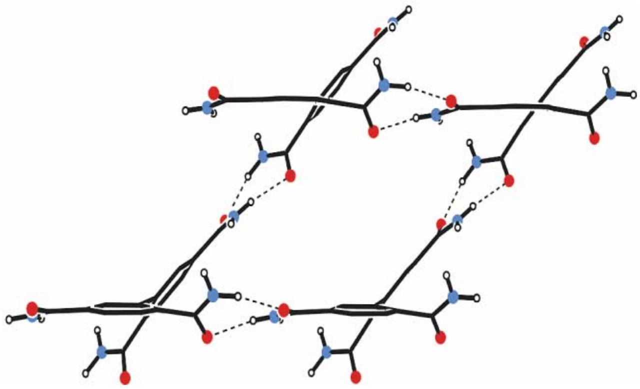


Figure 1. Segment of an infinite grid layer in the crystal of tetraamide **4** formed by intermolecular double hydrogen bonds. Oxygen and nitrogen atoms are depicted as red and blue circles, respectively.

hydrogen bonds are 2.03 and 2.25 Å), resulting in 3D hydrogen-bonded network (for parameters of all hydrogen bonds see Table 1).

2.2.3. Self-assembly of the 1:2 complex of 1,1′-biphenyl-2,2′,5,5′-tetracarboxylic acid 3 with 2,7-diazapyrene 8. Attempts to prepare an X-ray quality crystal of the free tetraacid **3** failed. However, a satisfactory crystal of the molecular complex of the tetraacid **3** with 2,7-diazapyrene[12] spacer **8** has been obtained and subjected to the crystallographic study. Composition of the addition complex corresponds to 1:2 stoichiometry.

Molecular components in the complex are linked via single hydrogen bonds between carboxyl substituents in the tetraacid **3** and nitrogen atoms in the diazapyrene base **8**. Classical, non-ionic, single hydrogen bonds are involved in the linkage, as evidenced, for example by their established parameters (Table 1) and bond lengths in the carboxyl groups (=O11 1.213(2) Å, =O21 1.196(2) Å, –O12 1.315(3) Å, –O22 1.322(2) Å). The carboxyl groups located at the upper and lower phenyls of the tetraacid **3** tectons are chained separately (via the inserted hydrogen-bonded diazapyrene spacers), in analogy with the self-assembling pattern established above for the tetraamide **4**.

Thus, infinite 2D-grid layers result, which are set up from huge (19 Å) rhombic compartments (Fig. 2). The grid layers (including the spacer molecules) are oriented along the *ab* plane in the crystal, with the biphenyls being collinear with the axis *c*. The empty space inside the resulting ‘valleys’ (flanked by the biphenyl ‘ridges’) is effectively filled by two independent grid layers also spreading along the *ab* plane (Fig. 3). Stacking of the resulting layer triads along the *c* axis is controlled by π–π interactions between the coplanar spacer molecules (Fig. 4). The established intermolecular distances (intercentroid 3.876 Å; interplanar 3.531 Å) correspond closely with the crystal parameters of the free diazapyrene[13] base (3.790 and 3.450 Å, respectively).

2.2.4. Self-assembly of (*S*)-1,1′-biphenyl-2,2′,3,3′,6,6′-hexacarboxylic acid, 5. Molecules of the hexaacid **5** are linked in the crystal by carboxyl–carboxyl double hydrogen bonds employing four of the six carboxyls available in each tecton. The carboxyl groups alternately placed in the positions 3 and 6 at the neighboring upper phenyls provide one hydrogen-bonded chain while the corresponding substituents in the 3′- and 6′-positions at the lower phenyls participate in another chain proceeding in the perpendicular direction. In this way, an infinite 2D square grid results (Fig. 5) which is

Table 1. Parameters of hydrogen bonds in the crystal structures

Compound	Specification		Distances (Å)		Bond angle (°) D H A
	D–H···A	D–H	H···A	D···A	
4	N1–H11···O2^{ai}	0.94(2)	1.96(2)	2.8839(18)	169.6(19)
	N1–H12···O1^{aii}	0.89(2)	2.03(2)	2.8969(18)	166.3(18)
	N2–H21···O1^{aiii}	0.91(2)	2.05(2)	2.9430(17)	169(2)
	N2–H22···O2^{aiv}	0.88(2)	2.25(2)	2.9155(17)	134.7(19)
$3{\cdot}(C_{14}H_8N_2)_2$	O12′–H12′···N1^{bi}	0.89(3)	1.77(3)	2.643(2)	170(3)
	O22′–H21′···N8^{bii}	1.06(4)	1.59(4)	2.629(2)	165(3)
5	O14–H14···O15^{ci}	0.98(4)	1.70(4)	2.6702(17)	172(3)
	O16–H16···O13^{cii}	1.03(3)	1.62(3)	2.6259(16)	164(2)
	O24–H24···O25^{ciii}	0.87(3)	1.80(3)	2.6709(17)	174(3)
	O26–H26···O23^{civ}	1.08(3)	1.57(3)	2.6256(16)	164(2)
	O12–H12···O2W	0.99(3)	1.54(3)	2.5266(17)	174(3)
	O22–H22···O1W	1.02(3)	1.50(3)	2.5222(17)	175(2)
	O1W–H11W···O4W^{cv}	0.86(3)	1.97(3)	2.8152(14)	170(2)
	O1W–H12W···O11^{cvi}	0.86(3)	1.90(3)	2.7001(17)	154(2)
	O2W–H21W···O21^{cvii}	0.91(3)	1.90(3)	2.6948(17)	144(2)
	O2W–H22W···O3W	0.88(3)	1.95(3)	2.8343(14)	179(3)
	O3W–H31W···O22	0.96(4)	1.98(4)	2.8973(18)	159(3)
	O4W–H42W···O12^{cviii}	0.94(4)	2.00(4)	2.8941(19)	157(4)

Symmetry transformations used to generate equivalent atoms: (ai) *x*, *y*−0.5, 0.5+*z*; (aii) 1.5−*x*, *y*, *z*−0.5; (aiii) *x*, 0.5+*y*, *z*−0.5; (aiv) 0.5+*x*, 0.5−*y*, *z*; (bi) 0.5−*x*, 0.5+*y*, 0.5−*z*; (bii) 1−*x*, *y*−1, 0.5−*z*; (ci) 0.5+*x*, 0.5+*y*, *z*; (cii) −0.5+*x*, −0.5+*y*, *z*; (ciii) −0.5+*x*, 0.5+*y*, *z*; (civ) 0.5+*x*, −0.5+*y*, *z*; (cv) 1.5+*x*, 1.5−*y*, 0.5+*z*; (cvi) *x*, 1−*y*, 2−*z*; (cvii) −0.5+*x*, 1.5−*y*, 2−*z*; (cviii) 1−*x*, *y*, 1.5−z.

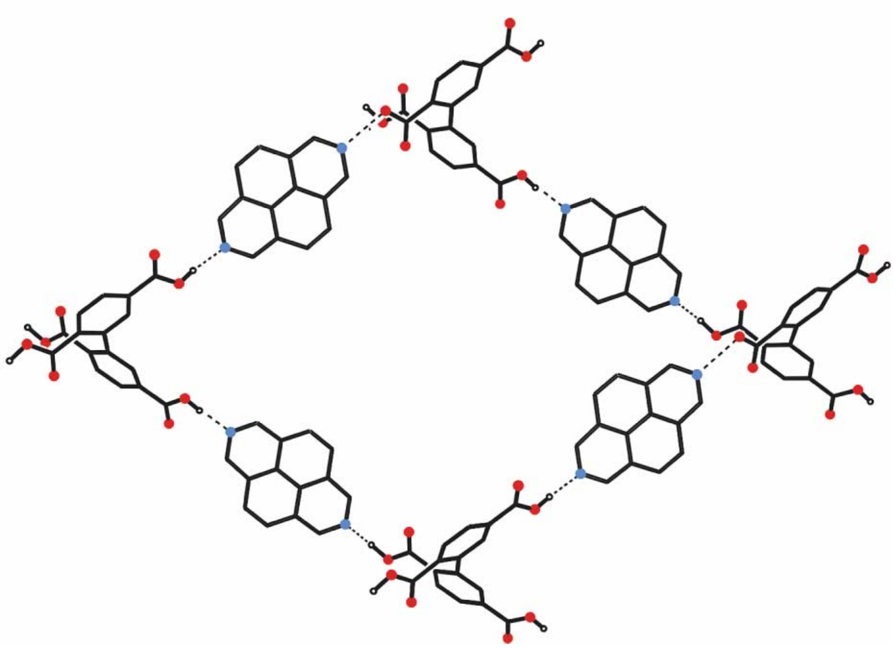


Figure 2. Segment of an infinite grid layer in the crystal of the molecular 1:2 complex of tetraacid **3** with 2,7-diazapyrene formed by intermolecular single hydrogen bonds. Oxygen and nitrogen atoms are depicted as red and blue circles, respectively.

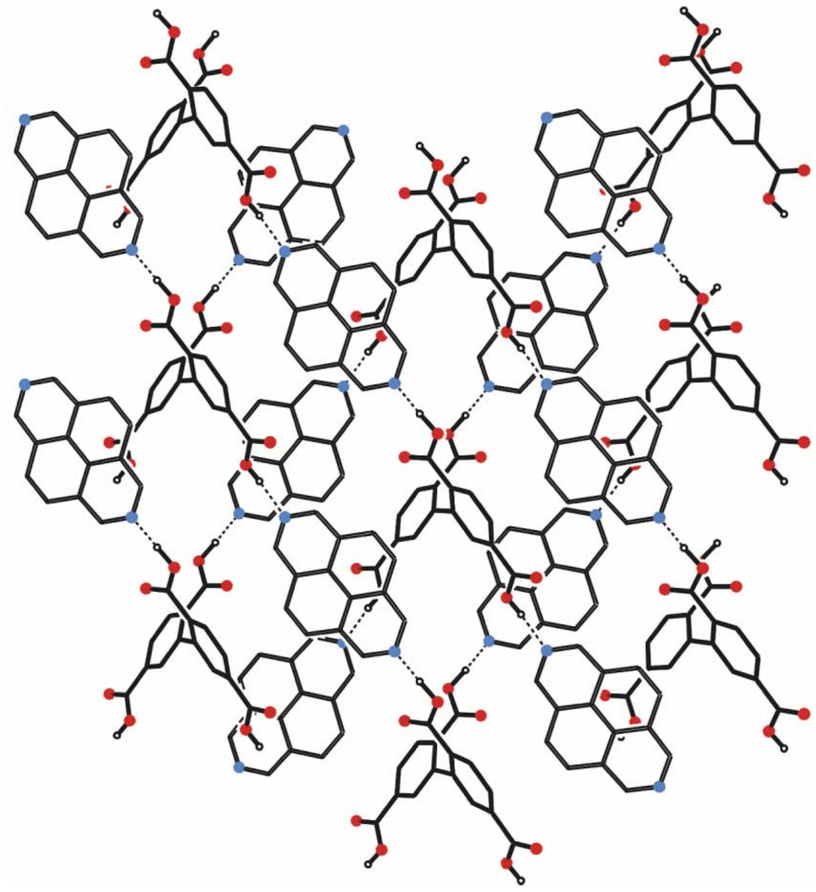


Figure 3. Pleating of individual grid layers from Fig. 2 into triads along the *ab* plane.

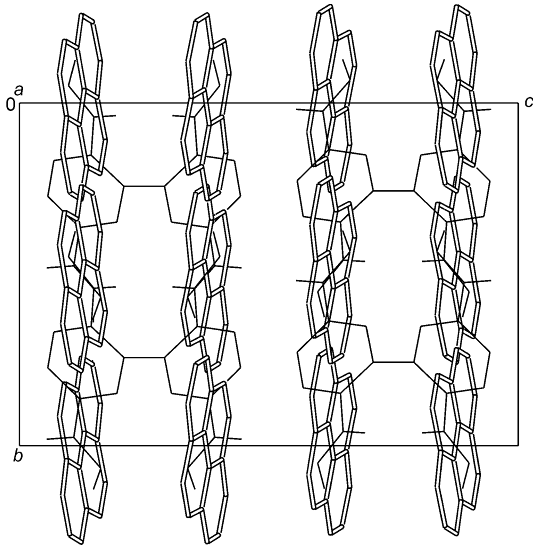


Figure 4. Stacking of individual grid layers from Fig. 2 along the *c* axis.

set up again from hydrogen bonded cyclotetrameric compartments. Except for the different geometry of the compartments (square versus rhomb), the 2D self-assembling pattern of the hexaacid **5** is analogous with that established for the tetraacid **3** (in the molecular complex) and the tetraamide **4**.

Within the individual cyclotetrameric compartments of the hexaacid **5** grid, the remaining (unpaired) carboxyls in the 2,2′-biphenyl positions are engaged in an independent system of hydrogen bonds, in which three molecules of water act as the hydrogen bond donors (Fig. 5). Two of the three water molecules simultaneously provide oxygen atoms (O1W, O2W) as the acceptors for the hydrogen bonds with the complementary 2,2′-positioned carboxyls in the neighboring layers (for detailed description of hydrogen bonds see Table 1).

2.3. Genealogical tree of the biphenyl self-assembly

2.3.1. The case of terephthalic Siamese twins. 2,2′,5,5′-Tetracarboxy- and tetracarbamoyl-substituted biphenyls **3** and **4** may be viewed upon as the Siamese twins from the terephthalic family. Both terephthalic acid[14,15] and the terephthaloyl diamide[16] are known to self-assemble with the formation of straight-chained ribbons organized via double hydrogen bonds (Scheme 3A). As we have now found, the Siamese twins, tectons **3** and **4**, replicate the same self-assembling motif in two criss-crossing chains (Scheme 3B), connecting separately the substituents in the upper and lower phenyl rings. An infinite 2D rhombic grid thus results, subdued to the dihedral angle between the planes of the twinned phenyl rings.

2.3.2. Comparison with the isophthalic Siamese twins. The corresponding positionally isomeric 2,2′,6,6′-tetrasubstituted biphenyl tectons **1** and **2**, which we have investigated earlier,[4–7] may be viewed as the Siamese twins from the related isophthalic family. Both isophthalic acid as well as isophthaloyl diamide[17] self-assemble via double hydrogen bonds with the formation of infinite zig-zag ribbon chains (Scheme 3C). The isophthalic Siamese twins replicate this self-assembling motif in two orthogonal chains. In contrast to the terephthalic twin tectons **3** and **4** which are chained in the upper–upper, lower–lower phenyl fashion, the corresponding isophthalic twins **1** and **2** exploit the alternate upper–lower, lower–upper phenyl bonding mode (Scheme 3D). An infinite zig-zag shaped grid thus results, which is almost orthogonal due to the enhanced repulsion between the four proximal 2,2′,6,6′-substituents at the twinned phenyls.

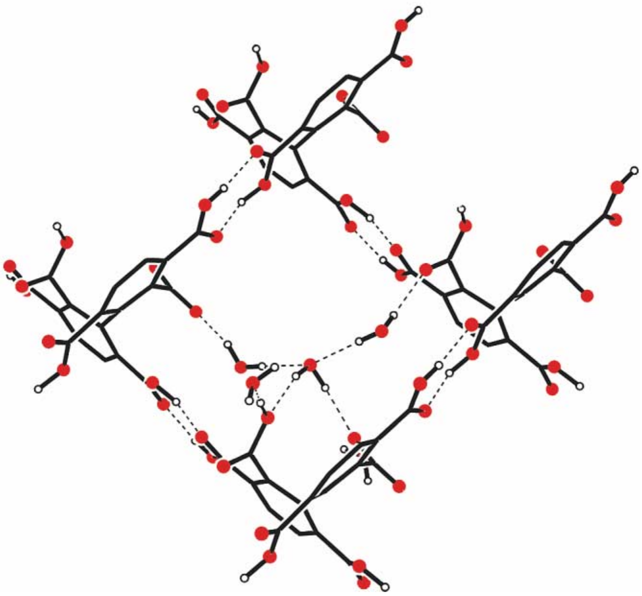


Figure 5. Segment of an infinite grid layer in the crystal of hexaacid (*S*)-**5** formed by intermolecular double hydrogen bonds. The unpaired carboxyls participate in an independent hydrogen-bonded network with molecules of water. Oxygen atoms are depicted as red circles.

2.3.3. The self-assembling dichotomy of 2,2′,3,3′,6,6′-hexasubstituted biphenyl tectons. In the hexaacid **5** participation of four of the six substituents in intermolecular (carboxyl–carboxyl) hydrogen bonds may give rise to two alternative 2D grid layers. Either 3,3′,6,6′- or 2,2′,6,6′-substituents may be involved. Out of the two scenarios, mimicking the self-assembling behavior either of the terephthalic or of the isophthalic Siamese twins (Scheme 3B and D, respectively), the former wins in the investigated crystal packing (Fig. 5).

2.4. Chirality in the self-assembly

In the 2,2′,5,5′-tetrasubstituted tectons **3** and **4**, the 2,2′-substituents oppose planarization of the biphenyl framework and the non-planar molecules are axially chiral (C_2 symmetry). The interconversion barrier imposed by the 2,2′-carboxy or 2,2′-carboxamide substituents along the biphenyl axis is however low and does not allow a customary separation of the individual rotamers (enantiomers).

Nonetheless, in the crystal of the tetracarboxamide **4**, the individual 2D layers are set up from enantiomerically uniform tectons. The cyclotetrameric rhombic compartments which are intrinsically chiral (C_1 symmetry) are accordingly homochiral within the individual layers. Layers set up from tectons of opposite chirality alternate in the crystal; the enantiomeric separation occurs on the level of individual layers.

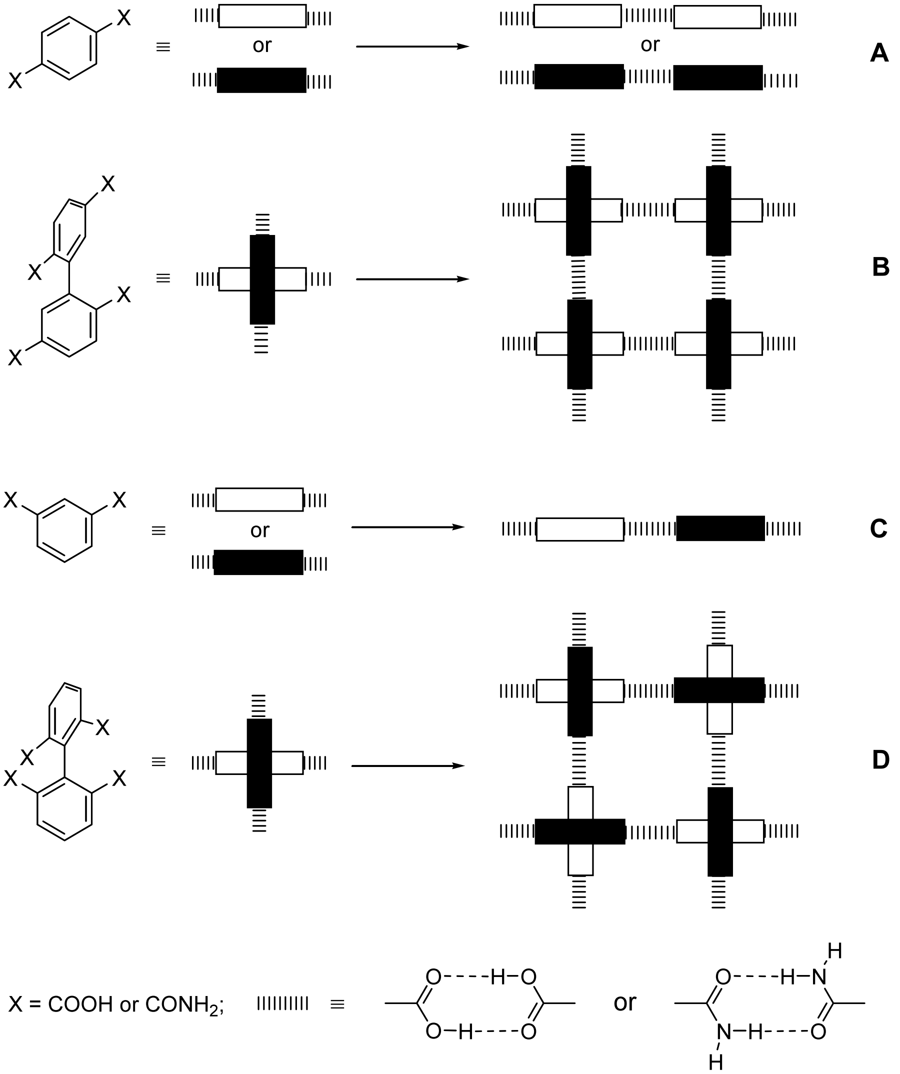
A similar situation exists in the crystal of the molecular complex of the tetracarboxylic acid **3** with 2,7-diazapyrene. Here, however, triads of homochiral layers (cf. Fig. 3 and Section 2.2.3) alternate (in place of the single homochiral layers) with the corresponding subunits of opposite chirality.

In the self-assembly of the hexaacid (*S*)-**5**, the problem of chirality is simplified by the enantiomeric uniformity of the employed tecton. All subunits in the crystal are accordingly enantiomerically uniform (homochiral).

3. Conclusions

Self-assembly of two biphenyl-2,2′,5,5′-tetrasubstituted tectons, **3** and **4**, has been subjected to crystallographic scrutiny. All four carboxyl or carbamoyl substituents in both tectons participate in the intermolecular hydrogen bonded network. Upper phenyl groups in the neighboring tectons are chained, in one direction, via the hydrogen-bonded substituents placed alternately in 2- and 5-positions, while the complementary 2′,5′-substituents at the lower phenyl groups organize a separate chain in another direction. Combination of the two chains leads to an infinite 2D rhombic grid layer, which is made up from cyclotetrameric compartments.

An analogous self-assembling pattern has been established for the higher 2,2′,3,3′,6,6′-hexasubstituted biphenyl homologue **5**, which selectively exploits the 3,3′,6,6′-substituents under formation of the infinite 2D rhombic grid.



Scheme 3. Comparison of the self-assembling patterns established for simple versus twinned terephthalic and isophthalic tectons. Black and white colors distinguish the relative position ('upper' or 'lower') of the individual molecular segments in the self-assembly.

Elements of chirality emerge in the self-assembly. Both the tetrasubstituted tectons **3** and **4** are axially chiral, but the low interconversion barrier does not allow enantiomeric separation. In the crystal, nevertheless, the individual 2D layers are built up from homochiral cyclotetrameric compartments (C_1 symmetry) which are set up from enantiomerically uniform tectons. Layers self-assembled from tectons of opposite chirality alternate in the crystal; enantiomeric separation thus occurs on the level of individual layers.

The homologous hexaacid (*S*)-**5** represents a stable enantiomer. All subunits in the investigated crystal are accordingly homochiral.

4. Experimental

Melting points were determined on a Kofler apparatus and are uncorrected. ^{1}H NMR spectra were measured on a Varian Unity XL-200 spectrometer (200 MHz, FT mode). Mass spectra were recorded on a ZAB-EQ (VG-Analytical) instrument. Thioglycerol-glycerol and 2-hydroxyethyl disulfide matrices were used for the FAB technique.

4.1. Synthesis

4.1.1. 1,1′-Biphenyl-2,2′,5,5′-tetracarboxylic acid, 3. Potassium permanganate (37.2 g; 236 mmol) was dissolved in hot water (195 ml) and added dropwise (90 min) to a boiling solution of 2,2′,5,5′-tetramethyl-1,1′-biphenyl[8] (3.70 g; 17.6 mmol) in pyridine (35 ml). The reaction mixture was kept under reflux for another 90 min, cooled down and the dissolved potassium salt of the product was separated from the manganese oxide by filtration. The precipitate was extracted with 0.3% aqueous solution of potassium hydroxide (2×100 ml) and the combined extracts were concentrated (100 ml) and acidified (6 M HCl) to pH 1. The deposited product was separated by filtration, washed with water and methanol and dried at 140°C; mp 300°C. Yield 5.35 g; 92%. ^{1}H NMR (DMSO-d_6) δ 7.68 (s, 2H); 8.00 (m, 4H); 12.8–13.6 (bs, 4H). Anal. calcd for $C_{16}H_{10}O_8$: C, 58.19; H, 3.05. Found C, 58.24; H, 3.24%.

4.1.2. 1:2 Complex of tetraacid 3 with 2,7-diazapyrene. 2,7-Diazapyrene[12] (100 mg; 0.49 mmol) and the tetraacid **3** (80 mg; 0.242 mmol) were dissolved in boiling methanol, the mixture was taken to dryness, washed with hot methanol (50 ml) and dried in vacuo. Yield 107 mg (59%), mp >350°C. ^{1}H NMR (DMSO-d_6) δ 7.69 (s, 2H); 8.00 (s, 2H); 8.39 (s, 8H); 9.61 (s, 8H); 13.0–13.5 (brs, 4H). Anal. calcd for $C_{44}H_{26}N_4O_8$: C, 71.54; H, 3.55; N, 7.58. Found C, 71.04; H, 3.70; N, 7.40%.

4.1.3. 1,1′-Biphenyl-2,2′,5,5′-tetracarboxamide, 4. Tetraacid **3** (200 mg; 0.606 mmol) was treated with thionyl chloride (5 ml) and dimethylformamide (one drop) under reflux (3 h), then cooled. The cooled mixture was taken to dryness on aspirator and the remaining thionyl chloride was removed by co-distillation with toluene (2×5 ml). The residue was dissolved in dioxane (10 ml) and the solution was added dropwise to conc. ammonium hydroxide (10 ml). The reaction mixture was taken to dryness after stirring for 2 h at room temperature and the crude product was crystallized from aqueous ethanol and recrystallized from water, mp 315–317°C. Yield 149 mg (75%). ^{1}H NMR (DMSO-d_6) δ 7.45 (brs, 2H); 7.47 (brs, 2H); 7.58–7.62 (m, 4H); 7.93 (dd, $J=8.0$ Hz and 1.6 Hz, 2H); 8.07 (brs, 4H). Anal. calcd for $C_{16}H_{14}N_4O_4{\cdot}2H_2O$: C, 53.04; H, 5.01; N, 15.46. Found C, 53.18; H, 4.99; N, 15.20%.

4.1.4. (*RS*)-3,3′,6,6′-Tetramethyl-1,1′-biphenyl-2,2′-dicarboxylic acid, (*RS*)-7. The diacid was obtained according to Gronowitz and Hansen,[10] mp 243.5–245.5°C (reported[10] mp 290–306°C (dec.)). ^{1}H NMR (DMSO-d_6) δ 1.86 (s, 6H); 2.28 (s, 6H); 7.21 and 7.13 (dd, $J=7.8$ Hz and 7.8 Hz, 4H). MS(FAB): 299 $(M+H)^+$.

4.1.5. (*S*)-3,3′,6,6′-Tetramethyl-1,1′-biphenyl-2,2′-dicarboxylic acid, (*S*)-7. Obtained according to Gronowitz and Skramstad[9] by resolution of the racemic acid via the quinine salt. The acid melted at 270–270.5°C and had $[\alpha]_D^{20}$ +84.6 (*c* 0.3; 0.1 M NaOH), in accord with the published data[9] (mp 265–270°C; $[\alpha]_D^{20}$ +80 (*c* 0.27; 0.1 M NaOH)). ^{1}H NMR spectrum was identical with that of the racemate.

4.1.6. (*S*)-1,1′-Biphenyl-2,2′,3,3′,6,6′-hexacarboxylic acid, (*S*)-5. A mixture of the diacid (*S*)-**7** (238 mg; 0.82 mmol), aqueous solution of KOH (130 mg in 10 ml of water) and potassium permanganate (2.9 g) was vigorously stirred at 85°C for 2 h. Excess of the permanganate was destroyed with 40% aqueous formaldehyde, the mixture was diluted with water (40 ml), filtered while hot, and the residue on the filter was thoroughly washed with hot water. The filtrate was mixed with Dowex 50X8 (evolution of gas) and then passed through a column of the same ion-exchanger. The filtrate was concentrated in vacuo and the residue crystallized from a very small amount of water; yield 290 mg (84%). Mp 184–186°C (dec.), $[\alpha]_D^{20}$ −127.9 (*c* 0.4; 0.1 M NaOH). ^{1}H NMR (DMSO-d_6) δ 8.03 and 7.84 (dd, $J=8.2$ and 8.2 Hz; 4H). An analytical sample was dried for 2 h in vacuo. Anal. calcd for $C_{18}H_{10}O_{12}{\cdot}1/2H_2O$: C, 50.60; H, 2.59. Found C, 50.31; H, 2.64%.

4.2. X-Ray diffraction analysis

Single crystals of the investigated tectons **4** and **5** were grown from their aqueous solutions by slow cooling. The molecular complex of the tecton **3** with 2,7-diazapyrene was crystallized from 30% aqueous dimethylformamide.

X-Ray data were collected on a Nonius KappaCCD diffractometer, MoK$_\alpha$ radiation ($\lambda=0.71073$ Å, graphite monochromator) at 150(2) K. The structures were solved by direct methods (SIR92[18]), full-matrix

Table 2. Crystallographic data

Compound	**4**	**3**·(diazapyrene)$_2$	**5**
Formula	$C_{16}H_{14}N_4O_4$	$C_{16}H_{10}O_8·2C_{14}H_8N_2$	$C_{18}H_{10}O_{12}·3H_2O$
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Aba*2	*C*2/*c*	*C*222$_1$
a (Å)	10.2830(2)	20.7880(7)	13.4410(2)
b (Å)	18.2590(5)	10.7060(4)	13.6780(2)
c (Å)	7.5180(3)	17.7470(7)	19.8730(3)
β (°)		119.962(2)	
Z	4	4	8
V (Å^3)	1411.56(7)	3421.9(2)	3653.57(9)
D_{calcd} (g cm^{-3})	1.535	1.434	1.717
Crystal dimensions (mm)	0.18 × 0.17 × 0.1	0.5 × 0.5 × 0.12	0.25 × 0.25 × 0.22
Appearance	Colourless prism	Yellow plate	Colourless prism
μ (mm^{-1})	0.114	0.101	0.154
h range	−13, 13	−26, 26	−17, 17
k range	−23, 23	−13, 13	−17, 17
l range	−9, 9	−22, 19	−25, 25
Reflections measured	12234	16697	29256
-Independent (R_{int})	1557 (0.033)	3710 (0.033)	4190 (0.031)
-Observed [$I > 2\sigma(I)$]	1440	3003	3931
Parameters refined	126	261	347
S	1.060	1.073	1.064
R	0.0320	0.0615	0.032
wR	0.0840	0.1727	0.084
$\Delta\rho_{\max}$; $\Delta\rho_{\min}$ (e Å^{-3})	0.185; −0.170	0.581; −0.396	0.260, −0.223

least-squares refinements on F^2 were carried out using the program SHELXL97.[19] All non-hydrogen atoms were refined anisotropically and converged ($(\Delta/\sigma)_{\max} = 0.002$). The positions of hydrogen atoms bonded to oxygen or nitrogen were found on difference Fourier map and refined isotropically. Those in CH moieties were fixed into idealised positions (riding model) and assigned temperature factors $H_{\text{iso}}(H) = 1.2\ U_{\text{eq}}$ (pivot atom). Crystal data, measurement and refinement details are summarized in Table 2.

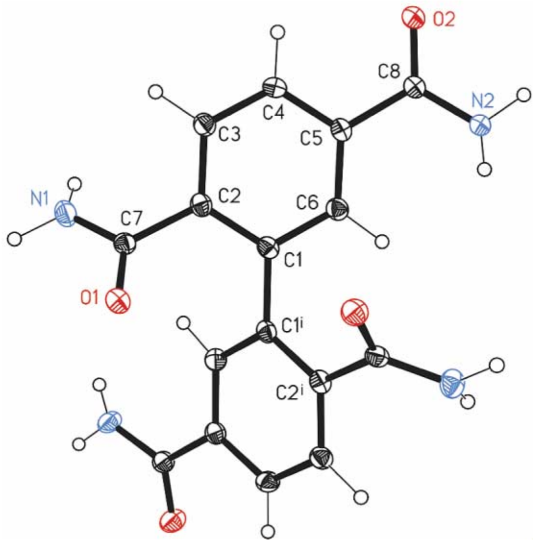


Figure 6. Perspective view of the molecule of tetraamide **4** with atom labeling. Ellipsoids for 50% probability, hydrogen atoms as spheres of arbitrary size.

Molecule of the tetraamide **4** consists of two symmetry-independent halves in the crystal, each half containing one phenyl group. The molecular structure is displayed in Fig. 6.

Two independent molecules (A and B) occur in the investigated crystal of the hexaacid **5**, differing each from the other only slightly in conformation. One molecule (A) is visualized in Fig. 7. In addition to the molecules of the hexaacid **5**, the crystal contains four

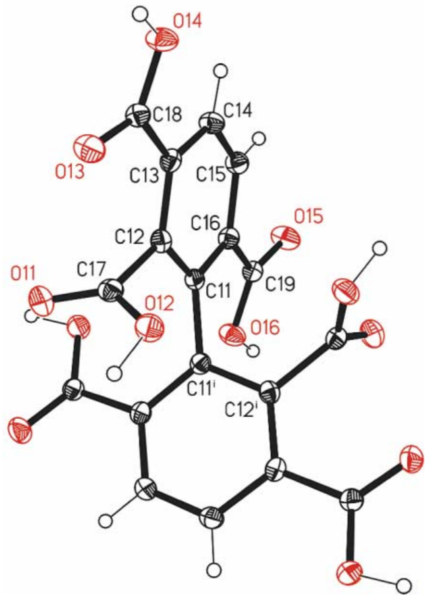


Figure 7. Perspective view of one molecule (A) of hexaacid (*S*)-**5** with atom labeling. Ellipsoids for 50% probability, hydrogen atoms as spheres of arbitrary size.

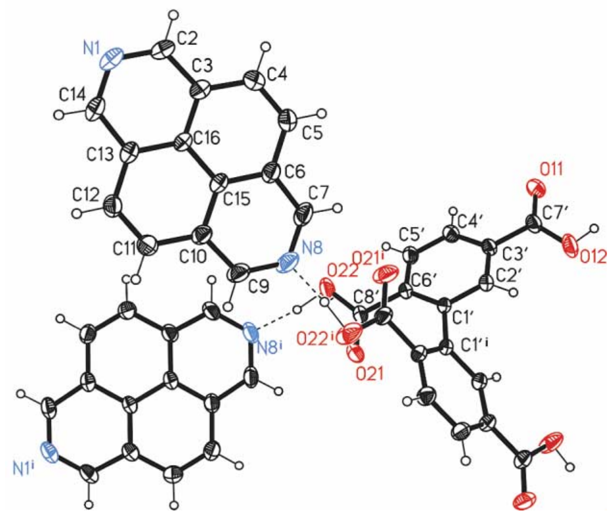


Figure 8. Perspective view of the molecular 2:1 complex of 2,7-diazapyrene **8** (left) and tetraacid **3** (right) with atom labeling. Ellipsoids for 50% probability, hydrogen atoms as spheres of arbitrary size.

different types of water molecules distinguished by hydrogen bonding; cf. Section 2.2.4 and Fig. 5.

The symmetry-independent part of the molecular complex **3**·(2,7-diazapyrene)$_2$ consists of one phenyl half of the molecule of the tetraacid **3** and one full molecule of the diazapyrene base. The established structure is depicted in Fig. 8.

Parameters of hydrogen bonds in the crystals of the presented tectons are collected in Table 1.

All crystallographic data for the investigated structures **3**–**5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers: **4**—CCDC 195740, **3**·(diazapyrene)$_2$—CCDC 195741, **5**—CCDC 195742. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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