KEYNOTE

1-Phenyl-1*H*-pyrrole-2,5-dicarboxylic acid derivatives as versatile hydrogen-bonding motifs for the formation of one-, two- and three-dimensional networks in the solid state †

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A series of 1-phenyl-1*H*-pyrrole-2,5-dicarboxylic acid derivatives were prepared and their solid state structures were investigated. Small structural changes in the monomeric subunit can lead to the formation of one-dimensional linear ribbons, two-dimensional sheets and three-dimensional networks. In each case a consistent feature of the solid state structures is the formation of bidentate hydrogen bonded contacts between the 2,5-carboxylic acid groups on adjacent pyrrole subunits. The exact nature of the crystal packing is strongly influenced by the substitution on the phenyl ring.

Introduction

The design of molecular subunits that self-assemble into well-defined structures in the solid state remains an area of intense interest.[1] Particular emphasis has been placed on the search for components that result in the ordered formation of one-,[2] two-[3] or three-dimensional[4] arrangements (Fig. 1). Hydrogen bonds, because of their strength, directionality and selectivity, have attracted most attention among efforts aimed at controlling solid state structures. Many hydrogen-bonding motifs that can direct the formation of predictable and ordered solid state structures have recently been reported. These have included the linear aggregation of diaryl ureas,[2a] the association of melamine and barbituric acid derivatives into hydrogen bonded tapes or rosettes,[2b,c] the formation of porous three-dimensional networks by pyridone and 2,4-diaminotriazine derivatives,[4b,c] and the design of functional networks of anthracene-bisresorcinal derivatives.[3d]

Our approach to this problem has centered on the hydrogen bonding properties of carboxylic acids, both with complementary acylaminopyridine derivatives[5] and with themselves.[6] In particular, we have been inspired by the solid state properties of trimesic acid. This remarkable molecule takes up a structure in the crystal in which all carboxylic acid groups are satisfied by bidentate hydrogen bonding to three neighboring molecules.[7] The result is a two-dimensional sheet structure in which six trimesic acid molecules define a cavity 14 Å in diameter. With simple trimesic acid these pores are filled by three perpendicular hydrogen bonded sheets in a triply concatenated arrangement.[8] Addition of certain alkane cosolvents[9] or substitution on the trimesic acid[10] can prevent concatenation and lead to the formation of planar sheet aggregates.

In an effort to isolate the essential ribbon and ring motifs seen in the structure of trimesic acid, we have investigated the solid state behavior of isophthalic acid derivatives and found that the nature of the aggregate depends critically on the substituent in the 5-position. In the case of 5-unsubstituted[11] and 5-methoxyisophthalic acid[12] a linear ribbon arrangement is formed (Fig. 2A). When certain long chain substituents (*e.g.* decyloxy- or octyloxy-) are present in the 5-position, then cyclic hexameric aggregates result as in Fig. 2B.[6a] In both cases the 120° angle between the hydrogen bonding groups dictates the overall shape of the aggregate, whether the ribbon angle in Fig. 2A or the hexameric stoichiometry in Fig. 2B.

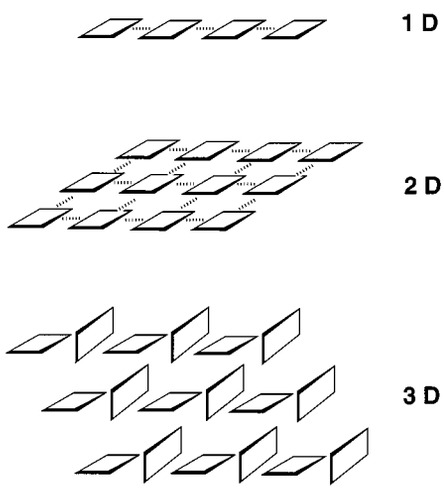

Fig. 1 One-, two- and three-dimensional arrangements of subunits

We were interested in determining the scope of these aromatic bis- and tris-carboxylic acids for controlling the formation of cyclic, one-, two- and three-dimensional structures in the solid state. One simple modification would be to vary the relative angle between the two hydrogen bonding groups. For example, with readily available *N*-phenylpyrrole-2,5-dicarboxylic acid derivatives the angle between the two carboxylic acid groups is approximately 135°. This should lead to more extended ribbon aggregates with the phenyl substituents projecting perpendicularly and potentially able to interact with adjacent strands. With the correct positioning of the strands this may lead to the formation and stabilization of pores within the solid (Fig. 2C). In the case of cyclic aggregation, *N*-phenylpyrrole-2,5-dicarboxylic acid would be expected (due to the 135° angle) to form a hydrogen bonded octamer in which the eight phenyl groups project into the central cavity (Fig. 2D). In this paper we describe the synthesis and solid state structures of several *N*-phenylpyrrole-2,5-dicarboxylic acid derivatives and show that they represent a robust and simple motif for crystal engineering (Table 1).

Synthesis

A wide variety of substituted *N*-phenylpyrrole-2,5-dicarboxylic acid derivatives were available by a three step sequence

† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/141.

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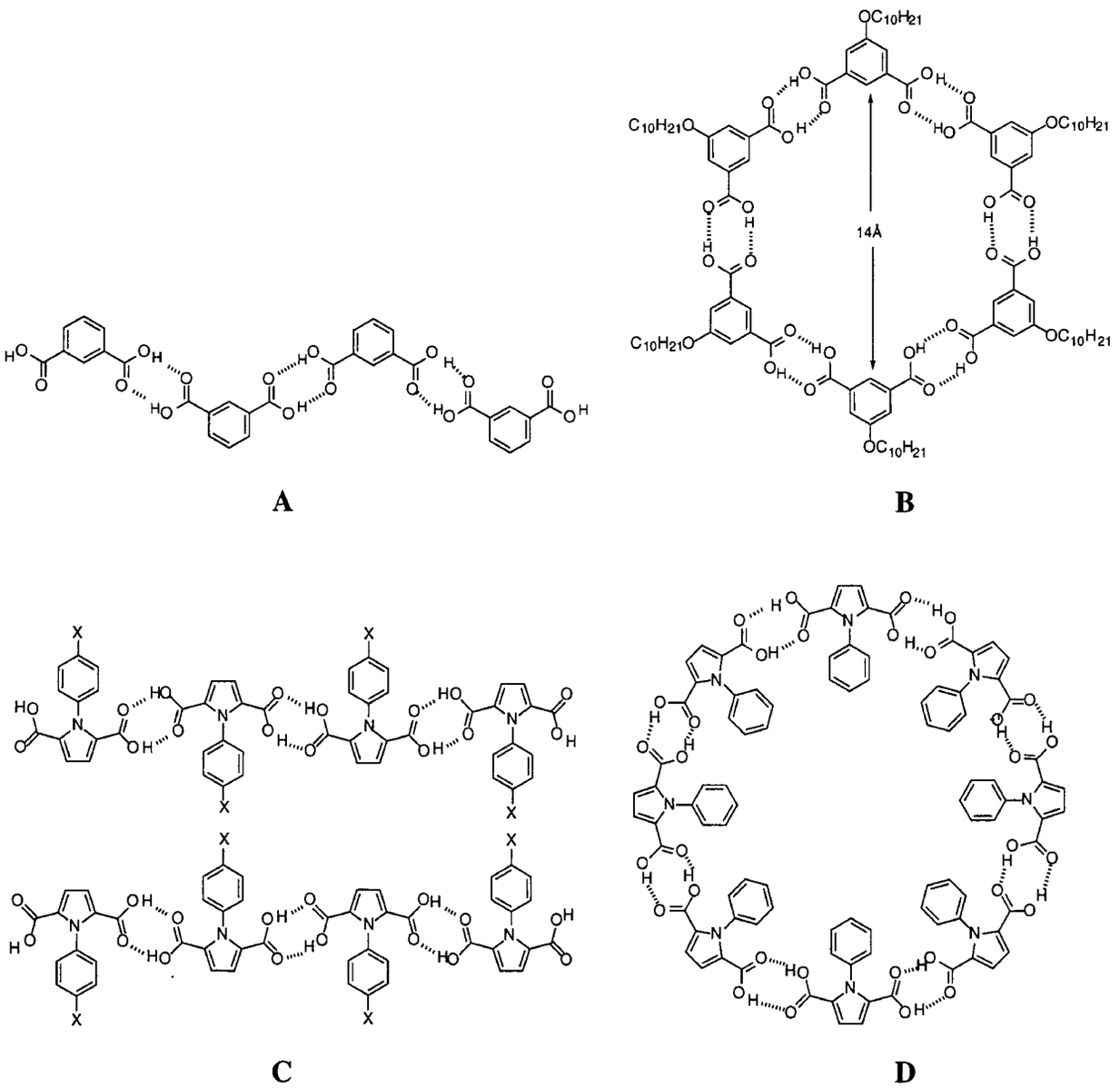
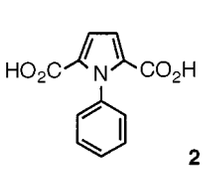


Fig. 2 Hydrogen bonding arrangement of (A) isophthalic acid and (B) 5-decyloxyisophthalic acid in the solid state; and possible hydrogen bonded packing arrangements for *N*-phenylpyrrole-2,5-dicarboxylic acid in (C) linear and (D) cyclic forms

from ethyl bromopyruvate and the corresponding aniline. Zinc promoted radical coupling of the bromoester gave 2,5-dihydroxyhexa-2,4-dienedioic acid diethyl ester (**1**).[13] Paal–Knorr reaction[14] with various aniline derivatives gave the corresponding diethyl pyrrole-2,5-dicarboxylates which were then hydrolyzed in basic ethanol to afford the final pyrrole-dicarboxylic acids (Scheme 1). In this way the parent *N*-phenyl- (**2**), 3,5-dimethylphenyl- (**3**), 4-carboxyphenyl- (**4**), 4-biphenyl- (**8**) and 4-hydroxyphenyl- (**9**) pyrroledicarboxylic acid derivatives were prepared. The use of a 4,4′-biphenyldiamine in the Paal–Knorr reaction allowed the formation of a bis(pyrrole-2,5-dicarboxylic acid) derivative **6**.

One-dimensional aggregates

1-Phenyl-1*H*-pyrrole-2,5-dicarboxylic acid (2)



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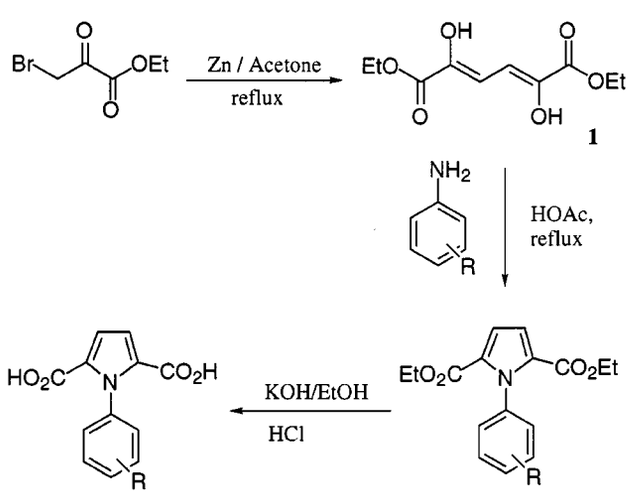
Unsubstituted 1-phenyl-1*H*-pyrrole-2,5-dicarboxylic acid might be expected to form either cyclic aggregates or extended one-dimensional ribbons of the type shown in Fig. 2. Diffraction quality crystals of **2** were grown by diffusing hexane into a THF solution of the diacid and were triclinic in the $P\bar{1}$ space group. X-Ray analysis showed that the diacid forms ribbon aggregates in the solid state through carboxylic acid dimer hydrogen bonding interactions (CO · · · OC 2.60–2.61 Å) (Fig. 3A). However, the ribbon is limited in size to four subunits stabilized by six hydrogen bonds. These four molecules comprise pairs of crystallographically independent hydrogen bonded molecules which are further linked to their centrosymmetrically related counterparts. Further extension of the strands was interrupted due to hydrogen bonding of the terminal carboxylic acid groups to disordered THF molecules. Interestingly, the complex does not take up an alternating projection of phenyl groups (as in Fig. 2C) but instead forms two adjacent pairs with the phenyl groups on the same side. Each pair corresponds to one quadrant of the octameric aggregate in Fig. 2D. The origin of this effect can be seen in the side view (Fig. 3B) of the hydrogen bonded ribbons, where each pair can be seen to project one phenyl group up and the other down to form an offset π–π stacking interaction with phenyl groups from

Table 1 X-Ray structure determination summary

Crystal data	**2**	**3**	**4**	**8**	**9**
Empirical formula	**2**·1/2 THF	$C_{15}H_9NO_4$	**4**·2/3 THF	**8**·THF	**9**·THF
Formula weight	263.22	267.23	383.37	252.93	308.24
Temperature/K	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength/Å	0.71073	1.54178	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	*Pbcn*	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Unit cell dimensions					
a/Å	6.967(3)	14.529(3)	5.695(5)	18.616(4)	14.219(3)
b/Å	9.831(3)	8.372(2)	10.315(7)	5.5570(11)	6.0854(12)
c/Å	20.245(6)	19.611(4)	16.789(6)	20.558(4)	18.510(4)
α/°	87.78(3)	90	92.28(4)	90	90
β/°	87.74(3)	90	96.30(6)	109.11(3)	90.98(3)
γ/°	78.52(3)	90	91.85(6)	90	90
Volume/Å^3	1357.1(9)	2385.4(8)	978.8(11)	2009.5(7)	1601.4(5)
Z	4	8	2	4	4
Density (calcd.)/g cm^{-3}	1.288	1.488	1.301	1.254	1.279
Absorption coefficient/mm^{-1}	0.098	0.920	0.101	0.089	0.098
F(000)	544	1104	404	800	632
Crystal size/mm	0.20 × 0.20 × 0.30	0.31 × 0.31 × 0.36	0.24 × 0.24 × 0.08	0.08 × 0.29 × 0.36	0.22 × 0.24 × 0.34
θ range for data collection/°	2.01 to 24.00	4.51 to 60.06	1.98 to 24.00	1.80 to 22.50	1.79 to 23.99
Limiting indices	$0 \le h \le 7$, $-11 \le k \le 11$, $-23 \le l \le 23$	$0 \le h \le 16$, $-1 \le k \le 9$, $-22 \le l \le 0$	$0 \le h \le 6$, $-11 \le k \le 11$, $-19 \le l \le 19$	$0 \le h \le 20$, $0 \le k \le 5$, $-22 \le l \le 20$	$0 \le h \le 16$, $0 \le k \le 6$, $-21 \le l \le 21$
Reflections collected	4646	1779	3431	2696	2609
Independent reflections	4248 (R_{int} = 0.0342)	1776 (R_{int} = 0.0276)	3082 (R_{int} = 0.0292)	2613 (R_{int} = 0.0093)	2509 (R_{int} = 0.0315)
Absorption correction	None	None	None	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Observed reflections, restraints, parameters	4244, 0, 378	1774, 0, 228	3082, 0, 236	2613, 0, 295	2509, 0, 241
Goodness-of-fit on F^2	1.057	1.000	1.072	1.020	1.055
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0602$, $wR2 = 0.1391$	$R1 = 0.0467$, $wR2 = 0.1576$	$R1 = 0.1376$, $wR2 = 0.3665$	$R1 = 0.0602$, $wR2 = 0.1315$	$R1 = 0.0694$, $wR2 = 0.1815$
R indices (all data)	$R1 = 0.1187$, $wR2 = 0.1829$	$R1 = 0.0676$, $wR2 = 0.1772$	$R1 = 0.2608$, $wR2 = 0.4985$	$R1 = 0.1142$, $wR2 = 0.1643$	$R1 = 0.1202$, $wR2 = 0.2228$
Extinction coefficient	0.008(2)	0.0011(3)	0.000(13)	0.0007(8)	0.004(3)
Largest diff. peak and hole/e Å^{-3}	0.278 and −0.175	0.232 and −0.257	0.678 and −0.240	0.272 and −0.252	0.516 and −0.230



Scheme 1

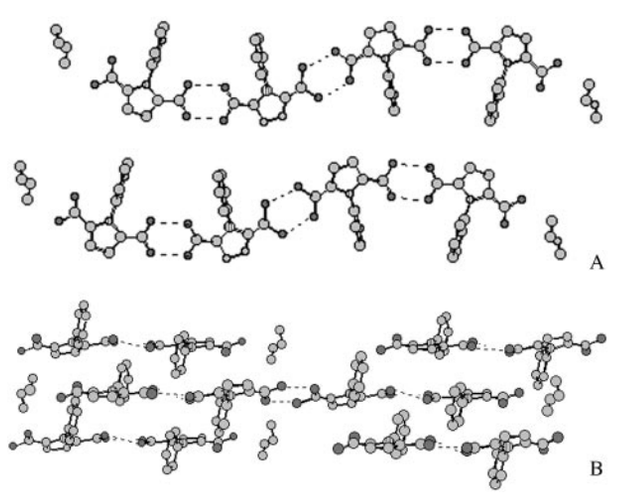


Fig. 3 X-ray structure of **2**, (A) top view (B) side view. Carboxylic acid hydrogens were not resolved.

the adjacent layers (closest phenyl-H · · · phenyl centroid, 3.6 Å).

1-(3,5-Dimethylphenyl)-1*H*-pyrrole-2,5-dicarboxylic acid (3)

The incorporation of substituents onto the phenyl ring might be expected to disrupt the interlayer packing seen in Fig. 3B and induce the formation of more extended aggregates. To test this the 3,5-dimethylphenyl derivative **3** was prepared and crystallized by the vapor diffusion method to give large orthorhombic crystals in the *Pbcn* space group. Once again, the bidentate carboxylic acid dimer motif was the dominating influence on the crystal packing (CO · · · OC was 2.62–2.64 Å with *θ* of 162°). However, in this case a continuous one-dimensional ribbon was formed with alternating and perpendicular projection of the phenyl groups (Fig. 4A). Adjacent ribbons are aligned in such a way as to position the 3,5-dimethylphenyl groups on each strand close to each other (4H · · · 4H, 2.72 Å). This results

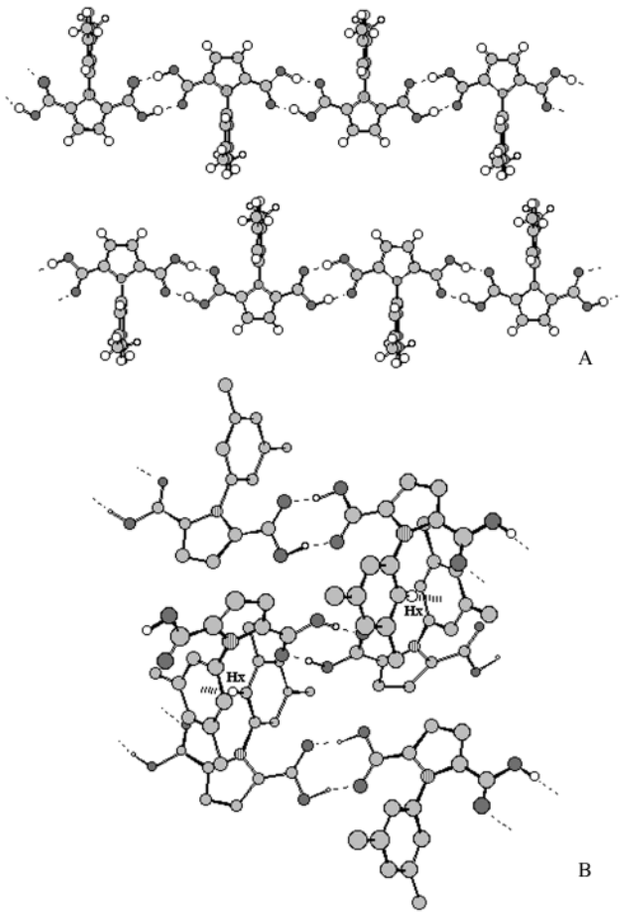
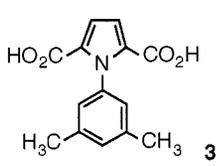


Fig. 4 Packing arrangement of **3**, (A) infinite linear strands and (B) a perpendicular strand penetrating through the interstrand cavity. H–π interactions are shown



3

in the formation of an almost rectangular cavity, 17.3 Å in length and 6.2 Å in width defined by the pyrrole rings of two and the phenyl rings of four subunits. These large pores were occupied by similar, perpendicularly oriented ribbons in an interpenetrating pseudo-catenated manner (Fig. 4B). Edge-to-face π–π interactions were observed between the phenyl-H (Hx in Fig. 4B) and phenyl rings of the concatenated strand with the distance Hx · · · centroid, 3.07 Å.

Two-dimensional aggregates

The close positioning of the 3,5-dimethylphenyl units in **3** clearly pointed to a further stabilization of the structure by incorporating complementary substituents into the phenyl 4-positions (as in Fig. 2C). For example, the 4-carboxyphenyl derivative should form, in addition to the parallel ribbons, a cross linking hydrogen bonding interaction between the two carboxylic acid 4-substituents. This would lead to a two-dimensional sheet structure in which large rectangular cavities would be stabilized by hydrogen bonding along the sides (through the pyrrole carboxylic acids) and edges (through the benzoic acids).

1-(4-Carboxyphenyl)-1*H*-pyrrole-2,5-dicarboxylic acid (4)

To test this idea tricarboxylic acid **4** was synthesized and recrystallized from THF–hexane. The crystals were triclinic in

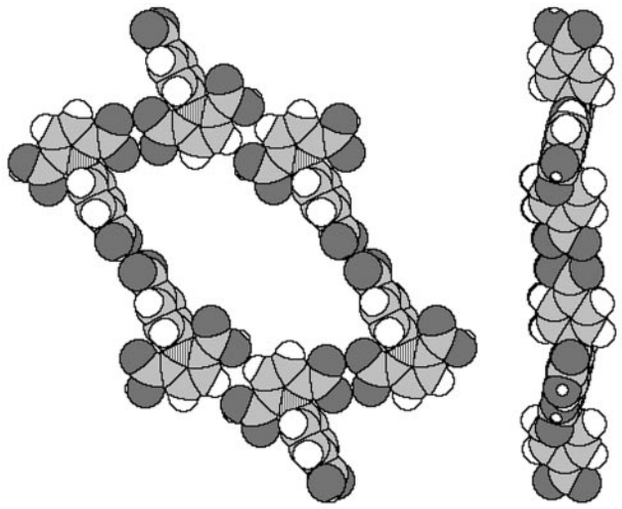
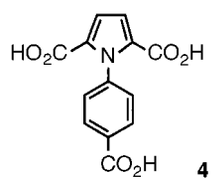


Fig. 5 Top and side views of the pores formed in the crystal structure of **4**, showing a rhombic shape with the size 15.61 × 15.13 Å



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the $P\bar{1}$ space group. The basic packing motif contains rhombic shaped cavities (Fig. 5) formed by cross linking the hydrogen bonded ribbons through benzoic acid dimer motifs with center inversion symmetry (CO · · · OC, 2.66–2.67 Å, $\theta = 156°$). The primary deviations from the idealized representation in Fig. 2C occur in the hydrogen bonded ribbons. Normal bidentate carboxylic acid interactions (CO · · · OC, 2.65 Å) alternate with a slipped positioning of the neighboring pair. This places the pyrrole-3H 2.44 Å from the corresponding carboxylate carbonyl, forming a stabilizing CH · · · O hydrogen bonding interaction.[15]

The cavities formed in this structure are 15.61 × 15.13 Å (pyrrole-N to pyrrole-N) in size and formed from the involvement of six subunit molecules (Fig. 6). Each is filled by disordered solvent molecules. The hydrogen bonded layers were packed in a slightly offset arrangement with an interlayer distance of *ca.* 4.0 Å. The controlling feature of the layer–layer interactions appears to be the slipped face-to-face stacking of the phenyl rings (centroid · · · centroid, 5.6 Å; closest phenyl-H · · · centroid, 3.8 Å). The result is a series of solvent-filled channels passing through the structure.

Three-dimensional networks

Extension of this strategy from two dimensions to three can be envisaged by building a subunit composed of two pyrrole-2,5-dicarboxylic acid units arranged in a perpendicular orientation (as in **5**). This should lead to an orthogonal projection of hydrogen bonded strands to form a three-dimensional network. For example, two pyrrole-2,5-dicarboxylic acid units linked through a 2,2′-disubstituted biphenyl will show a non-planar disposition of the carboxylic acid groups. In order to test this we have prepared the unsubstituted analog, biphenyl-4,4′-bis(pyrrole-2,5-dicarboxylic acid) (**6** where X = H), *via* the reaction of 4,4′-diaminobiphenyl with 2,5-dihydroxyhexa-2,4-dienedioic acid diethyl ester (**1**) followed by hydrolysis. While at this point we have been unable to obtain diffraction quality crystals of this compound, we have observed an analogous perpendicular disposition of two pyrrole rings in the crystal structure of 1-(biphenyl-4-yl)-1*H*-pyrrole-2,5-dicarboxylic acid (**8**) which replaces the covalent bond (in **6**) and

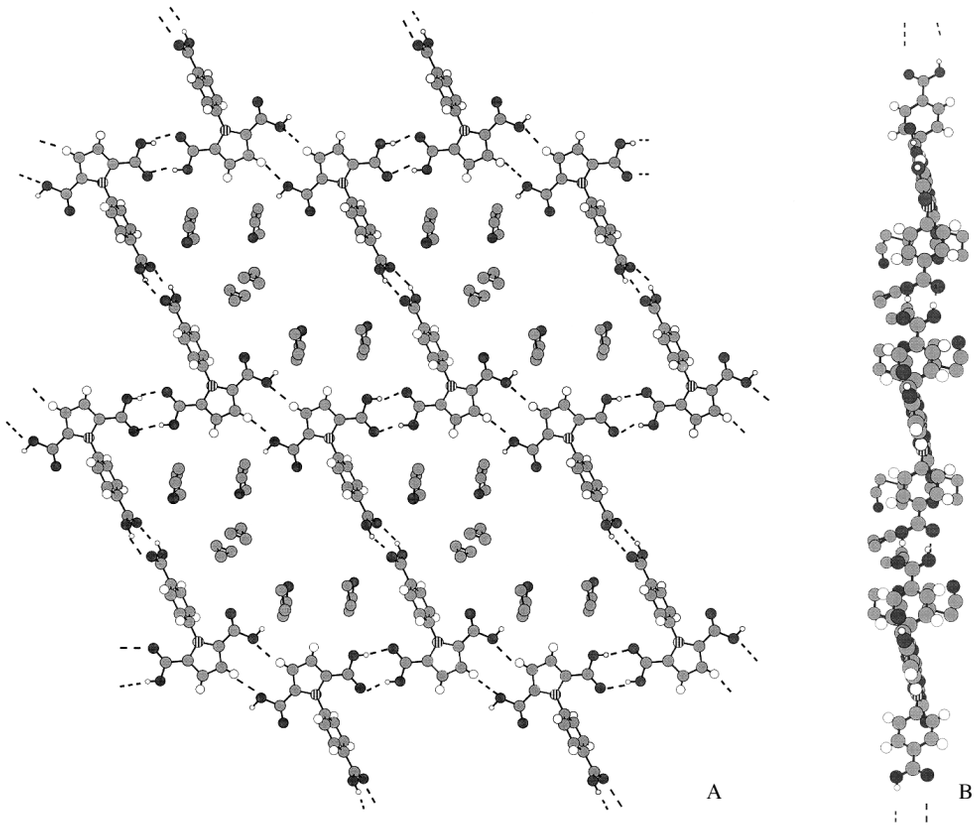
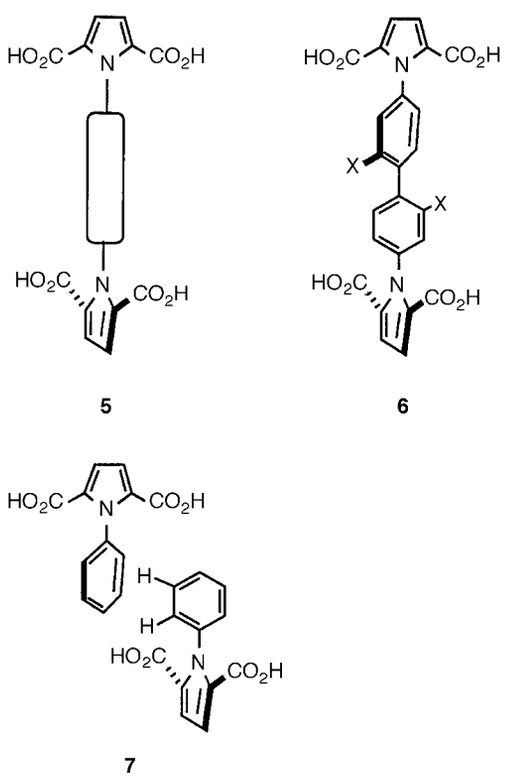


Fig. 6 Top view (A) and side view (B) of one layer structure of **4**; hydrogen bonds are linked and disordered solvent molecules are seen in the cavities

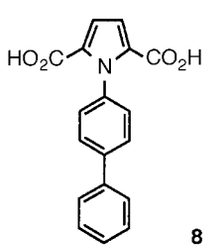


5 **6** **7**

positions the two pyrrole groups at right angles to each other (as in **7**).

1-(Biphenyl-4-yl)-1*H*-pyrrole-2,5-dicarboxylic acid (8)

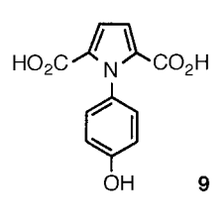
Crystals of **8** were grown by vapor diffusion from THF–hexane and were monoclinic with a $P2_1/n$ space group. The packing arrangement (Fig. 7) shows the formation of a dimeric aggregate in the solid state stabilized by two bidentate carboxylic



8

acid hydrogen bonds (CO · · · OC 2.60 Å, $\theta = 174°$), possessing 2_1 screw symmetry. The two biphenyl groups in the dimer are projected parallel to each other. Each biphenyl forms a double edge-to-face stacking interaction (H · · · centroid 2.84–3.21 Å) with the biphenyl of an adjacent, perpendicularly orientated hydrogen bonded dimer. Due to the size of the biphenyl groups the distance between hydrogen bonded dimers in the same plane increases to 18.6 Å. The additional space is filled by two ordered THF molecules which form hydrogen bonds (CO · · · O 2.58 Å) to the free carboxylic acid groups from dimers in the perpendicular plane (not shown in Fig. 7). A second hydrogen bond to the free carbonyl oxygen is formed from the biphenyl-4H (H · · · OC 2.41 Å, $\theta = 136°$), which also contributes to the overall stabilization of the three-dimensional structure.

1-(4-Hydroxyphenyl)-1*H*-pyrrole-2,5-dicarboxylic acid (9)



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A closely related structure is formed by hydroxyphenyl derivative **9**. Monoclinic crystals of **9** were grown by the vapor diffu-

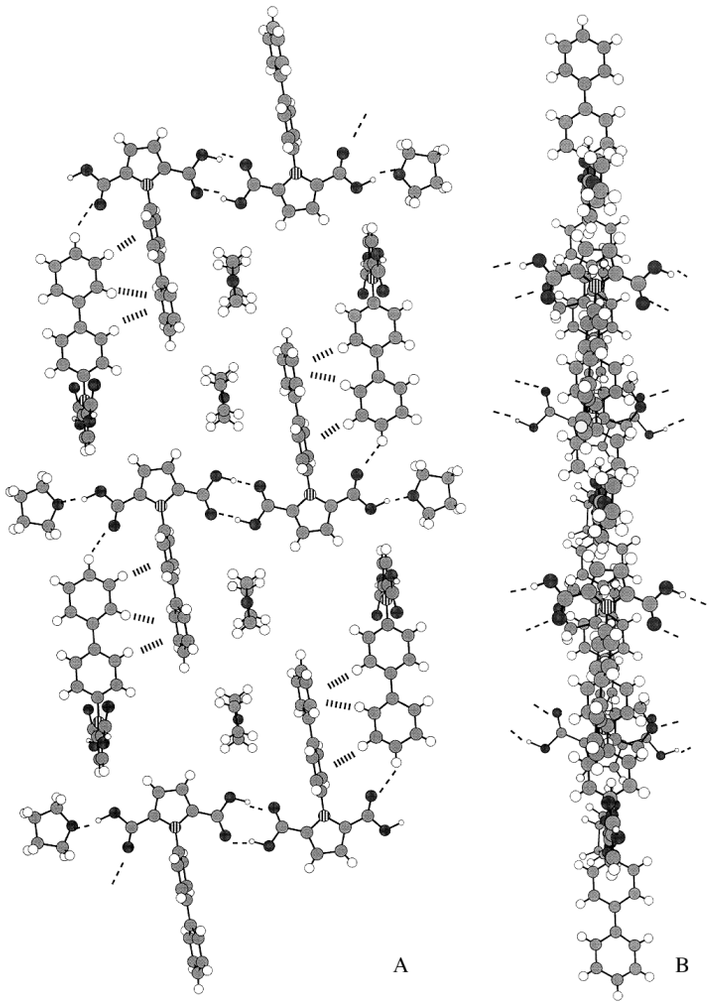

Fig. 7 Top view (A) and side view (B) of one layer crystal packing[16] of **8**. The hydrogen bonds are linked and the H–π interactions are shown.

sion method from THF–hexane mixtures in the $P2_1/n$ space group. Once again hydrogen bonded dimers were formed with an O···O distance of 2.62 Å (Fig. 8). Furthermore, edge-to-face interactions between the phenyl rings on perpendicular dimers (H···centroid, 3.09 Å) are seen, leading to a similar three-dimensional network to that of **8**. In this case, however, the phenyl-OH has taken the place of the biphenyl-4H in Fig. 7 to form a stabilizing hydrogen bond (PhO···OC 2.76 Å, $\theta = 174°$) to the pyrrole carboxylic acid not involved in dimer formation. Interestingly, only one THF molecule is found in each cavity of the H-bonded network, presumably due to the decreased pore size compared to **8**.

Conclusions

We have shown that simple 1-phenylpyrrole-2,5-dicarboxylic acid derivatives form versatile components for the assembly of solid state structures. In the case of unsubstituted or alkyl-substituted phenyl derivatives one-dimensional hydrogen bonded ribbons are formed. Incorporation of a self-complementary carboxylic acid group into the 4-position of the phenyl induces a hydrogen bonded alignment of the pyrrole diacid ribbons and the formation of two-dimensional sheet structures with large solvent-filled channels. Three-dimensional aggregates are formed when the interaction between the phenyl groups is of an edge-to-face type. This leads to the perpendicular disposition of the two pyrrole diacids and the formation of a three-dimensional hydrogen bonded lattice. These results point to the power of hydrogen bonding interactions in controlling the solid state structure of carboxylic acid derivatives, since in every case ribbons of bidentate carboxylic acid dimers are formed. However, this work also underlines the problems associated with trying to predict solid state structures based on these motifs. Despite the presence of a common 1-arylpyrrole-2,5-dicarboxylic core, we find that relatively minor variations in the substitution of the phenyl ring lead to large differences in the packing arrangements in the crystal. We are presently investigating further the solid state properties of di- and triacids of this type by modifying the relative angle between the hydrogen bonding groups and the range of hydrophobic substituents.

Experimental

General

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 (300 and 75 MHz). NMR chemical shifts are reported in ppm downfield from internal TMS. *J* values are given in Hz. Mass spectra were determined at the Department of Chemistry, University of Pittsburgh. EI and FAB mass spectra (MS) were obtained using a Varian MAT CH-5 or VG 7070 mass spectrometer under the direction of Dr Kasi V. Somayajula. Melting points were determined using an Electrothermal capillary melting point apparatus and are uncorrected.

2,5-Dihydroxyhexa-2,4-dienedioic acid diethyl ester (1)

Zinc (activated, 3.0 g, 0.046 mol) was suspended in 100 mL acetone and the suspension was refluxed for several minutes. To the above solution was added ethyl bromopyruvate (21.07 g, 0.097 mol) and the mixture was refluxed under argon for 45 min. Large amounts of a yellow solid appeared during reflux

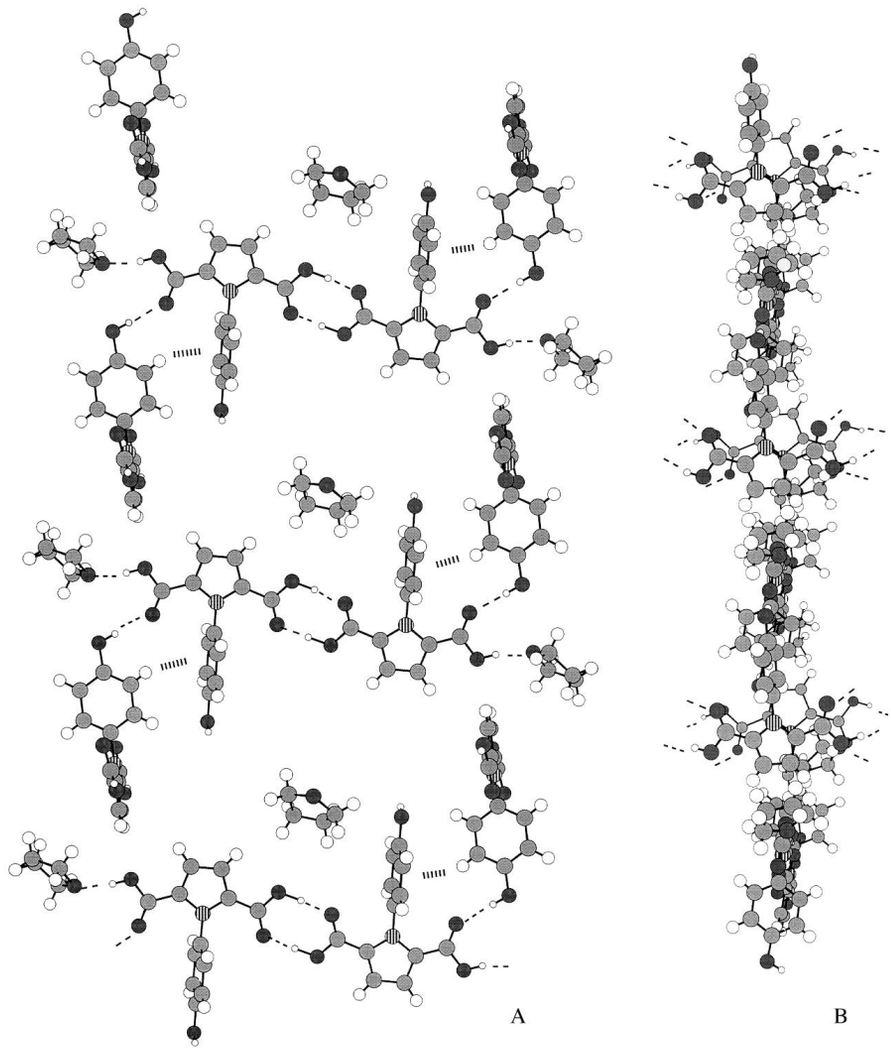

Fig. 8 Top view (A) and side view (B) of one layer crystal packing of **9**. The hydrogen bonding and H–π interactions are shown.

and were filtered off. The solid was washed twice with 1 M H_2SO_4 and was recrystallized from methyl ethyl ketone–toluene to give the first crop of product. The filtrate was poured into 50 mL 1 M H_2SO_4 and the resulting white precipitate was collected and recrystallized to give a second crop of product. Two crops were combined to give the white crystalline compound (1.230 g, 11%): mp 185–190 °C; δ_H(300 MHz, $CDCl_3$) 6.63 (s, 2H), 6.20 (s, 2H), 4.33 (q, *J* 7.1, 4H), 1.36 (t, *J* 7.1, 6H); HRMS *m*/*e* calcd. for $C_{10}H_{14}O_6$ 230.0790, found 230.0787.

Typical procedure for the synthesis of 1-phenylpyrrole-2,5-dicarboxylic acid derivatives.

1-Phenyl-1*H*-pyrrole-2,5-dicarboxylic acid (2)

To a solution of **1** (0.438 g, 1.9 mmol) in 60 mL glacial acetic acid was added aniline (0.354 g, 3.8 mmol) and the mixture was refluxed for 20 min under argon. The solvent was evaporated and the residue was chromatographed on silica gel using CH_2Cl_2 as the eluent. The correct fraction was collected and evaporated *in vacuo* to give diethyl 1-phenylpyrrole-2,5-dicarboxylate (0.350 g, 64%): mp 122–123 °C; δ_H(300 MHz, $CDCl_3$) 7.44 (m, 3H), 7.24 (m, 2H), 7.04 (s, 2H), 4.11 (q, *J* 7.1, 4H), 1.14 (t, *J* 7.1, 6H); HRMS *m*/*e* calcd. for $C_{16}H_{17}NO_4$ 287.1158, found 287.1151.

Diethyl 1-phenylpyrrole-2,5-dicarboxylate (0.057 g, 0.2 mmol) was dissolved in 30 mL absolute ethanol and KOH (0.195 g, 3.5 mmol) was added. The mixture was refluxed for 5 h. After removal of the solvent, the residue was dried *in vacuo*. The solid was then dissolved in 10 mL H_2O and the solution was titrated to pH = 3 with 1 M HCl. The precipitate was filtered off and dried *in vacuo* to give light yellow crystals (0.035 g, 76%): mp 140–144 °C; δ_H(300 MHz, DMSO-d_6) 12.55 (s, 2H), 7.38 (m, 3H), 7.22 (m, 2H), 6.94 (s, 2H); δ_C(75 MHz, DMSO-d_6) 160.6, 139.3, 129.5, 127.9, 127.9, 127.8, 116.3; HRMS *m*/*e* calcd. for $C_{12}H_9NO_4$ 231.0532, found 231.0533.

1-(3,5-Dimethylphenyl)-1*H*-pyrrole-2,5-dicarboxylic acid (3)

Mp 184 °C (dec.); δ_H(300 MHz, DMSO-d_6) 11.93 (s, 1H), 7.01 (s, 1H), 6.91 (s, 2H), 6.82 (s, 2H), 2.27 (s, 6H); δ_C(75 MHz, DMSO-d_6) 160.5, 139.1, 136.8, 129.5, 125.3, 116.2, 21.2; HRMS *m*/*e* calcd. for $C_{14}H_{13}NO_4$ 259.0845, found 259.0844.

1-(4-Carboxyphenyl)-1*H*-pyrrole-2,5-dicarboxylic acid (4)

Mp 238 °C (dec.); δ_H(300 MHz, DMSO-d_6) 11.60 (s, 3H), 7.93 (d, *J* 8.4, 2H), 7.36 (d, *J* 8.4, 2H), 7.00; δ_C(75 MHz, DMSO-d_6) 167.0, 160.5, 143.4, 130.2, 129.5, 129.1, 128.2, 116.7; HRMS *m*/*e* calcd. for $C_{13}H_9NO_6$ 275.0430, found 275.0426.

1-(Biphenyl-4-yl)-1*H*-pyrrole-2,5-dicarboxylic acid (8)

Mp 239–243 °C; δ_H(300 MHz, DMSO-d_6) 11.81 (s, 2H), 7.72 (m, 4H), 7.70 (m, 2H), 7.40 (m, 1H), 7.31 (m, 2H), 6.97 (s, 2H); δ_C(75 MHz, DMSO-d_6) 160.6, 146.9, 146.7, 146.4, 146.1, 145.9, 145.5, 139.4, 138.8, 129.6; HRMS *m*/*e* calcd. for $C_{18}H_{13}NO_4$ 307.0845, found 307.0857.

1-(4-Hydroxyphenyl)-1*H*-pyrrole-2,5-dicarboxylic acid (9)

Mp 243–245 °C; δ_H(300 MHz, DMSO-d_6) 11.94 (s, 2H), 9.56 *(s, 1H), 6.97 (d, J* 8.6, 2H), 6.89 (s, 2H), 6.70 (d, *J* 8.6, 2H); δ_C(75 MHz, DMSO-d_6) 159.2, 157.2, 129.1, 128.6, 116.3, 114.5,

74.4; HRMS *m/e* calcd. for $C_{12}H_9NO_5$ 247.0481, found 247.0475.

Biphenyl-4,4′-bis(1*H*-pyrrole-2,5-dicarboxylic acid) (6)

9 mL conc. HCl (37%) was dissolved in 100 mL absolute ethanol in an ice–water bath. *N*,*N*′-Diphenylhydrazine (1.84 g, 0.01 mol) was added to the above solution under argon and the mixture was stirred for 2.5 h. The precipitate was filtered off, washed with water and dried *in vacuo* to give a light yellow solid (0.216 g). The organic solvent was evaporated and the solution was titrated to pH = 12 with 1M NaOH. The white solid was filtered off and dried *in vacuo* (0.719 g). Two crops were combined to give biphenyl-4,4′-diamine (0.935 g, 51%): mp 116–118 °C; δ_H(300 MHz, DMSO-d_6) 7.19 (d, *J* 8.4, 4H), 6.57 (d, *J* 8.4, 4H), 4.99 (s, 4H); HRMS *m/e* calcd. for $C_{12}H_{12}N_2$ 184.1000, found 184,1003.

To a solution of **1** (0.230 g, 1.0 mmol) in 50 mL glacial acetic acid was added biphenyl-4,4′-diamine (0.100 g, 0.5 mmol) and the mixture was refluxed for 1 h under argon. The solvent was evaporated and the residue was purified by silica gel chromatography using acetone–CH_2Cl_2(3 : 100) as the eluent to give biphenyl-4,4′-bis[2,5-bis(ethoxycarbonyl)-1*H*-pyrrole] (0.145 g, 51%): mp 214–215 °C; δ_H(300 MHz, $CDCl_3$) 7.71 (d, *J* 8.5, 4H), 7.32 (d, *J* 8.3, 4H), 7.07 (s, 4H), 4.13 (q, *J* 7.1, 8H), 1.15 (t, *J* 7.1, 12H); HRMS *m/e* calcd. for $C_{32}H_{32}N_2O_8$ 572.2159, found 572.2149.

To a solution of biphenyl-4,4′-bis[2,5-bis(ethoxycarbonyl)-1*H*-pyrrole] (0.125 g, 0.22 mmol) in 40 mL absolute ethanol was added KOH (0.28 g, 5.0 mmol) and the mixture was refluxed for 5 h. The solvent was evaporated and the residue was dried *in vacuo* overnight. The solid was dissolved in 50 mL H_2O and the solution was titrated to pH = 4 with 1 M HCl. The precipitate was filtered off and washed with water several times and dried *in vacuo* to give the title compound (0.123 g, 84%): mp 290 °C (dec.); δ_H(300 MHz, DMSO-d_6) 11.81 (s, 4H), 7.77 (d, *J* 8.4, 4H), 7.34 (d, *J* 8.4, 4H), 6.98 (s, 4H); ES-MS *m/e* calcd. for $C_{24}H_{16}N_2O_8$ 460.39, found 461.11.

X-Ray structure determination

A Siemens P3 diffractometer controlled *via* Siemens P3/PC software was used for the collection of data. A Siemens SHELXTL package was used for the solutions and refinements of the X-ray structures.

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