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Crystal engineering using co-crystallisation of phenazine with dicarboxylic acids

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Co-crystallisation of phenazine **1** with six dicarboxylic acids was carried out in order to test the robustness of a "strong/weak" coupling, **IV**, in the design of supramolecular assemblies. Complexes of **1** with the *trans*-olefinic acids fumaric **2a** and mesaconic **2b** comprised 1 : 1 (base : acid) stoichiometric tapes assembled solely *via* the strong/weak coupling. Complexes of **1** with the corresponding *cis*-isomeric acids maleic **3a** and citraconic **3b** comprised 1 : 2 stoichiometric tapes in which the acid molecules were assembled to give centrosymmetric dimers. Complexes of **1** with the aliphatic dicarboxylic acids succinic **4a** and glutaric **4b** comprised 1 : 1 and 1 : 2 stoichiometric tapes respectively. In each of the co-crystal structures, tapes may be considered to form stacks in which the long axes of the tapes are parallel. In the 1 : 1 complexes, tapes in adjacent stacks are twisted relative to one another with a similar arrangement of C–H···O interactions occurring for each structure between stacks. In the 1 : 2 complexes, tapes in adjacent stacks are arranged with their long axes parallel. The exact packing arrangement varied from herringbone to a planar-sheet structure. The arrangement of C–H···O interactions also varied between each of the 1 : 2 complexes.

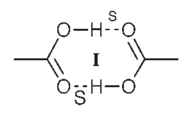
Introduction

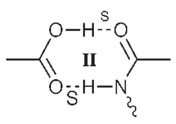
This work forms part of the continuing study of the design of molecular crystals using specific "couplings" or "synthons". The motivation for such research comes from the ability of molecular crystals to exhibit desirable chemical and physical properties.[1,2] These properties are dependent on both the nature of the individual molecules present and on the manner in which they are arranged within the crystal.[3–7] As a result, manipulation of crystal properties requires the control of both molecular and crystal structure. While control of molecular structure lies within the well established field of traditional organic chemistry, the control of crystal structure is part of the much newer field of research of "crystal engineering".[8] The ultimate aim of crystal engineering is to be able to predict the crystal structure adopted by a molecule or a set of molecules starting solely from a knowledge of the molecular structure[9] and to introduce specific functional groups to a molecule in order to direct crystal packing.

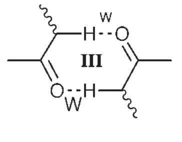
One strategy which has frequently been followed has been to identify couplings[10] or synthons[8] which can reliably be used in arranging for the juxtaposition of individual molecules to create extended molecular arrays. Such arrays will then form a subset of the crystal structure and hence reduce the number of packing modes.[11] A large number of possible synthons (couplings) have been described by Desiraju.[8] Frequently, couplings take the form of a cyclic arrangement and a number of cyclic couplings consisting of two non-covalent interactions were described by Pedireddi *et al.*[10]

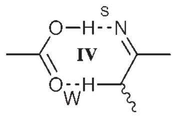
Hydrogen bonding has played a pivotal role in many crystal engineering strategies.[2,12–14] Robustness, highly directional nature and relatively high energy make the hydrogen bond of fundamental importance in the assembly of supramolecular architectures. By appropriate positioning of functional groups, extended molecular arrays have successfully been created including one-dimensional arrays (tapes,[3,11,15–18] ribbons[19,20] and rods[21,22]), sheets[4,6,7] and three-dimensional networks.[23,24] Apart from conventional strong hydrogen bonds as a tool for crystal engineering, weaker interactions such as C–H···O interactions have also been identified as being important in controlling the three-dimensional architecture of a crystal.[25,26] Couplings involving sets of C–H···O interactions have been used successfully to design and assemble a number of supramolecular motifs.[27–29]

Most research involving the use of $R_2^2(8)$ couplings to design supramolecular architectures has centred on couplings in which component interactions are of comparable strength[10] (*e.g.* couplings **I–III**). Pedireddi *et al.*, however, reported that cyclic motif **IV** which consists of both a "strong" and a "weak" hydrogen bond may be used in the design of new supramolecular assemblies.[10] This coupling is possible in crystals containing both an N-heterocycle (with the nitrogen atom substituted in an appropriate position within the aromatic ring) and a carboxylic acid group. Pedireddi *et al.* showed that co-crystals of phenazine and benzoic acid derivatives could couple *via* this motif. Suitable substitution of the benzoic acid allowed an extended network to be formed through the utilisation of additional C–H···O interactions. A molecular tape created solely from coupling **IV** was envisaged and the logical step was to co-crystallise phenazine with a dicarboxylic acid such as terephthalic acid. However, attempts to do this were unsuccessful due to solubility differences. Malonic acid was used as a terephthalic acid substitute with the acid–acid dimer (created *via* coupling **I**) substituting for the benzene ring of the terephthalic acid. An extended tape was produced from the 1 : 2 (base : acid) co-crystal.[10]









The aim of the present paper is to test further the robustness

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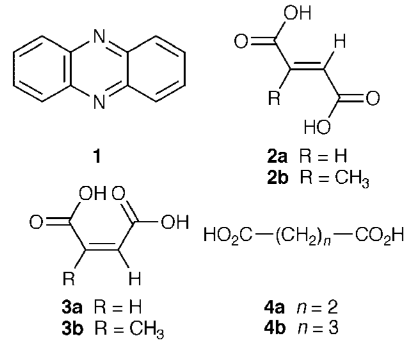
of coupling **IV** in the preparation of new molecular co-crystals and in the creation of supramolecular tapes. In particular, we wished to explore whether the stereochemistry of the acid moiety might be used to control the geometry of the tape. Hence, phenazine **1** was co-crystallised with each of the acids fumaric **2a** and maleic **3a** (and their methyl derivatives: mesaconic **2b** and citraconic **3b**). Complexes of **1** with a series of saturated aliphatic dicarboxylic acids $HO_2C(CH_2)_n$-CO_2H with $n=2$ or 3 were also prepared. The crystal structures of six complexes of **1** are reported and the hydrogen bond geometry assessed in terms of the specific couplings present. Extended tapes are produced in each case. The tertiary structure is assessed in terms of the packing of these tapes and the role of C–H···O interactions.



2c = 1+2a (1:1)
2d = 1+2b (1:1)
3c = 1+3a (1:2)
3d = 1+3b (1:2)
4c = 1+4a (1:1)
4d = 1+4b (1:2)

Experimental

Reagent grade chemicals were used. Co-crystals suitable for single-crystal X-ray diffraction were grown at room temperature by the process of slow evaporation.†

X-Ray diffraction was carried out using an Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo-K(α) radiation. All diffraction data were collected at room temperature. Cell parameters were obtained from 25 accurately centred reflections in the range $30<2\theta<40°$ ($16<2\theta<30°$ for **3c**) and refined using a least-squares routine. Data were collected in the range $1.5<2\theta<25°$ ($1.5<2\theta<22°$ for **3c**) using an ω–2θ scan type for most data collections with a variable scan speed dependent on the intensity of the reflection. Standard reflections were used to check the stability of the crystal; no loss in stability was observed. Data were processed and Lorentz-polarisation corrections applied using the TEXSAN[30] software package. No absorption correction was applied. The structures were solved by Direct Methods using SHELXS 86[31] and refined by full-matrix least squares using the SHELXL 93[32] package. Extinction coefficients were applied during the refinements of structures **2d**, **3c**, **4c**. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms involved in O–H···O or O–H···N hydrogen bonds were located from the difference Fourier map and refined isotropically. All other hydrogens were placed geometrically on their parent atoms ($d_{C-H}=0.93$) and refined with common and variable isotropic thermal parameters. Geometrical calculations were carried out using the SHELXL 97[33] package (no estimated standard deviations are given for calculations involving geometrically placed hydrogen atoms). Packing diagrams were produced using PLUTO,[34] TEXSAN and CERIUS^2.[35]

CCDC reference number 1145/207.

See http://www.rsc.org/suppdata/jm/a9/a908214j/ for crystallographic files in .cif format.

CSD Searches

Searches were carried out using the October 1998 release of the Cambridge Structural Database (CSD)[36] database using QUEST3D[37] version 2.3.7. Only entries which were error free at the 0.05 Å level were accepted. Disordered structures and those with $R>0.10$ were discarded as were organometallic entries and those having unmatched chemical and crystallographic connectivities. The visualisation package PLUTO was used to analyse the retrieved structures.

Results

Crystal structure of 2c (phenazine : fumaric acid)

1 : 1 Co-crystals form in the monoclinic crystal system with space group $P2_1/c$ (Table 1). The atomic numbering is shown in Fig. 1(a). An extended tape is generated *via* coupling **IV**, Fig. 1(b). A summary of the hydrogen bond geometries of coupling **IV** is given in Table 2. The dihedral angle between the least squares planes N1, C1–C6 and O1, O2, C7, C8 is 7.4(2)°.

Tapes form stacks (Fig. 1(c)) in which the tape axes and planes are parallel. Within these stacks, tapes are displaced parallel and perpendicular to the tape axis of the tape above or below. Stacks pack parallel to the *c* axis with adjacent stacks twisted by an angle, θ, of *ca.* 80° with respect to one another. A representative diagram of this is shown.

Table 1 Crystallographic data for the various complexes

Co-crystal	2c	2d	3c	3d	4c	4d
Empirical formula	$C_{16}H_{12}N_2O_4$	$C_{17}H_{14}N_2O_4$	$C_{20}H_{16}N_2O_8$	$C_{22}H_{20}N_2O_8$	$C_{16}H_{14}N_2O_4$	$C_{22}H_{24}N_2O_8$
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	5.3361(6)	26.83(3)	5.513(2)	6.6790(9)	5.2792(4)	5.6755(5)
b/Å	8.7650(8)	7.095(4)	6.733(2)	18.660(2)	9.057(1)	9.997(2)
c/Å	14.952(1)	19.61(3)	13.026(7)	8.933(1)	15.054(1)	10.866(1)
α/°	90	90	95.32(3)	90	90	116.61(1)
β/°	98.871(8)	127.46(7)	99.39(4)	105.13(2)	99.141(7)	95.12(1)
γ/°	90	90	100.24(3)	90	90	90.04(1)
V/Å^3	690.95(11)	2964(5)	465.7(3)	1074.7(2)	710.6(1)	548.4(1)
Z	2	8	1	2	2	1
μ/mm^{-1}	0.104	0.101	0.116	0.105	0.102	0.103
Reflections collected	1261	2689	1723	1844	1292	2017
Independent reflections	1212 ($R_{int}=0.0141$)	2601 ($R_{int}=0.0239$)	1644 ($R_{int}=0.0142$)	938 ($R_{int}=0.0527$)	1244 ($R_{int}=0.0138$)	1906 ($R_{int}=0.0222$)
$R1$ [$I>2\sigma(I)$]	0.0340	0.0407	0.0339	0.0477	0.0347	0.0463
$wR2$ [$I>2\sigma(I)$]	0.0919	0.1010	0.0887	0.1041	0.1011	0.1099

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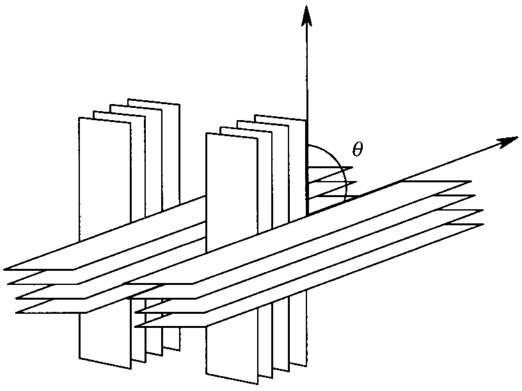
†Crystals of compound **2c** were grown from a 1 : 2 (base : acid) ratio of starting components in methanol, of **2d** from a 1 : 1 ratio in ethyl acetate, of **4c** from a 1 : 1 ratio of starting components in ethyl acetate–methanol, and of **3c**, **3d** and **4d** from a 1 : 2 ratio of starting components in ethyl acetate.



Both carbonyl and hydroxyl oxygens (O2 and O1 respectively) are involved in C–H···O interactions with aromatic hydrogens in adjacent stacks (C1–H1···O2 2.491, 3.319(2) Å, 148.4°; C6–H6···O1 2.867, 3.521(2) Å, 128.4°) (Fig. 1(d)).

Crystal structure of 2d (phenazine : mesaconic acid)

Monoclinic crystals of the 1 : 1 complex **2d** form in the space group $C2/c$. Fig. 2(a) shows the atomic numbering scheme. An acentric tape is generated *via* the self-assembly of molecules through coupling **IV** with the methyl groups lying on the same side of a tape (Fig. 2(b)). Coupling **IV** is present in two crystallographically distinct environments, referred to as (i) and (ii). Coupling (i) exists between the carboxyl moiety closest to the methyl substituent and **1**. The O···N distance is shorter in coupling (i) than in (ii) but the C···O distance is significantly longer (Table 2). The tapes are approximately flat with the dihedral angle between the least-squares planes of **1** and the carboxyl groups being 8.4(1)° for coupling (i) and 6.3(1)° for coupling (ii).

Tapes form stacks (Fig. 2(c)) in which the tape axes and planes are parallel and in which adjacent tapes are related by inversion symmetry leading to a centric space group. These stacks then pack parallel to the *c* axis and are twisted by an angle of *ca.* 30° with respect to one another.

C–H···O interactions are observed between the acid groups of one stack and the aromatic hydrogens in an adjacent stack (Fig. 2(d)) (C4–H4···O4 2.782, 3.429(5); C9–H9···O4 2.769, 3.644(5); C10–H10···O2 2.476, 3.210(6); C3–H3···O3 2.704, 3.603(6) Å). No inter-tape C–H···O contacts are observed involving O1 which is situated closest to the methyl group.

Crystal structure of 3c (phenazine : maleic acid)

1 co-crystallises with **3a** in the ratio 1 : 2 to yield triclinic crystals in the space group $P\bar{1}$. Fig. 3(a) shows the atomic numbering scheme. An extended molecular tape is formed (Fig. 3(b)). Within this tape motif, two types of coupling, **I** and **IV**, are observed. Table 2 summarises the interaction geometries. Coupling **I** is centrosymmetric. Coupling **IV** is distorted with the acid moiety at an angle of 35.4(1)° to the aromatic ring and the C–H···O component being longer and less linear than in complexes **2c** and **2d**. Since the carbonyl oxygen, O4, is not coplanar with the aromatic ring it is able to form a C–H···O interaction with an olefinic hydrogen on an acid molecule in an adjacent tape (C3–H3···O4 2.550, 3.365(2) Å) (Fig. 3(c)). These tapes are related by translation parallel to the *a* axis and can be considered to form a stack. Fig. 3(d) shows three such stacks viewed along the *a* axis. A C–H···O interaction is present between stacks (C5–H5···O2 2.655, 3.352(3) Å).

Within molecules of compound **3a** the carboxyl groups are twisted by 58.02(7)° with respect to one other. This twisting is necessary in the absence of an intramolecular hydrogen bond in order to overcome repulsion between oxygen atoms.

Crystal structure of 3d (phenazine : citraconic acid)

A 1 : 2 complex of **1** and **3b** forms in the space group $P2_1/n$. The atomic numbering is given in Fig. 4(a). Molecules are assembled into tapes (Fig. 4(b)) *via* an O–H···N hydrogen bond and centrosymmetric coupling **I** (Table 2). The interacting carboxyl moiety approaches **1** at an angle of 78.1(2)°. The O···N hydrogen bond distance is shorter than in the other co-crystals. The absence of the C–H···O component of coupling **IV** may allow the interacting hydroxyl group to approach closer to the aromatic ring. The absence of coupling **IV** also allows the formation of two additional C–H···O interactions between the aromatic hydrogens of molecule **1** and the adjacent carbonyl and hydroxyl oxygens of coupling **I** (C1–H1···O4 2.598, 3.364(6); C2–H2···O3 2.681, 3.589(6) Å) (Fig. 4(b)). This results in the tape being nearly planar (the angle between coupling **I** and **1** is *ca.* 5°). No intramolecular hydrogen bond is observed in molecules of **3b**; the dihedral angle between carboxyl moieties within one molecule is 79.6(2)°.

Tapes stack with their planes and long axes parallel. The carbonyl oxygen, O1, points out of the plane of the tape and forms a C–H···O interaction with an aromatic hydrogen from a molecule of **1** in a vertically adjacent tape (C10–H10···O1

Table 2 Selected hydrogen bond parameters for the various complexes

Co-crystal	D–H···O	H···A/Å	D···A/Å	D–H···O/°	Symmetry operator
Coupling **IV**					
2c	O1–H1O···N1	1.87(2)	2.764(2)	167(2)	$x-1,y,z$
	C5–H5···O2	2.41	3.303(2)	162	$x-1,y,z$
2d(i)	O1–H1O···N2	1.84(3)	2.736(4)	159(3)	$-x+\frac{3}{2},-y+\frac{3}{2},-z$
	C5–H5···O2	2.59	3.473(5)	159	$-x+\frac{3}{2},-y+\frac{3}{2},-z$
2d(ii)	O3–H3O···N1	1.96(3)	2.827(4)	164(2)	$-x+1,-y+1,-z$
	C11–H11···O4	2.33	3.219(4)	160	$-x+1,-y+1,-z$
3c	O3–H3O···N1	1.86(3)	2.741(2)	167(2)	$-x+1,-y,-z+2$
	C6–H6···O4	2.71	3.467(3)	140	$-x+1,-y,-z+2$
3d	O2–H2O···N1	1.73(8)	2.716(6)	164.9(9)	$-x+1,-y+1,-z+1$
4c	O1–H1O···N1	1.95(3)	2.792(2)	167(3)	x,y,z
	C5–H5···O2	2.42	3.314(2)	161	x,y,z
4d	O1–H1O···N1	1.83(4)	2.753(3)	167(3)	x,y,z
	C2–H2···O2	2.54	3.410(3)	157	x,y,z
Coupling **I**					
3c	O1–H1O···O2	1.63(3)	2.639(2)	176(3)	$-x+1,-y+1,-z+2$
3d	O4–H4O···O3	1.64(7)	2.631(5)	173(7)	$-x,-y+2,-z$
4d	O4–H4O···O3	1.66(4)	2.631(3)	176(4)	$-x+1,-y,-z$

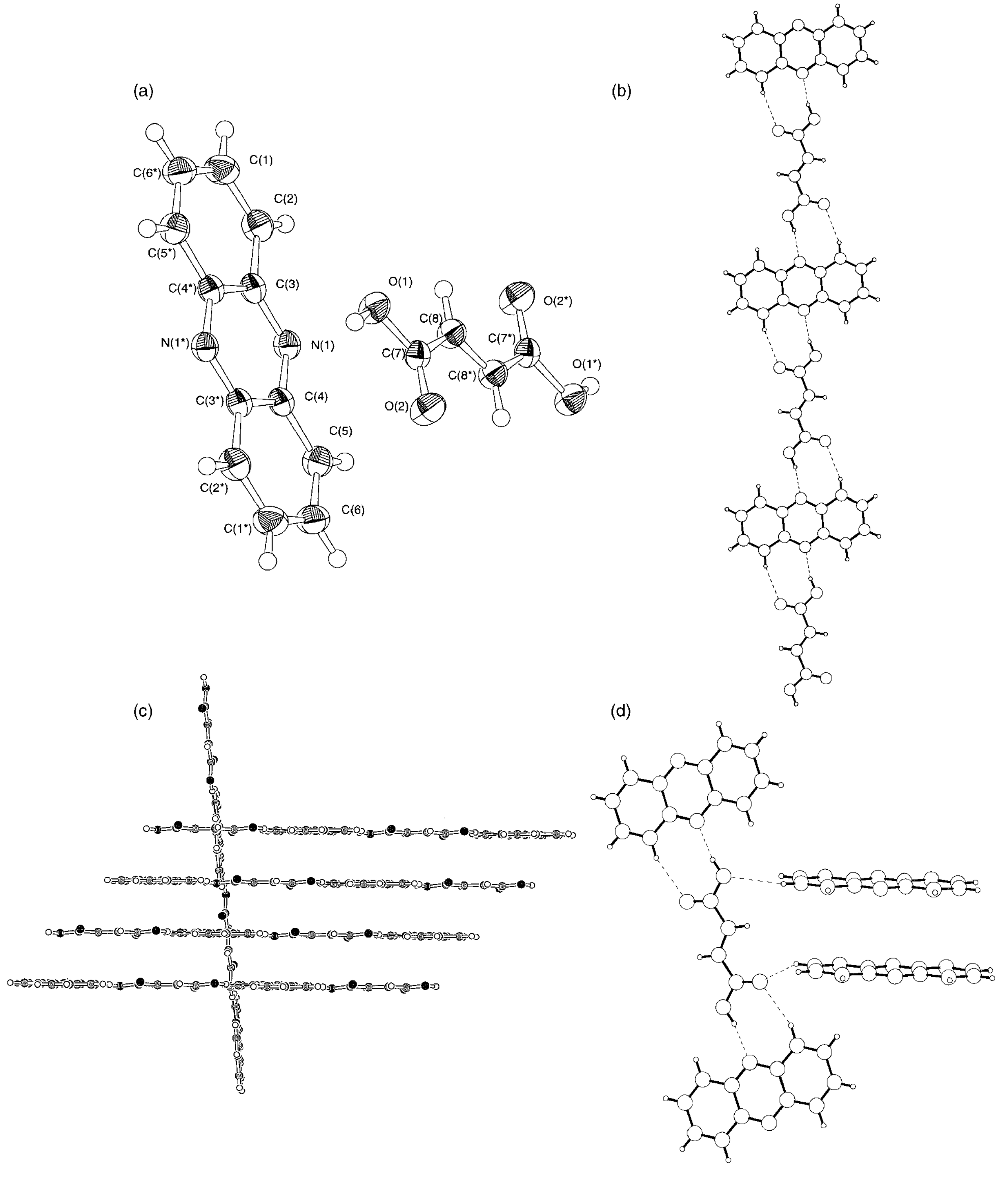


Fig. 1 (a) Numbering scheme for compound **2c** (**1** : **2a** in 1 : 1 ratio) with thermal ellipsoids at a 50% probability level. (b) Tape formed through coupling **IV**. (c) Packing diagram of **2c** showing a stack of tapes (horizontal motif). One tape from an adjacent stack has been included to highlight the inter-tape twisting. (d) View showing inter-stack C–H···O interactions.

2.647, 3.53(1) Å, 158°). Stacks are aligned in a herringbone arrangement (Fig. 4(c)) with van der Waals interactions taking place between methyl groups which are situated at the edges of the tapes. There are no significant C–H···O interactions between stacks.

Crystal structure of 4c (phenazine : succinic acid)

A 1 : 1 co-crystal forms in the monoclinic space group $P2_1/n$. Fig. 5(a) shows the atomic numbering. Fig. 5(b) shows the tape that is generated *via* coupling **IV**. The angle between the acid moiety and **1** is 10.0(2)°.

Tapes form stacks (Fig. 5(c)) in which the long axes and planes of the tapes are parallel and in which adjacent tapes are displaced both parallel and perpendicular to the tape axis. Adjacent stacks pack parallel to the *c* axis and are twisted by an angle of *ca.* 81° with respect to each other. C–H···O interactions take place between neighbouring stacks in a similar manner to those observed in co-crystal **2c** (C1–H1···O2: 2.538, 3.362(3); C6–H6···O1: 2.766, 3.467(3) Å) (Fig. 5(d)).

Crystal structure of 4d (phenazine : glutaric acid)

1 : 2 Co-crystals of **1** and **4b** form in the triclinic space group $P\bar{1}$. The atomic numbering is shown in Fig. 6(a). A tape is

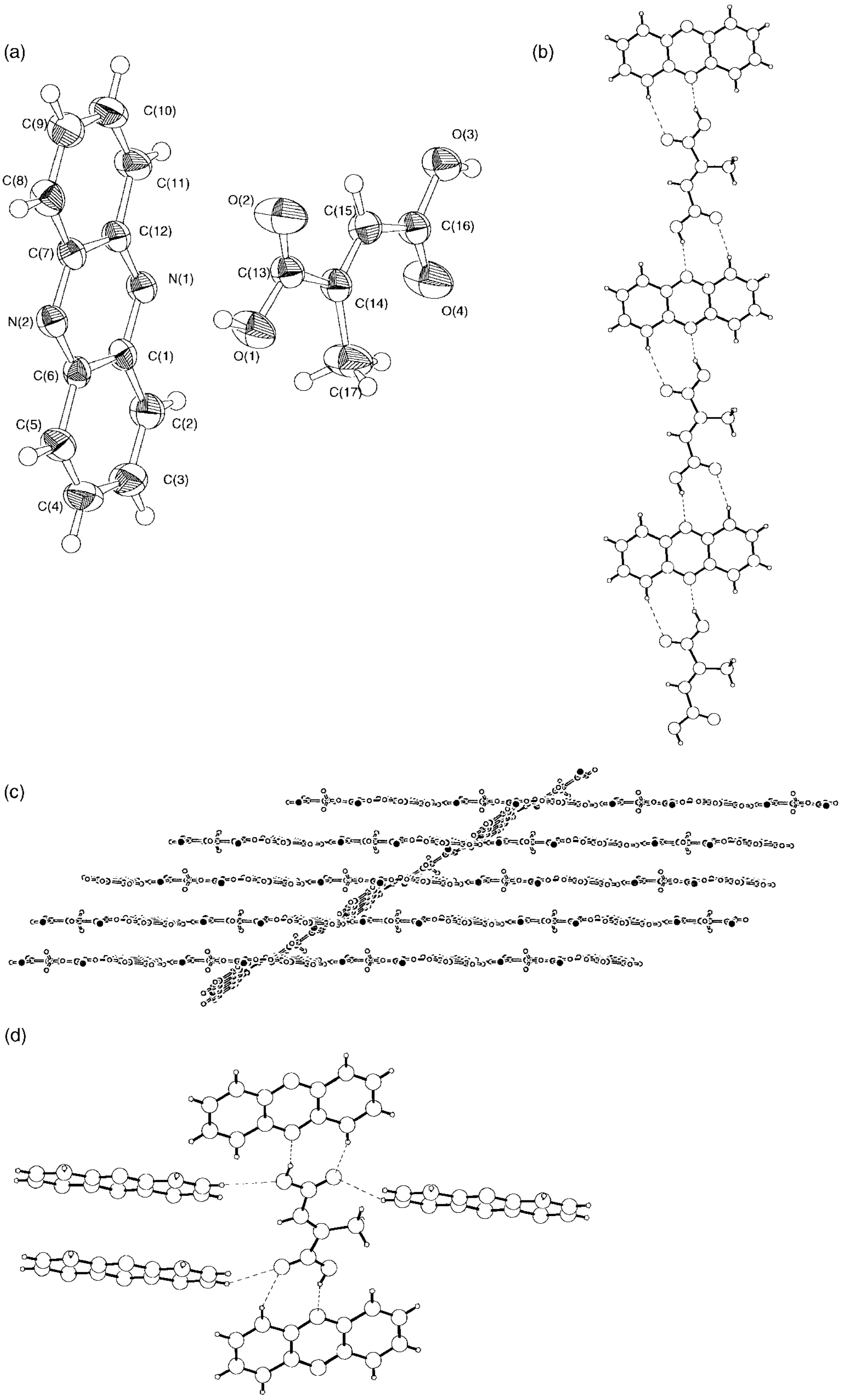


Fig. 2 (a) Numbering scheme for compound **2d** (**1** : **2b** in 1 : 1 ratio) with thermal ellipsoids at a 50% probability level. (b) Acentric tape is generated *via* coupling **IV**. (c) Packing diagram of **2d** showing stacking of tapes (horizontal motif). One tape from an adjacent stack has been included to show the inter-stack twisting. (d) View showing inter-stack C–H···O interactions.

generated (Fig. 6(b)) in which molecules are assembled *via* couplings **IV** and **I** (Table 2). The interplanar angle between the interacting carboxyl group and **1** is 13.6(2)°. In contrast to acids **3a** and **3b**, carboxyl groups on a given molecule of **4b** are only twisted by 7.0(2)° relative to one another. The carboxyl groups are further apart due to the longer aliphatic backbone and hence twisting is not now required to overcome oxygen–oxygen repulsion.

The structure consists of planar sheets (Fig. 6(c)) in which tapes fit together sideways connected by C–H···O interactions (C3–H3···O2 2.781, 3.700(3); C4–H4···O3 2.474, 3.368(4) Å).

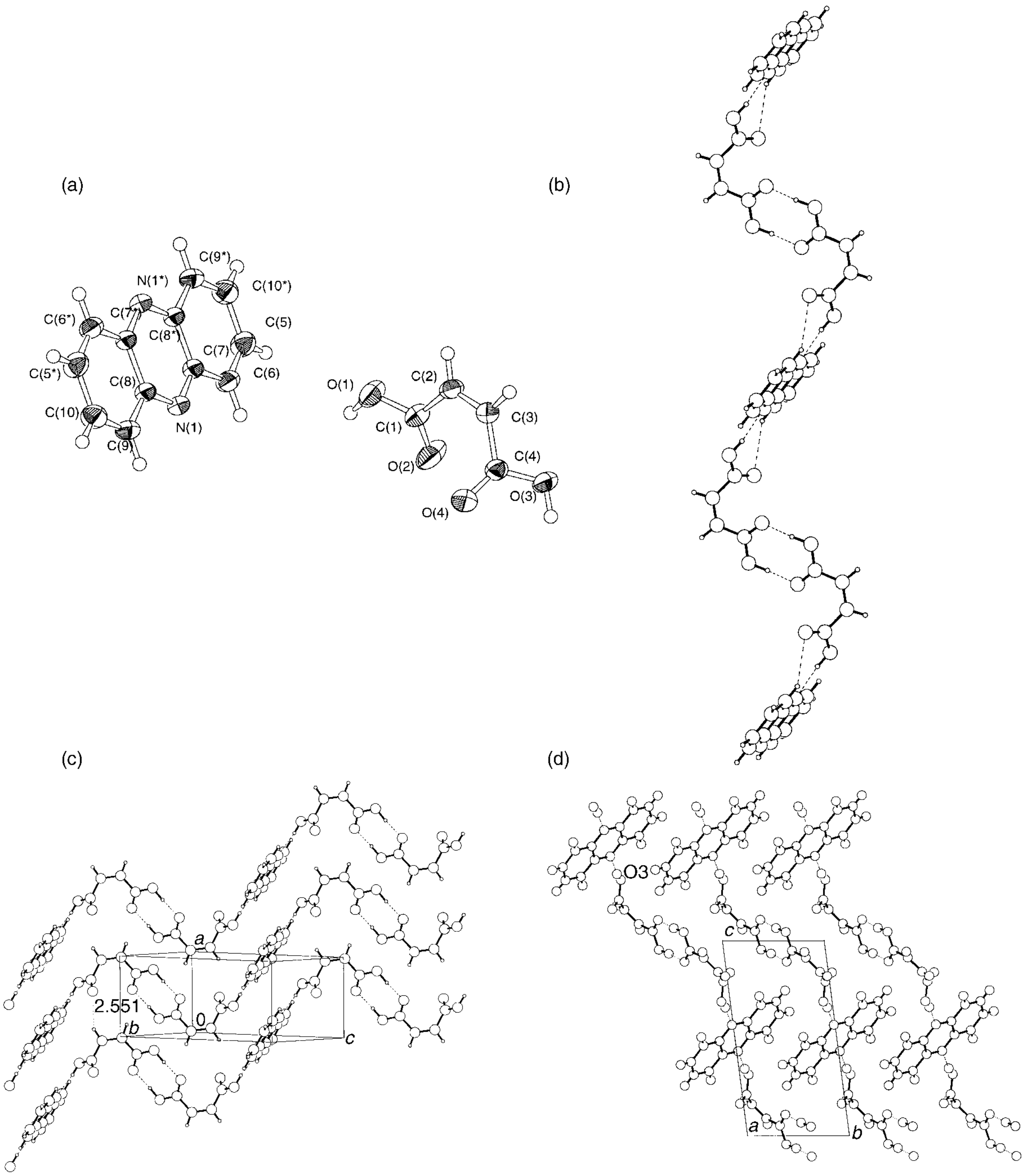


Fig. 3 (a) Numbering scheme for compound **3c** (**1**:**3a** in 1 : 2 ratio) with thermal ellipsoids at a 50% probability level. (b) Extended 1 : 2 tape generated through couplings **IV** and **I**. (c) Tapes stack parallel to the *a* axis with a C–H···O interaction between tapes as shown. (d) View down the *a* axis showing three stacks.

Discussion

Coupling IV in complexes 2c–2f

Coupling **IV** is present in five of the six structures reported. In all six structures the O–H···N component of coupling **IV** is present. The geometry of coupling **IV** in the 1 : 1 complexes (**2c**, **2d**, **4c**) is such that the interplanar angle between the acid moiety and **1** is between 7 and 10°. The geometry of the O–H···N hydrogen bond (Table 2) for the 1 : 1 complexes falls within the expected values for such an interaction.[38] The geometries of the C–H···O interactions (Table 2) for the 1 : 1 complexes may be representative of relatively strong C–H···O interactions.[29] Coupling **IV** is found in two of the three 1 : 2 co-crystals (**3c** and **4d**) and undergoes distortion, with the interplanar angle between the interacting carboxyl groups and **1** covering the range 14–78°. The O–H···N hydrogen bond is robust and is present in each of the 1 : 2 complexes (in general with shorter O···N distances than observed for most of the 1 : 1 co-crystals). However, the C–H···O interaction undergoes varying degrees of distortion from linearity as well as in length. In the two cases when the C–H···O interaction of coupling **IV** is distorted by twisting of the carbonyl oxygen out of the plane of the motif (*i.e.* in **3c** and **3d**) an alternative C–H···O interaction is formed.

Coupling IV from the CSD

An initial search was carried out in order to determine how many crystal structures had the appropriate functional groups for coupling **IV** to be possible *i.e.* crystal structures containing a carboxyl group and an N-heterocycle with the nitrogen atom in the correct position in the aromatic ring. This resulted in 51 structures (excluding duplicates) of which 20 contained the O–H···N hydrogen bond of coupling **IV**. Out of these 20

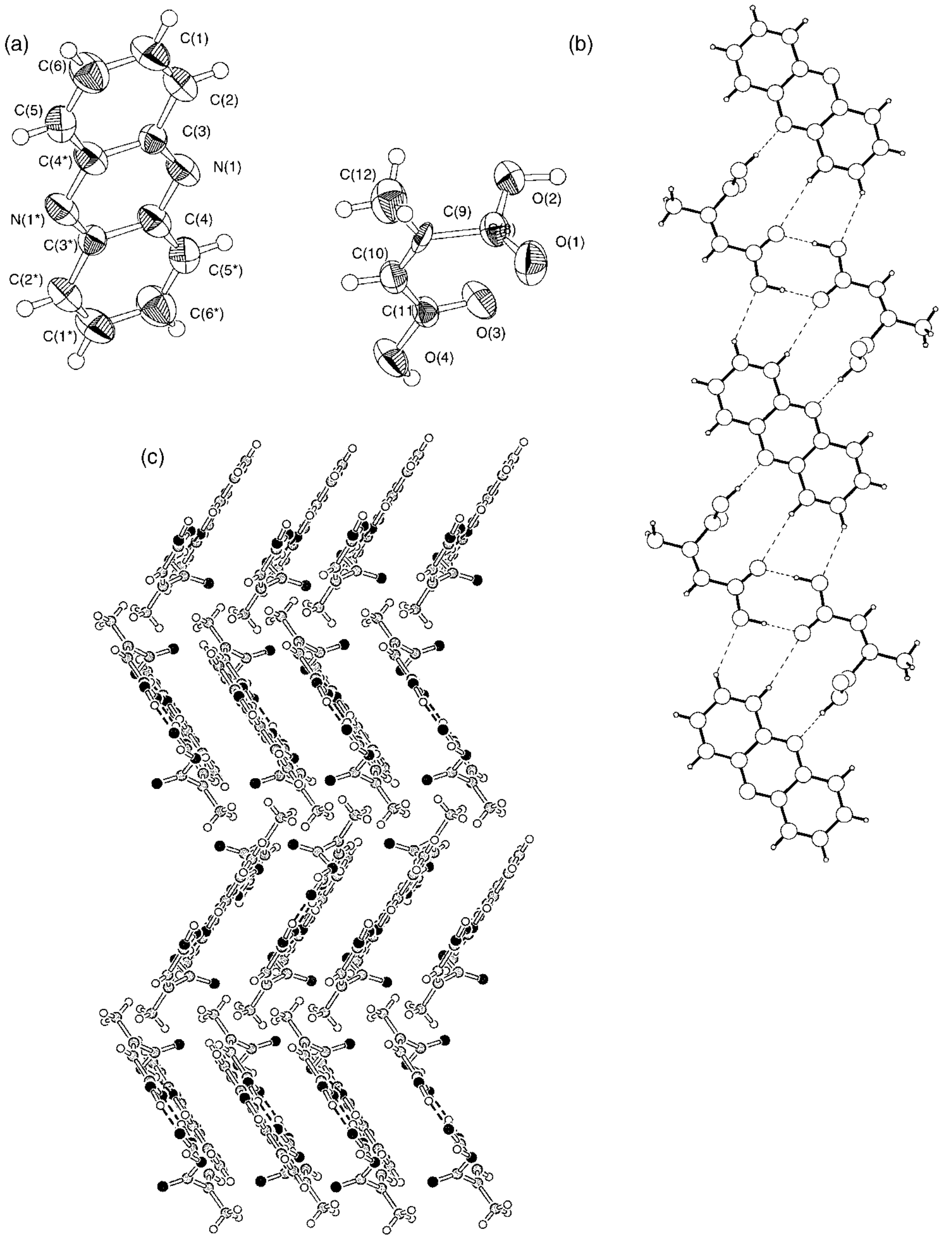
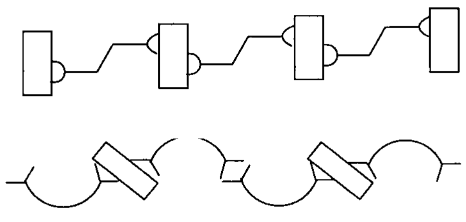


Fig. 4 (a) Numbering scheme for compound **3d** (**1** : **3b** in 1 : 2 ratio) with thermal ellipsoids at a 50% probability level. (b) Extended tape in which molecules assemble *via* an O–H···N interaction and coupling **I**. Note the presence of two intra-tape C–H···O interactions between coupling **I** and the aromatic hydrogens of adjacent molecules of **1**. (c) Packing diagram showing the herringbone arrangement of tapes in adjacent stacks.

structures, coupling **IV** was found in 11. These results show that coupling **IV** does exist in a number of quite different crystal structures, however, its robustness, as may be expected, is limited by the presence of competing interactions.

Description of tape motif

The tape motifs observed in complexes **2c**–**4d** can be divided into two classes according to stoichiometry and the type of couplings present. Complexes **2c**, **2d** and **4c** gave 1 : 1 tapes in which molecules were coupled purely by synthon **IV**. Complexes **3c**, **3d** and **4d** gave 1 : 2 tapes with the acid molecules forming centrosymmetric dimers through coupling **I**. The type of tape formed may be related to the position of the carboxyl moieties on the interacting acid molecule. Molecules in which the carboxyl groups point in opposite directions (*i.e.* for *trans*-olefinic and aliphatic acids with n even) form 1 : 1 tapes (see right). Molecules in which the acid groups point in the same direction (*i.e. cis*-olefinic and saturated aliphatics with n odd) form 1 : 2 tapes (see right). A similar result was obtained by Pedireddi *et al.* upon co-crystallising **1** with malonic acid (an aliphatic dicarboxylic acid having $n = 1$).



Figs. 1(b), 2(b) and 5(b) show that the hydrogen bonding in the 1 : 1 tapes runs approximately parallel with the tape axis. In the 1 : 2 tapes, the hydrogen bond network runs in a zigzag manner relative to the tape axis. The constituent molecules within each of the 1 : 1 tapes were coplanar (within *ca.* 10°) giving rise to near-flat tapes. The overall tape topology within the 1 : 2 complexes varied from one complex to another. In complexes of both **3d** and **4d** tapes are relatively flat although

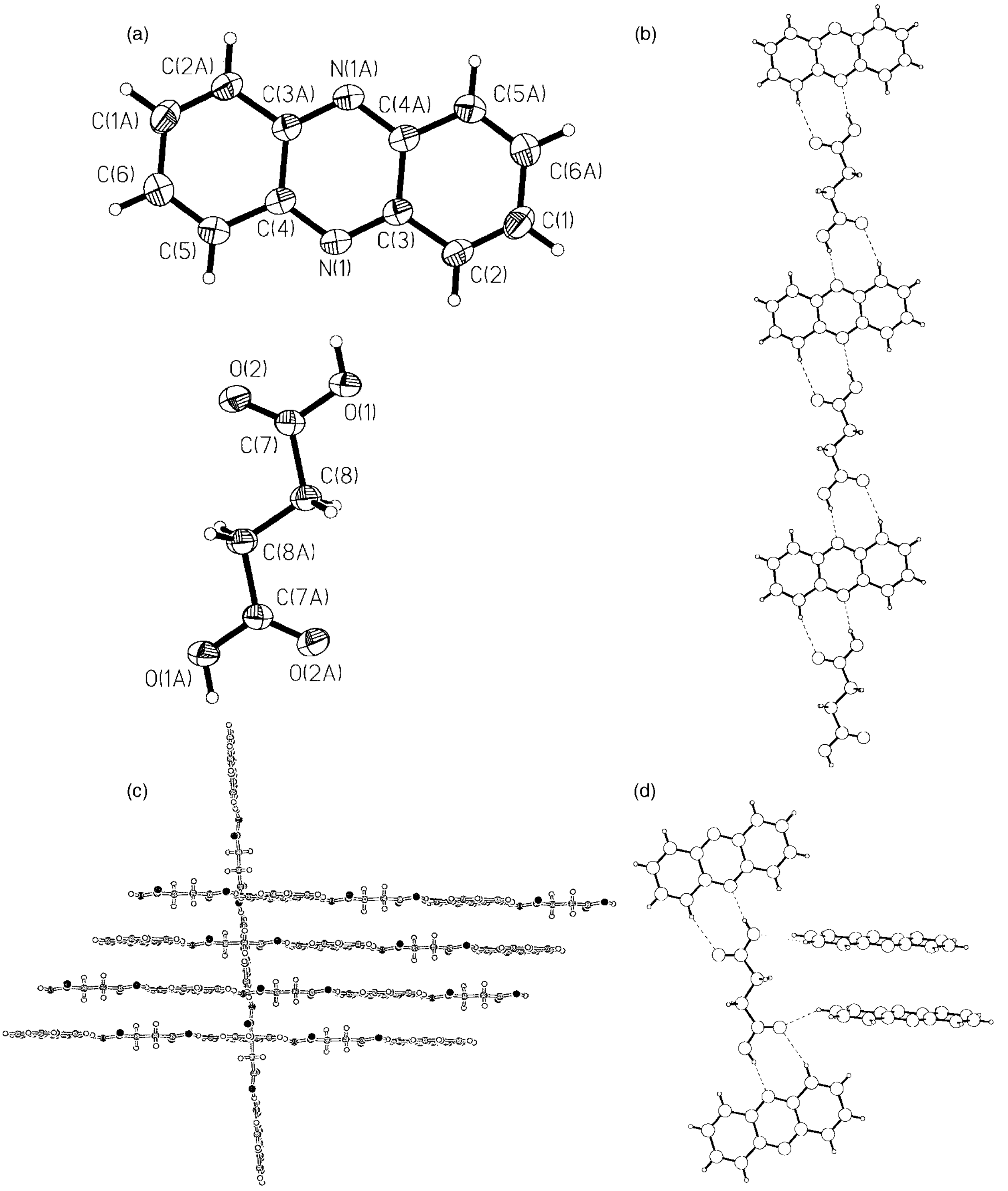


Fig. 5 (a) Numbering scheme for compound **4c** (**1** : **4a** in 1 : 1 ratio) with thermal ellipsoids at a 50% probability level. (b) Tape formed through coupling **IV**. (c) Packing diagram showing stacking of tapes (horizontal motif). One tape from an adjacent stack has been included to highlight inter-stack twisting of tapes. (d) View showing inter-stack C–H···O interactions.

the intra- and inter-tape interactions within these two complexes differ. Tapes of complex **3c**, however, are quite distorted from planarity with the plane of **1** being approximately normal to coupling **I**.

Packing of tapes

A key strategy in crystal engineering has been to try to reduce the number of packing arrangements open to a molecule by forcing it into a pre-designed network.[11,39] This may be a tape, sheet, or three-dimensional network. Much work has been carried out in order to find systems which reliably form tapes. In cases where tapes are consistently formed, the crystal engineering process reduces to the rationalisation of how those tapes pack in the crystal.

We have shown that it is possible to reproduce a tape motif by co-crystallising a number of different dicarboxylic acids with compound **1** through couplings **IV** and **I**. A number of points can be highlighted with respect to the packing of these tapes. The topology of the 1 : 1 tapes is similar as is the packing adopted. The 1 : 1 tapes all pack by forming stacks in which the long axes and the planes of the constituent tapes are parallel. The long axes of tapes in adjacent stacks are twisted by an angle, θ, relative to one another. In complexes **2c** and **4c** the angle is *ca.* 80°, whereas in **2d** the angle is 30°. In each structure C–H···O interactions are observed between oxygens in one stack and aromatic hydrogens in an adjacent stack (Figs. 1, 2 and 5(d)). In complex **2d**, however, formation of inter-stack C–H···O interactions is partially inhibited by the presence of the methyl group.

There are two questions that arise as a result of these observations. First, why do tapes in adjacent stacks twist and secondly, what determines the twist angle? A possible

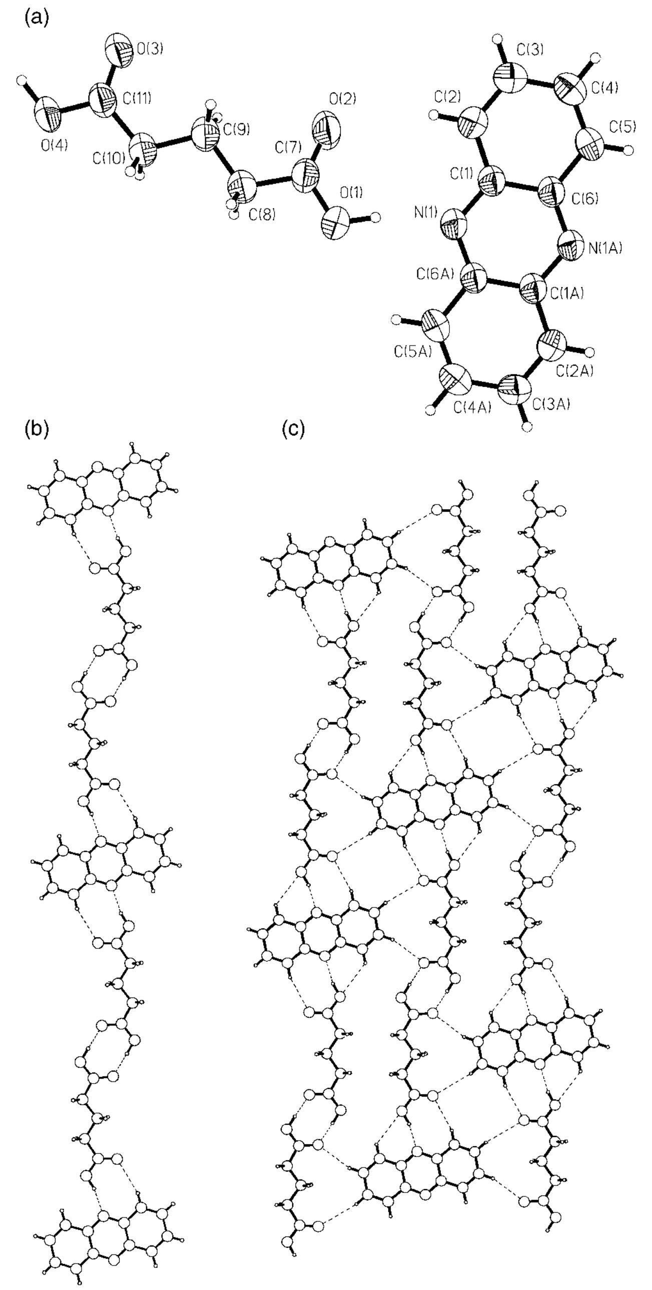
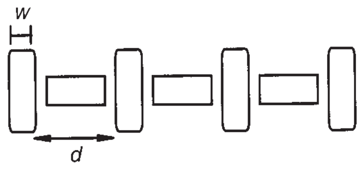


Fig. 6 (a) Numbering scheme for compound **4d** (**1** : **4b** in 1 : 2 ratio) with thermal ellipsoids at a 50% probability level. (b) Tape formed through couplings **IV** and **I**. (c) Packing diagram of **4d**. A planar sheet is formed through the edge-to-edge packing of tapes.

explanation was offered by Schwiebert *et al.*[15] who rationalised the twisting of *linear* tapes with the presence of a "scalloped" tape edge. They suggested that in their system sideways packing of the tapes would not lead to efficient packing due to steric effects. To overcome this, sideways adjacent tapes may twist allowing interlocking to occur and hence a closer approach.



A representation of a tape having scalloped edges is shown above. Along the edge of the tape there are protrusions of width *w* and hollows of width *d*. If *w*>*d* then sideways interlocking of tapes is hindered by steric effects. In such cases interlocking may occur by twisting of the tapes and hence a more efficient packing arrangement is achieved. If *d*>*w* then sideways interlocking is possible but may not be favoured since there will be voids. Once again, tapes may twist in order to achieve more efficient packing. If *w*=*d* and the shape of the protrusion allows it to fit snugly into the hollow then sideways packing of tapes may occur.

In complexes **2c** and **4c** *d*>*w* and therefore sideways interlocking is in theory possible. In addition, with tapes aligned sideways (*i.e.* in the absence of twisting), C–H···O interactions comparable to those observed experimentally are able to form. The twisting observed in complexes **2c** and **4c** may therefore be rationalised as a packing effect and not driven by the desire to form inter-stack C–H···O interactions since these appear possible even if the tapes were not twisted. In complex **2d** tapes are not symmetrical since within a given tape the methyl groups all lie on the same side. Consequently, the edge containing the methyl groups has *w*>*d* and the edge without the methyl moieties has *d*>*w*. Both of these situations may be expected to result in the tapes packing *via* a twisted arrangement. In complexes **2c** and **4c** tapes are twisted by about 80° whereas in **2d** the angle is about 30°. Whether the twist angle is determined solely by packing effects is not certain, however, because in all three structures, tapes are oriented in such a way that a number of inter-stack C–H···O interactions are observed (Figs. 1, 2, and 5(d)). In a paper describing the co-crystals formed between 2-pyridone and a series of even-numbered aliphatic dicarboxylic acids it is reported that each complex is comprised of infinite 1-D ribbons resulting from the bridging of 2-pyridone dimers by the dicarboxylic acid.[40] In three of the five structures reported, ribbons were arranged in a criss-cross manner. The angle of twisting between the ribbons decreased with increasing acid chain length. It may also be noted that with increasing chain length the ribbon changed from a planar to a "buckled" geometry.

The tapes and the packing of the 1 : 2 co-crystals are different from one another. There is, however, one common feature which is that in each of the 1 : 2 complexes all the tapes are arranged with their long axes parallel.

Complex **3c** consists of non-coplanar tapes having a zigzagged hydrogen bond arrangement. Tapes fit together with the protrusions of one tape slotting into the cavities of an adjacent tape leading to efficient packing as reflected in the calculated density. Here, C–H···O interactions are observed between both vertical and sideways adjacent tapes.

Complex **3d** consists of flat tapes which stack with their planes and long axes parallel. In contrast to the 1:1 complexes, however, no twisting of tapes is observed between adjacent stacks (*i.e.* $\theta = 0$). Tapes in adjacent stacks are tilted with respect to one another and offset along the stacking direction leading to a herringbone arrangement (Fig. 4(c)). The edges of the tapes of **3d** are scalloped in such a way that a sideways coplanar approach would result in an excess of void space, however, this does not lead to twisting of the tapes. That no twisting of tapes in adjacent stacks is observed in **3d** highlights the limitations of using a simplistic model such as that described earlier for the 1 : 1 complexes. The functional groups at the edges of tapes of **3d** are different from those of the 1 : 1 complexes. No oxygens are available at the tape edges to form C–H···O interactions with a sideways adjacent tape and hence inter-stack C–H···O interactions such as are observed in the 1 : 1 complexes are not possible. The tape edges consist rather of methyl and aromatic hydrogens allowing van der Waals type interactions. It may be that this difference in inter-stack interaction accounts for the difference in the structure adopted.

The tapes of complex **4d** are relatively flat and can be considered to form stacks. The edges of the tapes contain protrusions and cavities but unlike in the 1 : 1 complexes the angle θ between the long axes of tapes in adjacent stacks is zero. In addition, the planes of tapes in adjacent stacks are coplanar. The size and shape of the protrusions and cavities at the tape edges match well upon sideways interlocking. In addition such positioning of the tapes enables a number of sideways inter-tape C–H···O interactions to form (Fig. 6(c)). The result is a sheet containing strong O–H···N and O–H···O interactions in one dimension and weak C–H···O interactions in the perpendicular direction.

Conclusion

Coupling **IV** was successfully used in the design of supramolecular tapes. The O–H···N interaction was present in all six complexes. The C–H···O interaction of this coupling is subject to distortion as may be expected due to its weaker nature. The success of this coupling was increased when the carboxyl moieties were in a *trans* or *anti* conformation on the parent molecule. In a similar way, the co-crystal stoichiometry could be related to the position of the carboxyl groups on the carbon backbone. Molecules having carboxyl moieties positioned in a *cis* or pseudo *cis* (*i.e.* aliphatics having *n* odd) arrangement formed acid–acid pairs *via* coupling **I** leading to a 1:2 stoichiometry. The tapes of the 1:1 complexes all packed with their long axes non-parallel, C–H···O interactions being present between stacks. The tapes of the 1:2 complexes all packed with their long axes parallel. However, the exact packing of these tapes differed for each complex. Inter-tape C–H···O interactions were present in each of the 1:2 complexes.

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