

Unusual mixed solvent supramolecular crystal framework formed of a new tecton-like tetracarboxylic building block[†]

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A new tecton-like tetracarboxylic compound **1** featuring two isophthalic acid groups attached to both ends of a rigid 1,3-butadiyne spacer unit is synthesised using acetylene blocking/deblocking and coupling techniques. Crystallisation of **1** from DMSO-chloroform solution gives rise to the formation of an unusual mixed solvent crystalline framework structure **1a** containing DMSO and chloroform as secondary and tertiary components in 1:2:1 stoichiometric ratio. The X-ray crystal structure of **1a** shows interesting stacking mode and hydrogen-bonded, 3D network architecture with the two solvent species being involved in different behaviour pattern.

Keywords: tetracarboxylic acid; dimethyl sulphoxide; chloroform; crystalline complex; X-ray crystal structure

1. Introduction

Carboxylic acids featuring a well-defined shape have developed to a key position in the controlled assembly of supramolecular systems with a variety of uses in different branches of crystal engineering (1–3). This covers the carboxylic acids as hosts for crystalline inclusion formation (4) as well as their functional behaviour of a tecton (5), allowing the targeted formation of 2D and 3D hydrogen bond stabilised network structures (6, 7), although the carboxylic building blocks are brought differently into action in these particular fields. Although in the object of crystalline host–guest complexation the carboxylic groups are primarily intended for hydrogen bonding to the molecular guest species (8), they are used in the network construction for cyclic hydrogen-bonded pair formation (6, 7, 9–11). Moreover, rigid oligocarboxylic acid molecules are also very efficiently employed as coordinative linkers in the formation of open organic–inorganic hybrid frameworks (MOFs) (12, 13). This implies that for hydrogen-bonded guest inclusion, the carboxylic groups are endo in the attachment to the host molecule but at peripheral site in the tectones and linkers. With reference to the tectons, tetracarboxylic acids composed of two isophthalic acid groups connected at both ends of a linear spacer moiety, varying in the length, have been studied in their preference towards the formation of close packed, open parallel or

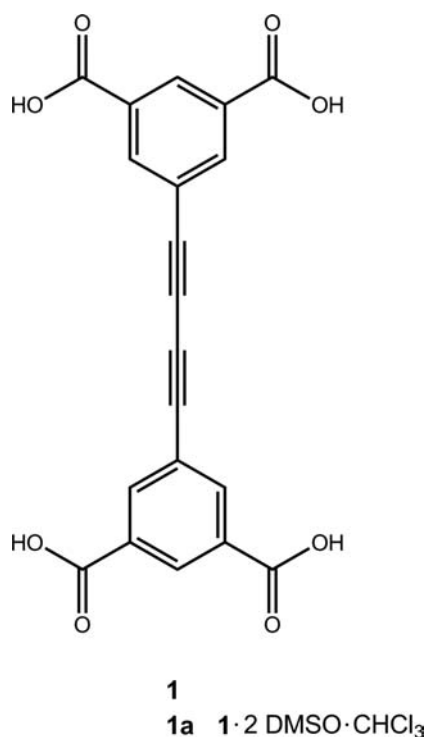
Kagomé networks (11, 14). In the case of biphenyl-3,3',5,5'-tetracarboxylic acid (two directly connected isophthalic acid groups), open parallel network formation is observed in the solid state structure, whereas the use of a very elongated 1,4-phenylene-bis(ethynylene) spacer unit between the isophthalic acid moieties produces a Kagomé assembly of the respective molecules adsorbed on highly oriented pyrolytic graphite, and the intermediate compound with a short ethynylene spacer results in the formation of a mixed pattern containing small areas of the two different motifs (14). Thus the length of the spacer unit in the tetracarboxylic molecules is shown to exert a distinct influence on the network structure to be formed.

Referring to the present compound **1** (Scheme 1), we describe the synthesis of a new member of this particular substance class of bisisophthalic acids featuring with the 1,3-butadiyne-1,4-diyl spacer unit, a molecule of medium length. Crystallisation of **1** from a solvent mixture of DMSO and chloroform yielded an interesting stacking mode and hydrogen-bonded, 3D mixed solvent containing network architecture of **1a** with the two solvent species being involved in different behaviour pattern, the structure of which is reported and discussed under the specific circumstances.

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Scheme 1. Chemical formulas of the compounds studied.

2. Results and discussion

2.1 Synthesis

Synthesis of title compound **1** was performed as specified in Scheme 2. This involves reaction of the starting compound dimethyl 5-iodoisophthalate (**2**) (15) with MEBYNOL using a Pd-catalysed Sonogashira coupling procedure (16, 17) to give the blocked acetylenic diester **3**. The 5-ethynylisophthalic acid (**4**) was prepared from **3** via removal of the blocking group with KOH in *n*-BuOH, yielding as an intermediate the dipotassium salt of **4**, which was converted into **4** by the reaction with hydrochloric acid. Sulphuric acid catalysed esterification of **4** with methanol gave the corresponding diester **5**. Alternatively, diester **5** could also be obtained in a selective single-step deblocking reaction from **3** using sodium hydride in toluene (18). Actually, compound **5** has already been described in the literature applying a similar synthetic route (19, 20), but being based on the rather costly TMS-acetylene instead of the cheaper MEBYNOL as the blocking reagent. Diester **5** was subjected to an Eglinton coupling reaction (21, 22) with copper(II) acetate in pyridine–methanol to produce the tetraester **6**. This ester was hydrolysed with LiOH in THF–H₂O followed by acidification with hydrochloric acid to yield tetracarboxylic acid **1**.

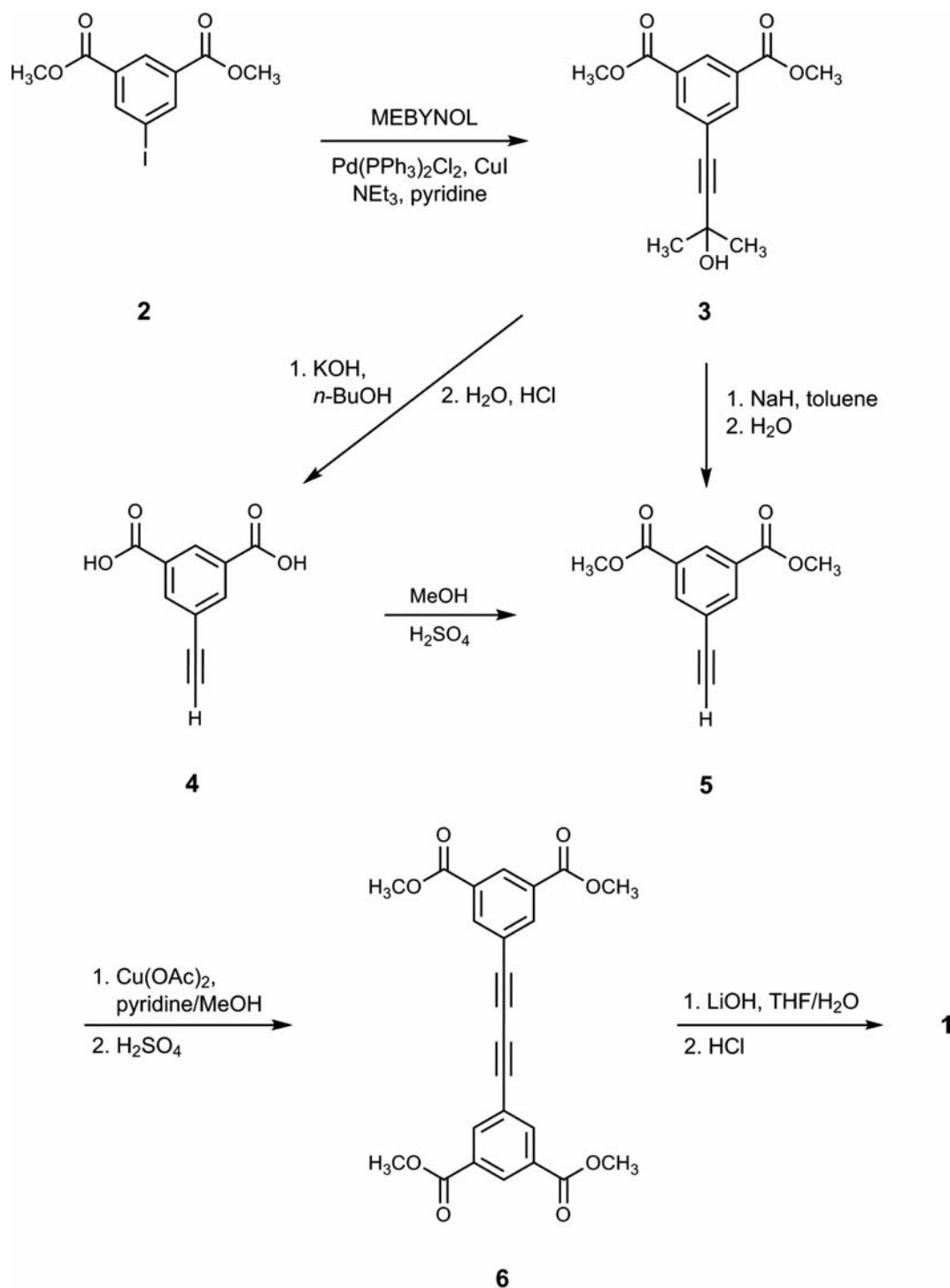
2.2 X-ray structural study

Crystallisation of tetracarboxylic acid **1** from a solvent mixture of dimethyl sulphoxide and chloroform yields a

ternary complex **1a** containing **1**, DMSO and chloroform in the stoichiometric ratio 1:2:1. Crystallographic data and selected refinement parameters of the structure are summarised in Table 1. Information regarding possible non-covalent interactions in the crystal structure is presented in Table 2. A perspective view of the molecular structure, including atom numbering scheme, is shown in Figure 1, whereas an illustration of the crystal packing is given in Figure 2. Figure 3 demonstrates the potential construction principle of the plain host lattice.

The crystal structure of **1a** has the monoclinic space group $P2_1/c$ with one host molecule, two molecules of DMSO and one molecule of CHCl₃ in the asymmetric cell unit (Figure 1). The bond lengths within the buta-1,3-diyne part of **1** are 1.432(2)/1.433(2) for C(sp²)–C(sp), 1.199(2)/1.201(2) for C≡C and 1.374(2) Å for the single C(sp)–C(sp) bond, and are similar to those found in 1,4-diphenylbutadiyne and its derivatives (23, 24). The high degree of molecular association in the crystal structure causes a slight bend of the host molecule along its diacetylene element (25), so that the dihedral angle between the planes of the aromatic rings is 11.5°. The carboxy groups are inclined at angles between 2.7(1) and 8.3(2)° with respect to the plane of the aromatic rings to which they are attached.

It is clear that assembly of the molecules via carboxylic pairing (9, 26) would result in a highly expanded and, thus, presumably too labile structure (27, 28). As a possible consequence of this, we did not succeed in growing a crystal of **1** in its solvent-free state. Instead, the distinctive donor/acceptor character of the crystal components induces a complicated network of non-covalent bonding between molecules. As depicted in Figure 2, all strong donor atoms of the tetracarboxylic acid are associated in the same fashion with DMSO molecules via O–H···O hydrogen bonds (29) [$d(\text{O} \cdots \text{O})$ 2.598(3)–2.651(3) Å], while a part of the acidic hydrogens of the DMSO molecules are coordinated to the carboxyl oxygens O(3), O(4) and O(7) of **1** or fulfil DMSO···DMSO interaction (30). Nevertheless, the donor–acceptor character of tetracarboxylic acid **1** requires the presence of a second solvent species having a complementary coordination behaviour compared with DMSO. This is realised by the chloroform molecule, more weakly interacting through C=O···H–C (31) and C=O···Cl–C contacts (32, 33) to different molecules of **1**. In more detail, the hydrogen atom of the chloroform molecule is connected to O(5) of **1** by a relatively strong C–H···O=C hydrogen bond [$d(\text{O} \cdots \text{H})$ 2.20 Å]. The observed angular parameters of the C=O···Cl–C contacts contributing to the chloroform coordination (C=O···Cl 85.6, 126.6°; C–Cl···O 158.2, 167.9°) agree well with the concept of the so-called ‘electrophil–nucleophil pairing’ (34), which considers the oxygen of C=O as an ‘electrophil’ approaching the halogen of C–X (X=Cl, Br, I) at an angle of ~100° (‘side on’), whereas the nucleophil X approaches the oxygen of C=O at ~165°



Scheme 2. Synthetic pathway for the preparation of compound **1**.

(‘head on’). From this angle, the solvent molecules are different in their effect for stabilisation of the lattice framework. Although DMSO does mainly bonding like assisting in stabilisation of the lattice construction, the chloroform is less effective in this way but, on the contrary, may be regarded as a volume stabilising component as it fills lattice voids left by the $1 \cdot 2$ DMSO network.

A view of the crystal structure in the direction of the *b*-axis reveals that the molecules of **1**, one equivalent of DMSO solvent and the molecules of CHCl_3 are arranged to corrugated layers, whereas the remaining solvent molecules are located between the molecular layers. A more instructive illustration of the lattice framework is shown in Figure 3, which represents a view along the stacking of plain **1**

Table 1. Crystallographic and structure refinement data of the compound studied (estimated standard deviations are in parentheses).

Compound	1a
Empirical formula	C ₂₀ H ₁₀ O ₈ · 2 C ₂ H ₆ SO · CHCl ₃
Formula weight	653.90
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	14.5144(6)
<i>b</i> (Å)	18.4714(7)
<i>c</i> (Å)	11.6806(5)
α (°)	90.0
β (°)	107.808(1)
γ (°)	90.0
<i>V</i> (Å ³)	2981.5(2)
<i>Z</i>	4
<i>F</i> (000)	420
<i>D</i> _c (mg m ^{−3})	1.457
μ (mm ^{−1})	0.500
Data collection	
Temperature (K)	153(2)
No. of collected reflections	56,412
Within the θ -limit ^a	1.5–29.1
Index ranges $\pm h$, $\pm k$, $\pm l$	−19/19, −25/25, −15/10
No. of unique reflections	7884
<i>R</i> _{int}	0.0373
Refinement calculations: full-matrix least-squares on all <i>F</i> ² values	
Weighting expression <i>w</i> ^a	$[\sigma^2(F_o^2) + (0.0612P)^2 + 1.3816P]^{-1}$
No. of refined parameters	369
No. of <i>F</i> values used [<i>I</i> > 2σ(<i>I</i>)]	6322
Final <i>R</i> -indices	
<i>R</i> (= $\sum \Delta F / \sum F_o $)	0.0390
<i>wR</i> on <i>F</i> ²	0.1203
<i>S</i> (= Goodness of fit on <i>F</i> ²)	1.079
Final $\Delta\rho_{\max}/\Delta\rho_{\min}/e \text{ Å}^{-3}$	0.65/−0.61

^a $P = (F_o^2 + 2F_c^2)/3$.

molecules. In this assembly, the longitudinal axes of molecules of consecutive layers are rotated by nearly 90°. From this it follows that every fourth layer in the stacking direction is congruent, thus producing an uncongested lattice structure. Nevertheless, the relatively close distance of 3.3 Å between the aromatic residues of consecutive molecules **1** suggests that arene stacking (35) has a decisive effect on the stabilisation of the lattice structure.

3. Conclusions

A new molecular building block **1** comprising two isophthalic acid moieties attached in the 5-position to both ends of a rigid rod-like diacetylene unit, which has been synthesised, is shown to create a complex (1:2:1) mixed solvent crystalline framework **1a** with DMSO and chloroform as secondary and tertiary components, the structure of which has been solved.

Table 2. Distances (Å) and angles (°) of possible hydrogen-bond type interactions of the compound studied.

Atoms involved	Symmetry	Distance		Angle D—H...A
		D...A	H...A	
1				
O(2)—H(2)···O(1B)	−1 + <i>x</i> , 1.5 − <i>y</i> , −1.5 + <i>z</i>	2.637(2)	1.82	163
O(4)—H(4)···O(1B)	1 − <i>x</i> , 1 − <i>y</i> , 1 − <i>z</i>	2.606(2)	1.77	174
C(2C)—H(2C1)···O(1B)	<i>x</i> , <i>y</i> , <i>z</i>	3.313(3)	2.56	134
O(6)—H(6)···O(1C)	<i>x</i> , <i>y</i> , <i>z</i>	2.598(2)	1.78	163
O(8)—H(8)···O(1C)	1 − <i>x</i> , 0.5 + <i>y</i> , 1.5 − <i>z</i>	2.651(2)	1.81	176
C(2C)—H(2C2)···O(3)	1 − <i>x</i> , 0.5 + <i>y</i> , 1.5 − <i>z</i>	3.310(3)	2.43	149
C(2B)—H(2B2)···O(4)	1 − <i>x</i> , 0.5 + <i>y</i> , 0.5 − <i>z</i>	3.535(3)	2.72	141
C(1A)—H(1A)···O(5)	<i>x</i> , <i>y</i> , <i>z</i>	3.093(3)	2.20	155
C(1B)—H(1B2)···O(7)	1 − <i>x</i> , 2 − <i>y</i> , 1 − <i>z</i>	3.143(3)	2.48	125

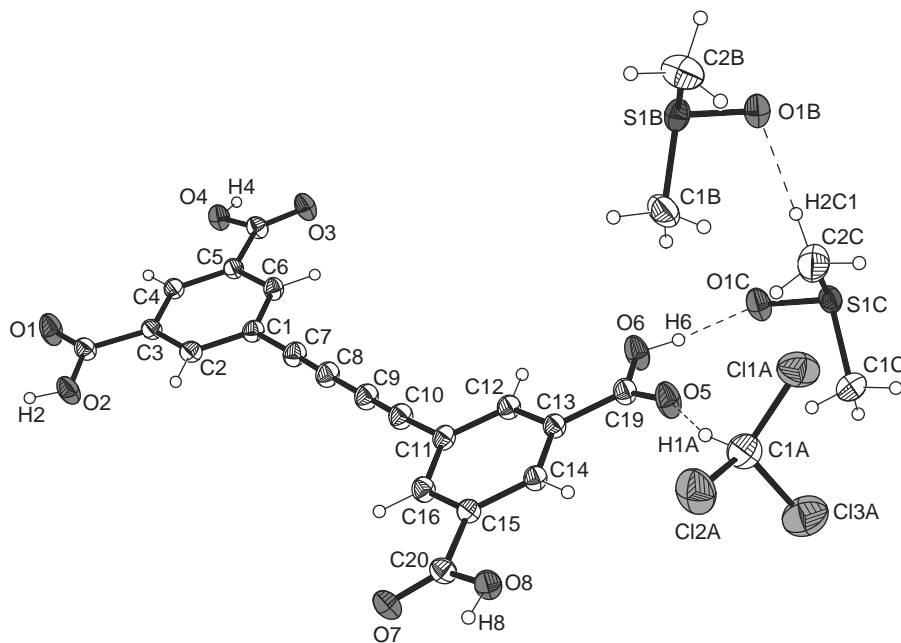


Figure 1. Perspective view of the asymmetric unit of **1a** ($1 \cdot 2 \text{ DMSO} \cdot \text{CHCl}_3$). Thermal ellipsoids are drawn at 50% probability level. Broken lines represent hydrogen bonds.

While other tetracarboxylic acids with similar well-defined shapes behave as tectons for the controlled assembly of hydrogen-bonded open frameworks rather than a close packed structure (11, 14), the present compound **1**, although corresponding to this molecular design, behaves markedly different in structure formation under the used condition. This can be attributed to geometric parameters of the molecule leading to a highly expanded labile crystal lattice on carboxylic pairing. Hence, as a way out, the molecule uses its secondary mode of synthon formation (26) which is aromatic stacking (35), allowing a partly overlap of the molecules and, thus, considerable shrinking of the lattice volume. The carboxylic groups being now extremely unsatisfied in terms of their hydrogen donor–acceptor property take the opportunity to interact with the coordinating solvent molecules, giving rise to a close packed structure.

Another line of reasoning is using metal ions strongly coordinating to the carboxylate groups of **1** in order to stabilise a porous framework structure (36). Actually, this has become possible as recently demonstrated by the generation and structural solution of a corresponding coordination polymer based on **1** and copper(II) (37), opening promising aspects of **1** in the actual field of metal-organic-frameworks (MOFs) (12, 13). Moreover, due to the molecular shape and functionality, compound **1** may also excite interest as tecton in the topical research area of surface-assisted 2D crystal engineering (6, 38–41).

4. Experimental

4.1 Methods and materials

The melting points (uncorrected) were measured on a hot-stage microscope PHMK (Rapido, Dresden). NMR spectra were recorded on a Bruker DPX 400 spectrometer (^1H 400 MHz, ^{13}C 100 MHz) in solutions using TMS as internal standard. IR spectra were recorded on a Nicolet 510 FT-IR spectrometer. MS were obtained using Hewlett-Packard MS 5989A (GC-MS) and Finnigan Mat 8200 (EI-MS) instruments. Elemental analyses were performed on a Heraeus CHN-Rapid analyser. Thin layer chromatography was carried out using Merck Silica gel 60 F₂₅₄ on aluminium backed plates. Solvents were purified and dried using standard laboratory procedures (42).

The following reagents were purchased from commercial sources: MEBINOL (Acros Organics) palladiumtriphenylphosphane dichloride (ABCR), copper(II) acetate, copper(I) iodide, lithium hydroxide and sodium hydride (60% in mineral oil) (Sigma-Aldrich). Dimethyl 5-iodoisophthalate was prepared as described in the literature (15).

4.2 Synthesis

4.2.1 Dimethyl 5-(3-hydroxy-3-methyl-1-butynyl)isophthalate (3)

A mixture of dimethyl 5-iodoisophthalate (**2**) (10.0 g, 31.2 mmol), 2-methylbut-3-yn-2-ol (MEBINOL, 3.20 g, 37.5 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (180 mg, 0.26 mmol) and CuI

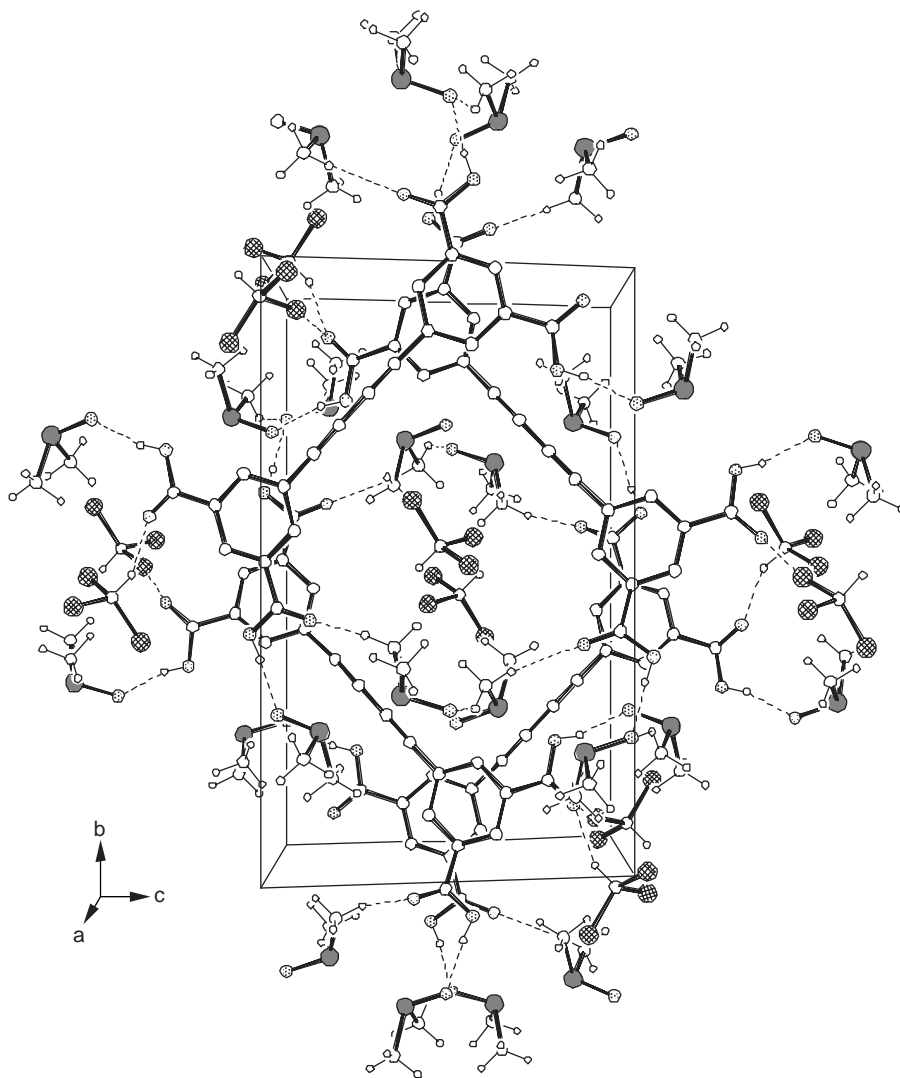


Figure 2. Packing excerpt of **1a** showing the mode of intermolecular interactions. Chlorine atoms are displayed as cross-hatched circles, oxygen atoms as dotted and sulphur atoms as shaded circles. Broken lines represent hydrogen-bond type interactions.

(40 mg, 0.21 mmol) in pyridine (25 ml) and triethylamine (60 ml) under Ar was heated to reflux for 1 h. After cooling to room temperature, the triethylammonium chloride, which has formed, was filtered off using celite and washed with diethyl ether. The filtrate was added dropwise under cooling to 6N hydrochloric acid. The aqueous phase was separated and extracted three times with diethyl ether. The combined organic layers were washed with 2N hydrochloric acid, aqueous sodium hydrogen carbonate and water, in this sequence, and dried with sodium sulphate. The solvent was evaporated and the crude product crystallised from toluene-*n*-hexane (1:1, v/v) to yield 76% of a white powder: Mp 104–106°C. IR (KBr, cm^{-1}): 3452 (OH), 3084 (C–H, Ar), 2981, 2955 (C–H), 2231 (C \equiv C), 1734 (C=O), 1636, 1605 (Ar), 1440 (C–H), 1347, 1259, 1202, 1176 (C–O), 1005, 917, 866 (Ar); ^1H NMR (CDCl_3): δ 1.63 (s, 6 H, CCH_3), 2.05 (s, 1

H, OH), 3.95 (s, 6 H, OCH_3), 8.25 (d, $^4J = 1.5$ Hz, 2 H, Ar-H), 8.60 (t, $^4J = 1.5$ Hz, 1 H, Ar-H); ^{13}C NMR (CDCl_3): δ 31.4 (CCH_3), 52.5 (OCH_3), 65.6 [$\text{C}(\text{CH}_3)_2\text{OH}$], 80.3 (Ar-C \equiv C), 95.7 (Ar-C \equiv C), 123.9, 130.1, 130.9, 136.6 (Ar-C), 165.6 (COOCH_3). MS (GC): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{O}_5$: 276.28. Found 276 [M^+]. Anal. calcd for $\text{C}_{15}\text{H}_{16}\text{O}_5$: C, 65.21%; H, 5.84. Found: C, 64.86; H, 5.97%.

4.2.2 5-Ethynylisophthalic acid (**4**)

To a solution of potassium hydroxide (11.6 g, 207.3 mmol) in *n*-butanol (250 ml) was added compound **3** (6.0 g, 21.7 mmol) and the mixture heated under reflux for 30 min. After cooling to room temperature, the precipitate which has formed was separated and washed with ethanol to yield 88% of an off-white powder of the dipotassium salt of **4**

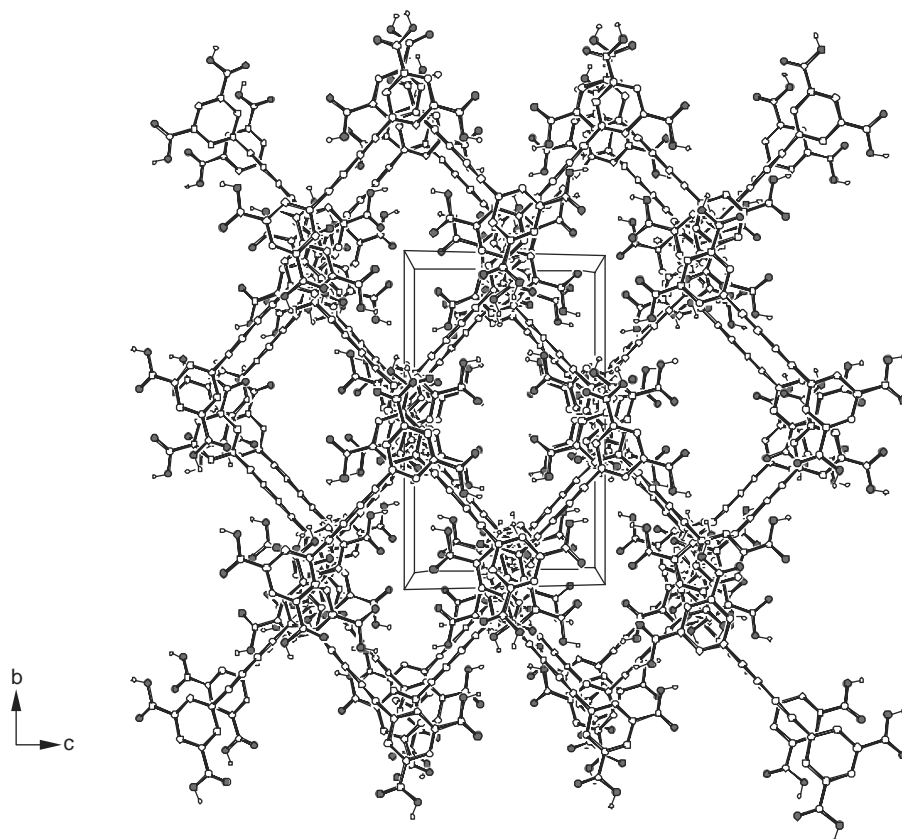


Figure 3. Illustration of the plain lattice of **1** (excluding solvent molecules) viewed along the crystallographic *a*-axis. Oxygen atoms are displayed as shaded circles. Only the hydrogens of the carboxy groups are displayed for clarity.

(Mp > 350°C). This was dissolved in water (20 ml) and acidified to pH 1 with 5N hydrochloric acid. The precipitate which has formed was separated, washed with water and dried for 4 h at 50°C under vacuum to yield 98% of a white powder: Mp 247–250°C. IR (KBr, cm^{-1}): 3297 (C—H, ethynyl), 3076 (C—H, Ar), 2983, 2933, 2876 (C—H), 2116 (C≡C), 1706 (C=O), 1599 (Ar), 1278, 1246 (C—O), 917, 860 (Ar); ^1H NMR ($[d_6]$ DMSO): δ 4.43 (s, 1 H, C≡C—H), 8.18 (s, 2 H, Ar—H), 8.47 (s, 1 H, Ar—H), 13.49 (s, 2 H, COOH); ^{13}C NMR ($[d_6]$ DMSO): δ 81.7 (C≡C—H), 82.7 (C≡C—H), 122.8, 130.1, 132.1, 136.0 (Ar—C), 165.8 (COOH). MS (EI): m/z calcd for $\text{C}_{10}\text{H}_6\text{O}_4$: 190.15. Found: 189.9 $[\text{M}^+]$. Anal. calcd for $\text{C}_{10}\text{H}_6\text{O}_4$: C, 63.16; H, 3.18. Found: C, 62.88; H, 3.42%.

4.2.3 Dimethyl 5-ethynylisophthalate (**5**)

Via esterification of 4. A mixture of diacid **4** (5.70 g, 30.0 mmol) in dry methanol (25 ml) and conc. sulphuric acid (1.20 g, 12.2 mmol) was heated to reflux for 5 h under dry conditions. The most part of the alcohol was evaporated and the residue added to five times the amount of iced water. The organic layer was separated and the aqueous phase extracted three times with diethyl ether. The combined organic layers

were washed with conc. aqueous solution of sodium carbonate and water, in this sequence, and dried with sodium sulphate. Evaporation of the solvent and crystallisation from ethanol yielded 55% of colourless needles; mp 134–136°C (lit. (19) 130–131°C). Spectroscopic data correspond with the literature (19).

Via deblocking of 3. To a solution of **3** (6.0 g, 21.7 mmol) in dry toluene (300 ml), sodium hydride (60% in mineral oil, 1.56 g, 39.0 mmol) was added and the mixture heated for 1 h to 75°C. After cooling to room temperature, the mixture was carefully quenched with water. The organic layer was separated, washed with water and dried with sodium sulphate. Evaporation of the solvent and crystallisation from ethanol yielded 60% of the compound.

4.2.4 Tetramethyl 5,5'-(1,3-butadiyne-1,4-diyl)diisophthalate (**6**)

A solution of diester **5** (0.50 g, 2.30 mmol) in pyridine–methanol (10 ml, 1:1, v/v) was heated for 30 min under an atmosphere of argon, in order to remove oxygen. After cooling to room temperature, copper(II) acetate (0.60 g,

3.22 mmol) was added and the mixture heated to reflux for 4 h under argon. The mixture was then cooled to room temperature and dropped slowly into 18N sulphuric acid under cooling with ice. The solid which has formed was dissolved in diethyl ether. The ethereal solution was washed with water and dried with sodium sulphate. The solvent was evaporated and the crude product crystallised from acetone–chloroform (1:1, v/v) to yield 88% of a colourless solid; mp 221–222°C. IR (KBr, cm^{-1}): 3079, 3037, 3008 (C–H, Ar), 2951 (C–H), 1729 (C=O), 1634, 1595 (Ar), 1438 (C–H), 1331, 1271, 1131, 1110 (C–O), 999, 914, 875 (Ar); ^1H NMR (CDCl_3) δ 3.97 (s, 12 H, CH_3), 8.37 (s, 4 H, Ar-*H*), 8.67 (s, 2 H, Ar-*H*); ^{13}C NMR (CDCl_3) δ 52.6 (CH_3), 75.1 (C–C \equiv C), 80.2 (C–C \equiv C), 122.6, 131.2, 131.3, 137.4 (Ar-C), 165.3 (COOCH_3); MS (GC): m/z calcd for $\text{C}_{24}\text{H}_{18}\text{O}_8$: 434.39. Found: 434 [M^+]. Anal. calcd for $\text{C}_{24}\text{H}_{18}\text{O}_8$: C, 66.36; H, 4.18. Found: C, 66.18; H, 4.15%.

4.2.5 5,5'-(1,3-Butadiyne-1,4-diyl)diisophthalic acid (**1**)

Tetraester **6** (0.20 g, 0.46 mmol) was dissolved in THF (15 ml). Lithium hydroxide (0.80 g, 19.0 mmol) was added and the suspension mixed with water (4.5 ml). The mixture was stirred for 15 h at room temperature and then diluted with water (20 ml). The solution was acidified with 3N hydrochloric acid and the precipitate, which has formed, was dissolved with a mixture of diethylether and THF. The ethereal solution was dried with sodium sulphate and evaporated to yield after drying at 100°C under vacuum 83% of a colourless solid: Mp > 350°C. IR (KBr, cm^{-1}): 3415 (br, H_2O), 3038 (C–H, Ar), 2637, 2551 (COOH), 1703 (C=O), 1595, 1542, 1510 (Ar), 1142 (C–O), 914 (Ar). ^1H NMR ($[d_6]\text{DMSO}$): δ 8.30 (s, 4 H, Ar-*H*), 8.50 (s, 2 H, Ar-*H*), 13.62 (s, 4 H, COOH); ^{13}C NMR ($[d_6]\text{DMSO}$): δ 74.5 (C–C \equiv C), 80.6 (C–C \equiv C), 121.4, 131.0, 132.3, 136.6 (Ar-C), 165.6 (COOH). MS (EI): m/z calcd for $\text{C}_{20}\text{H}_{10}\text{O}_8$: 378.29. Found: 378.1 [M^+]. Anal. calcd for $\text{C}_{20}\text{H}_{10}\text{O}_8 \cdot \text{H}_2\text{O}$: C, 60.61; H, 3.05. Found: C, 60.28; H, 2.93%.

4.3 X-ray crystallography

Single crystals of **1a** suitable for X-ray crystallographic analysis were grown from a solution of **1** in DMSO–chloroform. Intensity data were collected on a Bruker Kappa APEX II diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using ω - and φ -scans. Reflections were corrected for background and Lorentz polarisation effects. Preliminary structure models were derived by application of direct methods (43) and were refined by full-matrix least squares calculation based on F^2 for all reflections (43). All hydrogens were included in the models in calculated positions and were refined as constrained to bonding atoms.

Analysis of hydrogen bonds was carried out by using the HTAB instruction of the SHELXTL program. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication number CCDC-780477. Copies of data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, E-mail: deposit@ccdc.cam.ac.uk).

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References

- (1) Tiekink, E.R.T., Vittal, J., Eds. *Frontiers in Crystal Engineering*; Wiley: Hoboken, NJ, 2006.
- (2) Braga, D., Grepioni, F., Eds. *Making Crystals by Design: Methods, Techniques and Applications*; Wiley: Weinheim, Germany, 2007.
- (3) Jones, W., Rao, J.N.R., Eds. *Supramolecular Organization and Materials Design*; Cambridge University Press: New York, 2008.
- (4) Weber, E. In *Comprehensive Supramolecular Chemistry*; MacNicol, D.D., Toda, F., Bishop, R., Eds.; Elsevier: Oxford, 1996; Vol. 6, pp 535–592.
- (5) Metrangola, P.; Resnati, G. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J.L., Steed, J.W., Eds.; CRC Press: Boca Raton, FL, 2004; pp 1484–1492.
- (6) Elemans, J.A.A.W.; Lei, S.; De Feyter, S. *Angew. Chem., Int. Ed.* **2009**, *121*, 7434–7469.
- (7) Burrows, A.D. Structure and Bonding. In *Supramolecular Assembly via Hydrogen Bonds I*; Mingos, D.M., Ed.; Springer-Verlag: Berlin-Heidelberg, 2004; Vol. 108, pp 55–96.
- (8) Weber, E.; Czugler, M. Topics in Current Chemistry. In *Molecular Inclusion and Molecular Recognition – Clathrates II*; Weber, E., Ed.; Springer-Verlag: Berlin-Heidelberg, 1988; Vol. 149, pp 45–135.
- (9) Meléndez, R.E.; Hamilton, A.D. Topics in Current Chemistry. In *Design of Organic Solids*; Weber, E., Ed.; Springer-Verlag: Berlin-Heidelberg, 1998; Vol. 198, pp 97–129.
- (10) Kolotuchin, S.V.; Thiessen, P.A.; Fenlon, E.E.; Wilson, S.R.; Loweth, C.H.; Zimmerman, S.C. *Chem. Eur. J.* **1999**, *5*, 2537–2547.
- (11) Blunt, M.; Lin, S.; Gimenez-Lopez, C.M.; Schröder, M.; Champness, N.R.; Beton, P.H. *Chem. Commun.* **2008**, 2304–2306.
- (12) Batten, S.R.; Neville, S.M.; Turner, D.R. *Coordination Polymers*; Royal Society of Chemistry: Cambridge, UK, 2009.
- (13) Chen, L.; Hong, M.-C. *Design and Construction of Coordination Polymers*; Wiley: Weinheim, Germany, 2009.
- (14) Zhou, H.; Dang, H.; Yi, J.-H.; Nanci, A.; Rochefort, A.; Wuest, J.D. *J. Am. Chem. Soc.* **2007**, *129*, 13774–13775.
- (15) Mazik, M.; König, A. *J. Org. Chem.* **2006**, *71*, 7854–7857.
- (16) Doucet, H.; Hierro, J.C. *Angew. Chem., Int. Ed.* **2007**, *46*, 834–871.
- (17) Rafael, C.; Carmen, N. *Chem. Rev.* **2007**, *107*, 874–922.

- (18) Havens, S.J.; Hergenrother, P.M. *J. Org. Chem.* **1985**, *50*, 1763–1765.
- (19) Bhagwat, S.S.; Roland, D.M.; Main, A.J.; Gude, C.; Goldstein, R.; Cohen, D.S.; Dotson, R.; Mathis, J.; Lee, W. *Biorg. Med. Chem. Lett.* **1992**, *2*, 1623–1626.
- (20) Crisp, G.T.; Turner, P.D. *Tetrahedron* **2000**, *56*, 8335–8344.
- (21) Simándi, L.I. In *The Chemistry of Functional Groups*, Suppl. C; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; pt 1, pp 529–534.
- (22) Fedenok, L.G.; Berdnikov, V.M.; Shvartsberg, M.S. *J. Org. Chem. USSR* **1973**, *9*, 1806–1809.
- (23) Back, S.; Lutz, M.; Spek, A.L.; Lang, H.; van Koten, G. *J. Organomet. Chem.* **2001**, *620*, 227–234.
- (24) Thomas, R.; Mallajosula, S.S.; Lakshmi, L.; Pati, S.K.; Kulkarni, G.U. *J. Mol. Struct.* **2009**, *922*, 46–50.
- (25) Schindler, D.; Eißmann, F.; Weber, E. *Org. Biomol. Chem.* **2009**, *7*, 3549–3560.
- (26) Desiraju, G.R. *Angew. Chem., Int. Ed.* **1995**, *34*, 2311–2327.
- (27) Kitaigorodsky, A.I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973.
- (28) Kitaigorodsky, A.I. *Organic Chemical Crystallography*; Consultant Bureau: New York, 1961.
- (29) Csöregi, I.; Czugler, M.; Ertan, A.; Weber, E.; Ahrendt, J. *J. Incl. Phenom.* **1990**, *8*, 275–287.
- (30) Ruffani, A.; Seichter, W.; Weber, E. *J. Incl. Phenom. Macrocycl. Chem.* **2010**, Doi: 10.1007/s10847-010-9850-0.
- (31) Desiraju, G.R.; Steiner, T. *The Weak Hydrogen Bond*; IUCr Monographs on Crystallography, Oxford University Press: New York, 1999; Vol. 9, pp 29–121.
- (32) Rissanen, K. *CrystEngComm* **2008**, *10*, 1107–1113.
- (33) Metrangolo, P.; Meyer, M.; Pilati, T.; Resnati, G.; Terraneo, G. *Angew. Chem., Int. Ed.* **2008**, *120*, 6206–6220.
- (34) Ramasubbu, N.; Parthasarathy, R.; Murray-Rust, P. *J. Am. Chem. Soc.* **1986**, *108*, 4308–4314.
- (35) Dance, I. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J.L., Steed, W.J., Eds.; CRC Press: Boca Raton, FL, 2004; pp 1076–1092.
- (36) Hausdorf, S.; Seichter, W.; Weber, E.; Mertens, F.O.R.L. *Dalton Trans.* **2009**, 1107–1113.
- (37) Böhle, T.; Schindler, D.; Hauptvogel, I.M.; Mertens, F.O.R.L.; Weber, E.; paper in preparation.
- (38) Bonifazi, D.; Mohnani, S.; Llanes-Pallas, A. *Chem. Eur. J.* **2009**, *15*, 7004–7025.
- (39) Payer, D.; Comisso, A.; Dmitriev, A.; Strunskus, T.; Lin, N.; Wöll, C.; De Vita, A.; Barth, J.V.; Kern, K. *Chem. Eur. J.* **2007**, *13*, 3900–3906.
- (40) Kampschulte, L.; Lackinger, M.; Maier, A.-K.; Kishore, R.S.K.; Griessl, S.; Schmittl, M.; Heckl, W.M. *J. Phys. Chem.* **2006**, *B110*, 10829–10836.
- (41) Schütte, M.; Stolle, C.; Kurth, D.G. *Supramol. Chem.* **2003**, *15*, 549–555.
- (42) Leonard, L.; Lugo, B.; Procter, G. *Praxis der Organischen Chemie*; VCH: Weinheim, Germany, 1994; pp 53–68.
- (43) Sheldrick, G.M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

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