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Crystal structure of 1,1'-biphenyl-2,2',3,3'-tetracarboxylic and 1,1'-biphenyl-2,2',3,3',5,5',6,6'-octacarboxylic acids: solid-state chiralization and dissociation

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Abstract—X-ray diffraction analysis revealed unexpected stereochemical features accompanying crystal self-assembly of the two title oligocarboxylic acids.

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1. Introduction

Currently we are interested in the self-assembly of symmetrical 1,1'-biphenyl oligocarboxylic acids. As part of a more extensive study¹ on porous architectures, we have recently investigated the self-assembling behavior of two isomeric tetracarboxylic acids, **1** and **2**, which may be viewed upon as the Siamese twins belonging, respectively, to the terephthalic and isophthalic families. Self-assembling patterns of the twin tectons have been correlated with those established earlier for the parent benzene dicarboxylic acids. Both terephthalic as well as isophthalic tectons tend to form 1D ribbons organized

via intermolecular double hydrogen bonds (Scheme 1a and b).

The Siamese twins 1 and 2 replicate this self-assembling motif in two divergent directions giving rise to 2D infinite grids set up from open cyclotetrameric compartments.²

The isomeric Siamese twin 3 awaits analogous scrutiny. The parent phthalic acid tecton is known³ to self-assemble via intermolecular double hydrogen bonds under the formation of zig-zag 1D ribbons (Scheme 1c). The twin tecton 3, on replication with this motif in two divergent



Scheme 1.

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(orthogonal) directions, would tend to yield nonporous corrugated 2D layers or infinite helices.

More interesting, in this context, is the homologous octacarboxy-substituted twin tecton **4**, which on replication of the phthalic acid self-assembling motif in four orthogonal directions might provide access to infinite anisotropic open-pore 3D structures set up from coaxial helices; we have recently discovered such patterns in the cyclodextrin series.^{1f,g}

We herein report the X-ray structure of the two twin tectors **3** and **4**.



2. Results and discussion

2.1. Synthesis

1,1'-Biphenyl-2,2',3,3'-tetracarboxylic acid **3** was prepared by Ullmann coupling of dimethyl 3-iodophthalate⁴ by modification of a known procedure.⁵ The corresponding octacarboxylic acid **4** was prepared analogously (Scheme 2), starting from 3-bromo-1,2,4,5-benzenetetracarboxylic acid⁶ **5** easily accessible by permanganate oxidation of bromodurene.

2.2. X-ray crystallographic analysis

2.2.1. Molecular structure of 1,1'-biphenyl-2,2',3,3'-tetracarboxylic acid 3. The investigated crystal of tecton 3 corresponds to the monohydrate. The molecular structure (Fig. 1) exhibits nearly orthogonal orientation of the coupled phenyl groups (dihedral angle 88.69°). Phenyl groups in the individual molecules are almost ideally planar, the observed displacements of the individual ring carbons being close to 0.013 Å (at C3) or less. Although more significant displacements occur at the pivotal carbons of the adjacent carboxyls, as evident from the pertinent torsion angles C7–C2–C3–C8 (-8.78°) and C7'– C2'–C3'–C8' (-4.91°), the observed values are markedly smaller than those reported by Ermer⁷ for the parent phthalic acid (20.3°).



Scheme 2. Reagents and conditions: (i) Cu, $240 \,^{\circ}$ C; (ii) NaOH, H₂O, EtOH; (iii) HCl; (iv) KMnO₄, Py, $110 \,^{\circ}$ C; (v) SOCl₂; (vi) MeOH; (vii) Cu, DMF, $150 \,^{\circ}$ C.



Figure 1. Molecular structure of tetraacid 3 (only one enantiomer is shown). Ellipsoids for 50% probability.

Planes of both carboxyl groups placed in the inner (2,2'-) positions of the twin molecule **3** are almost perpendicular with respect to the adjacent phenyl rings (dihedral angle 75.36° and 82.86°, respectively). Whereas planes of the outer carboxyls (3,3'-) attached to C3 and C3' are turned out much less, the corresponding dihedral angles were only 15.08° and 9.32°, respectively. Also these findings differ markedly from the arrangement found⁷ in the parent phthalic acid, which exhibits mild, and comparable, deviation of both the neighboring carboxyls from the plane of the benzene ring, the corresponding dihedral angles being 30.5° and 32.0°, respectively.

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Finally, the intramolecular single hydrogen bond between the inner carboxyls distinguishes the twin molecule 3 (Fig. 1) from the parent phthalic acid. This might suggest that the arrangement of carboxyl groups in the two compared molecules depends on the absence or presence of the intramolecular hydrogen bond. A caveat against such a conclusion provides however the known crystal structure of benzene-1,2,3-tricarboxylic,⁸ benzene-1,2,4-tricarboxylic,⁹ and benzene-1,2,4,5-tetra-carboxylic¹⁰ acids. Notably, in all the three phthalic acid homologues, which do not exhibit intramolecular hydrogen bonds, values of the torsion angles about carboxylic groups closely resemble the pattern found in the biphthalic acid 3 rather than that in the parent phthalic acid. According to Ermer,⁷ the distinct geometry in phthalic acid can be rationalized in terms of specific packing (intermolecular) forces accompanying the crystal self-assembly.

2.2.2. Chiral aspects of the crystal self-assembly of the tecton 3. Orthogonal arrangement of the coupled phenyls accounts for the axial chirality of tecton 3 in the investigated crystal. Both enantiomers with otherwise identical geometries are present in the unit cell and are held together by hydrogen bonds mediated by water molecules (Fig. 2).

Homochiral tectons are organized in stacks along axis b via direct single hydrogen bonds connecting the carboxyl at position 3 with the corresponding group placed at position 2 in the neighboring molecule. Alternation of the homochiral stacks with the antipode stacks along axis c gives rise to zones of high and low polarity, in which the water-mediated hydrogen bonds between carboxyls or the aromatic moieties, respectively, prevail. The resulting architecture thus differs fundamentally from the prediction based on the helical elaboration of the phthalic acid motif (Scheme 1c).

2.2.3. Molecular structure of 1,1'-biphenyl-2,2',3,3', 5,5',6,6'-octacarboxylic acid 4. The investigated crystal corresponds to the tetrahydrate. The molecular structure of the twin tecton 4 (Fig. 3) resembles in most respects that described above for the tetracarboxysubstituted twin 3. Thus, the coupled phenyl groups in 4 are nearly planar and mutually orthogonal, with the dihedral angle between the planes of the adjacent aromatic rings being 83.18°. The pivotal carbons of all the individual carboxyls are displaced only mildly from the plane of the neighboring aromatic ring, the pertinent values of the torsion angles C17-C12-C13-C8 (3.94°), C19-C15-C16-C110 (-12.42°), C27-C22-C23-C28 (7.98°), and C29–C25–C26–C210 (-12.09°) closely approaching those established for tetraacid 3.

Also the dihedral angles between the planes of the individual carboxyl groups and the corresponding aromatic rings in the tecton **4** follow an analogous pattern as found for the lower homologue **3**, the inner 2,2',6,6'-carboxyls being much more turned out ($63.92-79.50^{\circ}$) than those in the outer 3,3',5,5'-positions ($10-16^{\circ}$). Furthermore, the intramolecular hydrogen bond involving the



Figure 2. Perspective view on stacking of molecules of tetraacid 3 and water. Scheme of stacks differing in chirality below.

inner 2,2'-carboxyls can be found in both twin tectons 3 and 4.

A striking difference exists, however, concerning the nature of this particular bond in the two compared molecules. While a simple uncharged intramolecular hydrogen bond results in tetraacid **3**, the corresponding hydrogen bonding in octaacid **4** is accompanied by the dissociation of the participating acceptor carboxyl group in the 2-position. This is a surprising observation, since carboxyl dissociation is very uncommon in the crystallography of carboxylic acids.[†] Two water molecules (from total four symmetrically independent ones) bind the liberated proton in the complex $H_5O_2^+$ ion (Fig. 4) by a strong symmetrical hydrogen bond (the distances of hydrogen H1a to the both acceptor atoms O1w and O2w are identical within the accuracy limits).

2.2.4. Chiral aspects of the crystal self-assembly of the tecton 4. In contrast to the tetra-substituted twin tecton 3, the orthogonal arrangement of the coupled phenyl rings, alone, cannot promote axial chirality in the octa-substituted homologue 4, owing to the persisting planes of symmetry. In the investigated crystal of tecton 4, however, the introduction of an intramolecular hydrogen bond (along with the accompanying deprotonization) chiralizes the intrinsically achiral molecule.

[†]We are aware of only one, a peculiar precedent concerning trifluoroacetic acid. For the tetrahydrate an ionic structure $(H_5O_2)[(CF_3-COO)_2H]$ · $6H_2O$, which is analogous to the present case, was confirmed by X-ray analysis, whereas the perdeuterated tetrahydrate was found to be molecular (non-ionic); Ref. 11.



Figure 3. Molecular structure of octaacid 4 (only one enantiomer is shown). Ellipsoids for 50% probability.



Figure 4. Hydrogen bonding of the complex $H_5O_2^+$ ion in the crystal of the tetrahydrate of octaacid 4.

Both enantiomers can be discerned in the elementary cell containing eight molecules of tecton **4** (four enantiomeric pairs) accompanied by 32 molecules of water (Fig. 5).

Homochiral molecules are stacked along the *b* and *c* axis, while along the *a* axis, chirality alternates. The neighboring tectons are linked by single intermolecular hydrogen bonds between the proximate carboxyls, each molecule being interconnected with six surrounding counterparts. The direct hydrogen bonds between proximal carboxyls are complemented by indirect ones involving water molecules. Also the complex ion $H_5O_2^+$ arising from the dissociation of the carboxylic group (Fig. 4) participates in the 3D hydrogen bonded network, which in turn results in very dense crystal packing $(d_c = 1.7227 \,\mathrm{g \, cm^{-3}})$. In this way, the crystal architecture differs fundamentally from the prediction based of the helical elaboration of the phthalic acid motif (Scheme



Figure 5. Perspective view on the unit cell in the crystal of the tetrahydrate of octaacid 4. Scheme of chirality of individual molecules of 4 below.

1c), as similarly observed above for the lower homologue **3**.

2.2.5. Concluding remarks on the predictability of the crystal packing of the investigated twin tectons. The observed discord between the actual crystal structure of the twin tectons 3 and 4 and the prediction based on a multidirectional replication of the self-assembling motif outlined in Scheme 1c contrasts with the successful correlations we attained previously with the akin tectons 1 and 2 on basis of the corresponding Scheme 1a and b. Low stability of the key motif from Scheme 1c may be responsible for this failure. As already noted by Ermer in his analysis,⁷ expression of this motif in the crystal of phthalic acid imposes a severe strain in the structure of the parent molecule. Less strained alternatives, which avoid the geometrically demanding double hydrogen bonds can accordingly prevail in crystal packing of the twins 3 and 4.

3. Experimental

Melting points were determined on a Kofler apparatus and are uncorrected. ¹H NMR spectra were measured on a Varian Unity XL-200 and a Bruker 400 spectrometer (200 and 400 MHz, respectively, FT mode) in deuteriochloroform or in hexadeuteriodimethyl sulfoxide. Mass spectra were recorded on a ZAB-EQ (VG-Analytical) instrument. Thioglycerol–glycerol and 2-hydroxyethyl disulfide matrices were used for the FAB technique.

3.1. Synthesis

3.1.1.1,1'-Biphenyl-2,2',3,3'-tetracarboxylic acid 3. This tetraacid was prepared⁵ by saponification of the tetramethyl ester, which was obtained by Ullmann coupling

of dimethyl 3-iodophthalate.⁴ Yield 76%, mp 274–275°C, lit.⁵ 265°C. ¹H NMR (DMSO-*d*₆): δ 13.0 (s, 4H); 7.87 (dd, J = 7.7 and 1.3Hz, 2H); 7.53 (t, J = 7.7Hz, 2H); 7.44 (dd, J = 7.7 and 1.3Hz, 2H). Anal. Calcd for C₁₆H₁₀O₈·H₂O: C, 55.18; H; 3.47. Found C, 54.99; H, 3.36. The monocrystal (monohydrate) for X-ray analysis was obtained by slow crystallization from water.

3.1.2. 3-Bromo-1,2,4,5-benzenetetracarboxylic acid 5. To a stirred solution of 3-bromo-1,2,4,5-tetramethyl-benzene (25g; 117 mmol, prepared in 77% yield by bromination¹² of 1,2,4,5-tetramethylbenzene) in pyridine (200 mL) was added a hot solution of potassium permanganate (248g; 1.57 mol) in water (1330 mL) at 115 °C for 8h. After an additional 5h heating, the deposited manganese dioxide was filtered off, and washed with 0.3% aqueous KOH $(2 \times 300 \text{ mL})$. The combined filtrates were collected and concentrated to 500 mL. After acidification with concd HCl to pH1, the precipitated tetraacid was filtered off, washed with water, acetone, and dried. Yield 31.4g (80%), mp >350°C, lit.⁶ 240–265°C. ¹H NMR ($D_2O/$ NaOD): δ 8.60 (s, 1H). Anal. Calcd for C₁₀H₅BrO₈ (333.05): C, 36.06; H, 1.51; Br, 23.99. Found: C, 35.96; H, 1.58; Br, 23.51.

3.1.3. Tetramethyl 3-bromo-1,2,4,5-benzenetetra-carboxylate 6. A mixture of tetraacid 5 (3.33 g; 10.0 mmol), thionyl chloride (40 mL; 550 mmol), and a drop of DMF was heated at reflux for 8 h. The excess of thionyl chloride was then removed in vacuo and the residue heated to reflux with methanol (50 mL) for 1 h. After filtration, the solvent was removed, and the crude tetraester crystallized successively from methanol and toluene/petro-leum ether. Yield 73%, mp 135°C. ¹H NMR(CDCl₃): δ 8.65 (s, 1H); 4.01 (s, 6H); 3,96 (s, 6H). FAB MS: *m*/*z* 389/391 [M+H]⁺; 357/359 [M+H–CH₃OH]⁺. Anal. Calcd for C₁₄H₁₃O₈Br (389.05): C, 43.21; H, 3.37; Br, 20.53. Found C, 43.40; H, 3.42; Br, 20.48.

3.1.4. Octamethyl 1,1'-biphenyl-2,2',3,3',5,5',6,6'-octacarboxylate 7. A mixture of bromotetraester 6 (2.5g; 6.42 mmol) and activated¹³ copper bronze (2.5 g; 39.3 mmol) in DMF (7.5 mL) was heated 3.5 h at 150 °C. After dilution with water (50 mL), the mixture was extracted with ethyl acetate $(3 \times 50 \text{ mL})$. The combined extracts were washed with water (20mL), dried over Na₂SO₄, and evaporated. The residue was subjected to column chromatography (silica gel 250g; toluene/ethyl acetate/ethanol 90:8:2 to 90:8:4). After separation of the side product (tetramethyl 1,2,4,5-benzenetetracarboxylate; 634mg; 2.04mmol; 32%), the desired octaester was eluted (1.107g; 1.79mmol; 56%). Mp after crystallization from toluene 174–176°C. ¹H NMR (200 MHz; CDCl₃): δ 8.41 (s, 2H); 3.91 (s, 12 H); 3.60 (s, 12 H). FAB MS: m/z 619 $[M+H]^+$; 587 $[M+H-CH_3OH]^+$. Anal. Calcd for $C_{28}H_{26}O_{16}$ (618.12): C, 54.38; H, 4.24. Found C, 54.36; H, 4.27.

3.1.5. 1,1'-Biphenyl-2,2',3,3',5,5',6,6'-octacarboxylic acid 4. A mixture of octaester 7 (500 mg; 0.808 mmol) and aqueous 2.6 M NaOH (5 mL) was heated at reflux for 8 h. After acidification with concd HCl to pH 1, the octaacid was allowed to crystallize in a refrigerator overnight, filtered off, washed with a small amount of water, and dried in vacuo at 120 °C. Yield 338 mg (89%), mp >350 °C. FAB MS: m/z 573 [M+3Na]⁺; 551 [M+2Na]⁺; 529 [M+Na]⁺; 507 [M+H]⁺. HR FAB MS: m/z for C₂₀H₁₀O₁₆+H calcd 507.0047; found 507.0031. ¹H NMR (DMSO- d_6): δ 13.30 (s, 8H); 8.13 (s, 2H). The monocrystal (tetrahydrate) for X-ray analysis was obtained by slow cooling of hot aqueous solution.

3.2. X-ray diffraction analysis

X-ray data were collected on a Nonius Kappa CCD diffractometer, MoK_{α} radiation ($\lambda = 0.71073$ Å, graphite monochromator) at 150(2) K. The structure was solved by direct methods (SIR92¹⁴), full-matrix least-squares refinements on F^2 were carried out using the program SHELXL97¹⁵. All nonhydrogen atoms were refined anisotropically and converged ((Δ/σ)_{max} = 0.003). The positions of the hydrogen atoms bonded to oxygen were found on a difference Fourier map and refined isotropically. Those in CH moieties were fixed into idealized positions (riding model) and assigned temperature factors H_{iso} (H) = 1.2 U_{eq} (pivot atom). Crystal data, measurement and refinement details are summarized in Table 1. Parameters of hydrogen bonds are collected in Table 2.

All crystallographic data for the investigated structures **3** and **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers: **3**-CCDC 250626, **4**-CCDC 250625. Copies of the data can be obtained, free of charge, on application

Table 1. Crystallographic data

Compound	3 ·H ₂ O	4 ·4H ₂ O
Formula	$C_{16}H_{12}O_{8}H_{2}O$	$C_{20}H_9O_{16}H_3O\cdot 3H_2O$
$M_{ m r}$	348.26	578.34
Crystal system	Triclinic	Monoclinic
Space group	P-1 (No. 2)	C2/c (No. 15)
<i>a</i> , Å	7.5640(4)	20.8270(10)
b, Å	9.1680(4)	12.9211(10)
<i>c</i> , Å	12.0240(7)	19.3320(10)
α, °	87.827(3)	
β, °	76.165(3)	121.007(2)
γ, °	66.436(2)	
Z	2	8
$V, Å^3$	740.56(7)	4459.0(4)
$D_{\rm c},{\rm gcm^{-3}}$	1.562	1.723
Crystal dimensions, mm	$0.25 \times 0.1 \times 0.025$	$0.4 \times 0.25 \times 0.075$
Appearance	Colorless bar	Colorless plate
μ , mm ⁻¹	0.131	0.160
h Range	-9, 9	-25, 25
k Range	-10, 11	-15, 15
<i>l</i> Range	-15, 15	-23, 19
Reflections measured	12,956	24,721
Independent (R_{int})	3333 (0.0310)	4294 (0.0378)
Observed $[I > 2\sigma(I)]$	2532	3474
Parameters refined	250	425
S	1.011	1.055
R	0.0460	0.0443
wR^2	0.1172	0.1206
$\Delta \rho_{\rm max}$; $\Delta \rho_{\rm min}$, eÅ ⁻³	0.460; -0.409	0.317; -0.350

Table 2.	Parameters	of hydrogen	bonds in the	investigated	crystals
					-

Compound	Specification		Distances (Å)		
	O–H···O	O–H	$H{\cdots}O$	00	$O{-}H{\cdots}O$
3 ·H ₂ O	O6–H60···O1	0.92(2)	1.82(3)	2.7150(17)	161(2)
	O4–H40· · · O5 ^{ai}	0.95(3)	1.73(3)	2.6759(18)	174(2)
	O2–H20···O1w	0.99(3)	1.69(3)	2.6310(17)	159(2)
	O8–H80· · · O1w ^{aii}	0.90(2)	1.85(3)	2.7103(18)	158(2)
	O1w–H1b· · · O1 ^{aiii}	0.91(4)	1.90(4)	2.797(2)	170(3)
	O1w−H1a· · ·O7 ^{aiv}	0.91(4)	2.13(4)	2.8703(17)	138(3)
	$O1w-H1a\cdots O3^{av}$	0.91(4)	2.46(4)	3.219(2)	141(3)
4 ·4H ₂ O	O1w–H1a···O2w	1.21(3)	1.21(3)	2.412(2)	176(3)
	$O1w-H1b\cdots O15^{bi}$	1.00(5)	2.15(5)	2.870(2)	128(4)
	O1w–H1b· · · O15 ^{bii}	1.00(7)	2.05(5)	2.816(2)	132(4)
	O1w-H1c···O23 ^{biii}	0.98(3)	1.67(3)	2.635(2)	166(3)
	O2w-H2a···O13 ^{biv}	0.98(4)	1.70(5)	2.665(2)	167(4)
	O2w−H2b···O22 ^{bii}	0.85(3)	1.88(3)	2.703(2)	162(3)
	$O3w-H3a$ ··· $O27^{bv}$	0.99(3)	1.79(3)	2.707(2)	153(3)
	O3w−H3b···O25 ^{bvi}	0.98(4)	1.88(4)	2.832(2)	165(4)
	O4w–H4a···O17	1.01(4)	1.81(4)	2.793(2)	163(3)
	O4w–H4b···O3w ^{bvii}	1.11(4)	1.74(4)	2.824(2)	164(3)
	O12–H12···O21	1.00(3)	1.52(3)	2.5109(19)	172(3)
	O14–H14· · · O4w ^{bviii}	0.95(4)	1.58(4)	2.523(2)	173(3)
	$O28-H15\cdots O22^{bii}$	0.97(4)	1.63(4)	2.5823(19)	164(3)
	O16–H16· · ·O11 ^{bix}	0.90(3)	1.81(3)	2.7081(19)	175(3)
	$O16-H16\cdots O12^{bix}$	0.90(3)	2.52(3)	3.0460(19)	118(2)
	$O18-H18\cdots O11^{bv}$	0.90(3)	1.81(3)	2.7086(19)	171(3)
	$O24-H24\cdots O3w^{bx}$	0.96(3)	1.63(3)	2.582(2)	174(3)
	O26–H26···O21 ^{bxi}	0.93(4)	1.79(4)	2.693(2)	165(3)

Symmetry transformations used to generate equivalent atoms:

(ai): x, 1 + y, z; (aii): -x, -y, 1 - z; (aiii): -x, 1 - y, 1 - z; (aiv): -1 + x, 1 + y, z; (av): -1 + x, y, z; (bi): x, -y, -1/2 + z; (bii): 3/2 - x, -1/2 + y, 3/2 - z; (biii): 3/2 - x, 1/2 - y, 1 - z; (biv): -1/2 + x, -1/2 - y, -1/2 + z; (bv): 3/2 - x, 1/2 + y, 3/2 - z; (bvi): 1/2 + x, 1/2 - y, 1/2 + z; (bvii): -1/2 + x, -1/2 + y, z; (bviii): 1/2 + x, -1/2 + y, z; (bviiii): 1/2 + x, -1/2 + y, z;

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