

## Hydrogen bonding and $\pi$ - $\pi$ interactions in 1-benzofuran-2,3-dicarboxylic acid and its 1:1 cocrystals with pyridine, phenazine and 1,4-phenylenediamine

Hatem M. Titi and Israel Goldberg\*

School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University,  
Ramat-Aviv, 69978 Tel-Aviv, Israel

Correspondence e-mail: goldberg@post.tau.ac.il

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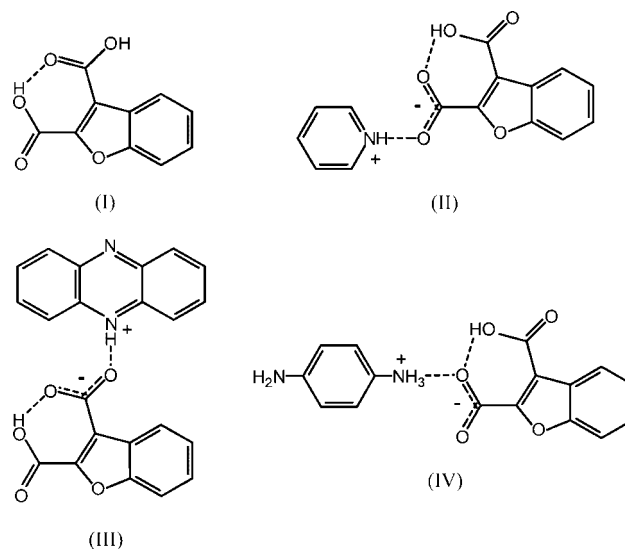
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The structure of 1-benzofuran-2,3-dicarboxylic acid (BFDC),  $C_{10}H_6O_5$ , (I), exhibits an intramolecular hydrogen bond between one  $-COOH$  group and the other, while the second carboxyl function is involved in intermolecular hydrogen bonding to neighbouring species. The latter results in the formation of flat one-dimensional hydrogen-bonded chains in the crystal structure, which are  $\pi$ - $\pi$  stacked along the normal to the plane of the molecular framework, forming a layered structure. 1:1 Cocrystallization of BFDC with pyridine, phenazine and 1,4-phenylenediamine is associated with H-atom transfer from BFDC to the base and charge-assisted hydrogen bonding between the  $BFDC^-$  monoanion and the corresponding ammonium species, while preserving, in all cases, the intramolecular hydrogen bond between the carboxyl and carboxylate functions. The pyridinium 2-carboxylato-1-benzofuran-3-carboxylic acid,  $C_5H_6N^+ \cdot C_{10}H_5O_5^-$ , (II), and phenazinium 3-carboxylato-1-benzofuran-2-carboxylic acid,  $C_{12}H_9N_2^+ \cdot C_{10}H_5O_5^-$ , (III), adducts form discrete hydrogen-bonded ion-pair entities. In the corresponding crystal structures, the two components are arranged in either segregated or mixed  $\pi$ - $\pi$  stacks, respectively. On the other hand, the structure of 4-aminoanilinium 2-carboxylato-1-benzofuran-3-carboxylic acid,  $C_6H_9N_2^+ \cdot C_{10}H_5O_5^-$ , (IV), exhibits an intermolecular hydrogen-bonding network with three-dimensional connectivity. Moreover, this fourth structure exhibits induction of supramolecular chirality by the extended hydrogen bonding, leading to a helical arrangement of the interacting moieties around  $2_1$  screw axes. The significance of this study is that it presents the first crystallographic characterization of pure BFDC, and manifestation of its cocrystallization with a variety of weakly basic amine molecules. It confirms the tendency of BFDC to preserve its intramolecular hydrogen bond and to prefer a monoanionic form in supramolecular association with other components.

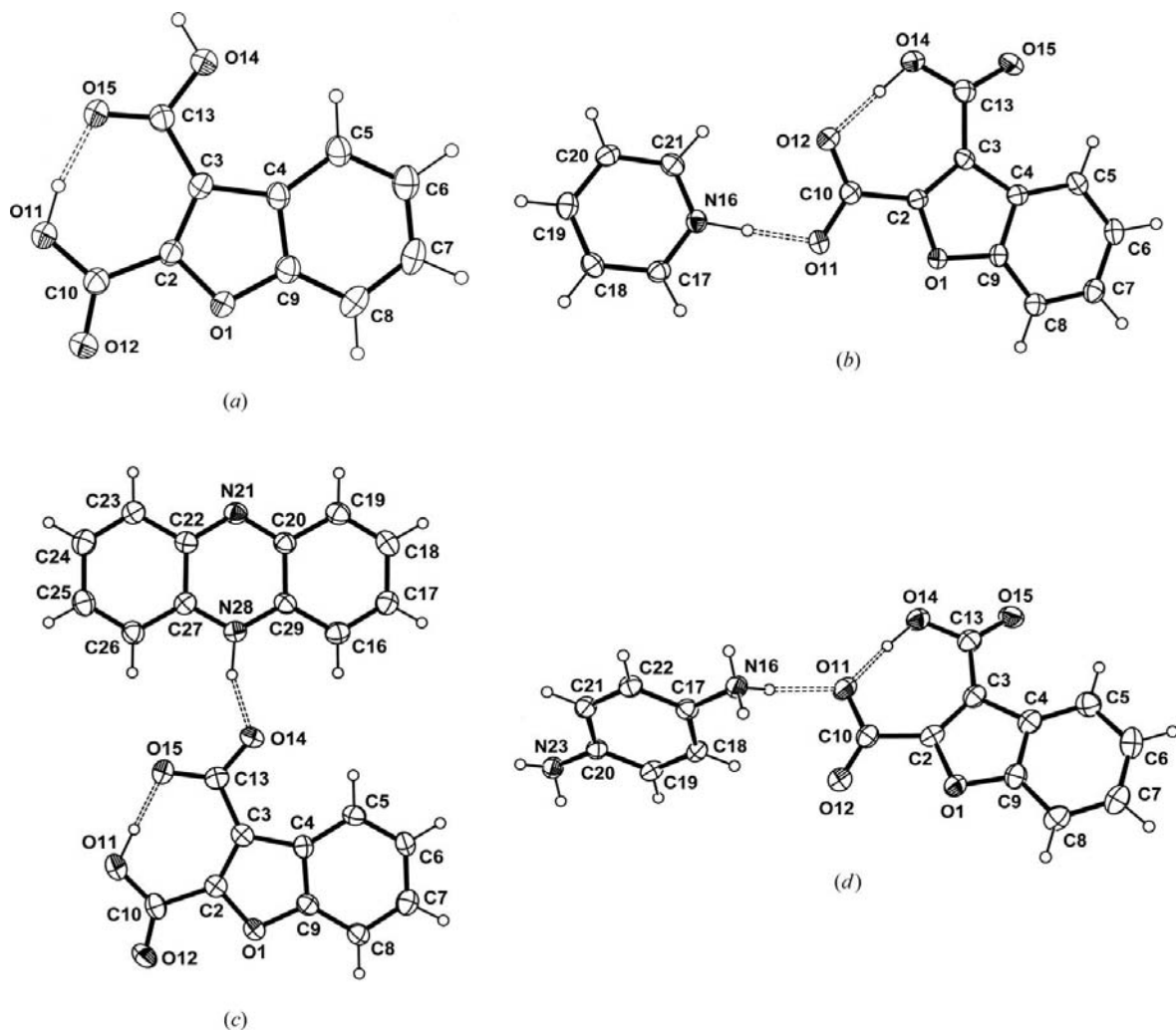
The aromaticity of the flat benzofuran residue plays an important role in directing either homo- or heteromolecular  $\pi$ - $\pi$  stacking in the first three structures, while the occurrence of a chiral architecture directed by multiple hydrogen bonding is the dominant feature in the fourth.

### Comment

This study is part of an extended research project directed at the detailed evaluation of the structural features and functionality of the 1-benzofuran-2,3-dicarboxylic acid (BFDC) building block, along with the formulation of new supramolecular materials of this compound with a variety of transition metals and complimentary organic ligands. In recent publications (Koner & Goldberg, 2009*a,b,c*), we showed that BFDC can be readily deprotonated, singly or doubly, to the corresponding anions  $BFDC^-$  and  $BFDC^{2-}$ , and can form coordination compounds with 2+ and 3+ metal ions. The monoanions (obtained under weak basic conditions) engage in the formation of discrete complexes, while the dianions (available in higher pH environments) can afford extended coordination polymers. It also appeared that the first deprotonation of BFDC occurs favourably on the carboxylic acid group which is closer to the electron-withdrawing etheral site. In the resulting  $BFDC^-$  anion, the H atom of the second carboxyl function is involved in an intramolecular hydrogen bond to the carboxylate group. The structure of free BFDC



has not been reported before, and its supramolecular/coordination chemistry has not been studied prior to our work. Within the above context, this presentation describes the first crystallographic characterization of pure BFDC, (I). In addition, the structures of the 1:1 cocrystals of BFDC with pyridine, phenazine and 1,4-phenylenediamine, the formation of which is associated with H-atom transfer from the acidic BFDC to the corresponding Lewis base, are also described, *viz.* (II), (III) and (IV), respectively. The four compounds crystallized serendipitously during our attempts to formulate coordination polymers of this ligand with various lanthanide metal ions.



**Figure 1**

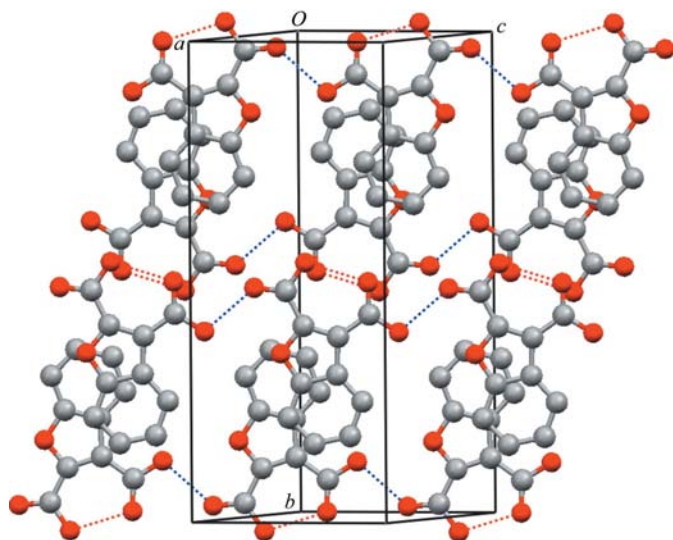
The asymmetric units in (a) (I), (b) (II), (c) (III) and (d) (IV). Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K and H atoms are shown as small spheres of arbitrary radii. Intra- and intermolecular hydrogen bonds are indicated by dashed lines.

Ellipsoid plots of compounds (I)–(IV) are shown in Fig. 1. The only conformational degrees of freedom in the BDFC framework involve free rotations of the carboxyl/carboxylate functions with respect to the rigid aromatic benzofuran residue. They are efficiently utilized for optimization of the intra- and intermolecular hydrogen bonding in (I)–(IV).

The observed structure of (I) involves the formation of an intramolecular hydrogen bond between the two *ortho*-substituted carboxylic acid functions (Fig. 1*a*). The more acidic of the two groups (C10/O11/O12) acts as an H-atom donor in this bond (O11—H11...O15; Table 1), with graph-set notation *S*(7) (Bernstein *et al.*, 1995). The aromatic benzofuran fragment (O1/C2–C9) is essentially planar. The two carboxylic acid groups are slightly twisted with respect to this plane, with dihedral angles of 9.2 (2) and 5.8 (2)° for fragments C10/O11/O12 and C13/O14/O15, respectively. Additional H-atom donor (O14—H14) and acceptor (O12) sites diverge outward from the flat molecular structure and are accessible to intermolecular hydrogen bonding (Table 1). This gives rise to the formation of supramolecular hydrogen-bonded chains of BDFC, involving molecular units displaced along the *c* axis of

the crystal structure [graph-set notation *C*(7)]. The chain assemblies are flat, lying parallel to the (100) plane of the crystal structure at approximately  $x = \frac{1}{4}$ . Neighbouring symmetry-related hydrogen-bonded chains are centred at either  $x = \frac{1}{4}$  or  $x = \frac{3}{4}$  and are roughly parallel to one another, yielding a layered intermolecular arrangement (Fig. 2).

In addition to the common dispersion forces that stabilize the crystal packing in molecular crystals, the two following sets of van der Waals type interactions between adjacent chains in (I) deserve specific attention. Along the *a* axis of the crystal structure, the chain arrays related by the glide-plane symmetry are offset stacked on top of one other. The mean interplanar distance between the partly overlapping benzofuran residues (O1/C2–C9) at  $(x, y, z)$  and  $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$  is 3.27 (1) Å. More specifically, there is an apparent  $\pi$ – $\pi$  interaction between both the furan and the benzene rings at  $(x, y, z)$  and the benzene ring at  $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$ . The corresponding ring-centroid distances, the dihedral angles between the planes concerned and the interplanar spacings are 3.8272 (10) Å, 1.27 (9)° and 3.3163 (8) Å, and 3.8579 (11) Å, 0° and 3.3525 (8) Å, respectively. Along the *b* axis, the crystal

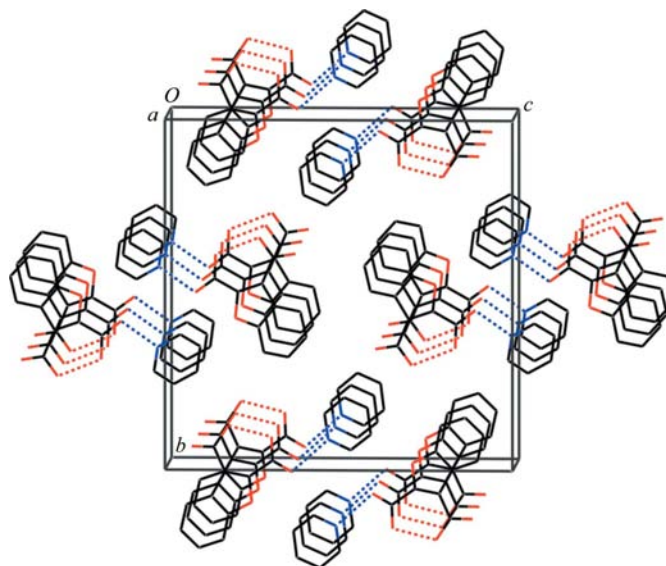


**Figure 2**

Ball-and-stick illustration of the crystal structure of (I). Note the partial overlap between BFDC molecules stacked along the *a* axis. Intra- and intermolecular hydrogen bonds in this layered structure are denoted by dashed lines.

packing is further stabilized by weak C—H...O interactions between molecules interrelated by the screw-axis symmetry (Table 1), which involve the aryl termini of one molecule and the carboxylic acid O atoms of an adjacent unit at the same *z* level but shifted along the *b* axis. The entire crystal packing is thus stabilized by O—H...O hydrogen bonding,  $\pi$ - $\pi$  stacking and weak C—H...O interactions along the *c*, *a* and *b* axes, respectively.

Furandicarboxylic acids have been shown to be relatively strong acids (Xing & Glen, 2002; Ostrow & Mukerjee, 2007) with  $pK_a$  values below 3. The extended benzofuran aromatic framework provides an even higher stabilization of the negative charge after deprotonation, thus lowering this value even further. Not surprisingly, therefore, weakly basic environments are adequate to effect ionization of BFDC (Koner & Goldberg, 2009a). Cocrystallization of BFDC with pyridine was indeed associated with H-atom transfer from BFDC to the pyridine base, yielding the charge-assisted hydrogen-bonded heteromeric entity (II) of the two ions thus formed. This H-atom transfer occurred as expected from the more acidic carboxyl group C10/OH11/O12 to the N16 pyridine site (Fig. 1*b*). The molecular structure of the BFDC<sup>-</sup> ion is further characterized by an intramolecular hydrogen bond from the second carboxylic acid group (C13/O14/O15) to the deprotonated carboxylate group (Table 2). The graph-set notations for the inter- and intramolecular hydrogen bonds of (II) are *D* and *S*(7), respectively. The two interacting moieties are essentially planar but they deviate slightly from coplanarity, the dihedral angle between the O1/C2—C9 and N16/C17—C21 planes being 13.13 (7)°. They are offset stacked in segregated columns along the *a* axis of the crystal structure of (II), as shown in Fig. 3. The interplanar distance between neighbouring pyridinium units (N16/C17—C21), with minor overlapping between them at (*x*, *y*, *z*) and (1 + *x*, *y*, *z*) along

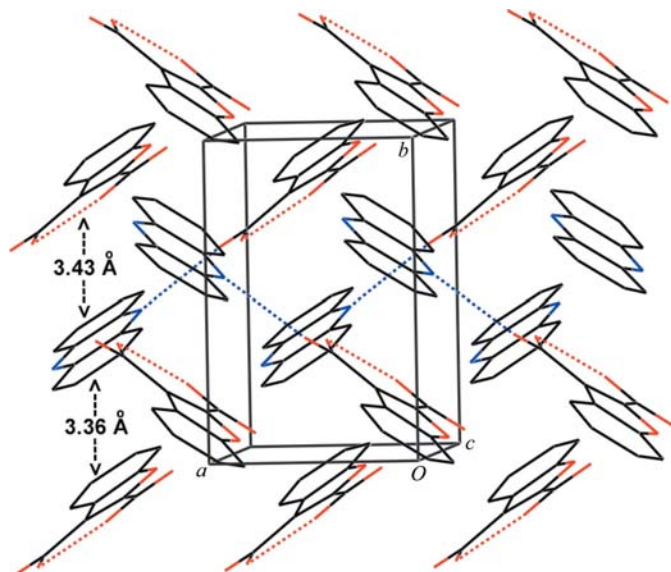


**Figure 3**

Wireframe presentation of the crystal structure of (II), viewed approximately down the *a* axis, showing the segregated stacking of the BFDC<sup>-</sup> and pyridinium components. Hydrogen bonds are indicated by dashed lines.

the stack, is 3.324 (7) Å, while that between the correspondingly better overlapping benzofuran rings (O1/C2—C9) is slightly larger at 3.393 (6) Å. In the latter case, the specific interaction between the benzene ring at (*x*, *y*, *z*) and the furan ring at (*x* + 1, *y*, *z*) is characterized by a ring-centroid distance of 3.7401 (12) Å, a dihedral angle between the two planes of 0.33 (10)° and an interplanar spacing of 3.3936 (8) Å. A series of relatively short C—H...O approaches between neighbouring molecules of the two components (Table 2) contributes to the stabilization of the columnar crystal packing of (II).

The observed structure of (III) is also characterized by an intercomponent hydrogen bond (N28—H...O14; Table 3) associated with H-atom transfer from one of the carboxylic acid groups to the aromatic N-atom site (Fig. 1*c*). The molecular structure also accommodates an intramolecular O11—H...O15 hydrogen bond (Table 3). Somewhat surprisingly, the hydrogen bonding between the BFDC<sup>-</sup> anion and the phenazine cation this time involves the apparently less acidic carboxyl group C13/O14/O15 (see below). A possible explanation for this deviation from the more commonly observed trend in earlier examples (Koner & Goldberg, 2009*a,b,c*), as well as in compounds (II) and (IV) of this work, relates to the comparable size and flat shape of the aromatic BFDC<sup>-</sup> and phenazine cation components (the two species are essentially planar). The individual moieties of the hydrogen-bonded pair are coplanar. In the crystal structure, the hydrogen-bonded dimers stack along [110] in an offset manner, and yet the preferred organization in this structure represents mixed stacking [rather than homomeric as in (II)], with alternating and partially overlapping BFDC<sup>-</sup> and phenazine units (Fig. 4). The mean interplanar separations from the electron-deficient phenazine framework (C16—C20/N21/C22—C27/

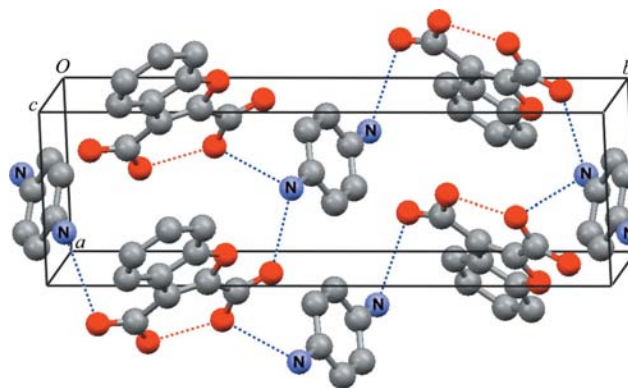


**Figure 4**

The crystal packing of (III) (wireframe). Note the arrangement of the BFDC<sup>-</sup> and phenazinium units in an alternating manner in heteromeric stacks (along the *b* axis, as marked by the interplanar distances) with partial overlap between them. Neighbouring columns are related to one another by the glide symmetry. Hydrogen bonds are indicated by dashed lines.

N28/C29) at (*x*, *y*, *z*) and the two adjacent electron-rich BFDC<sup>-</sup> (O1/C2–C10/O11/O12/C13/O14/O15) planes at (*x* + 1, *y* + 1, *z*) and (*x* + 1, *y*, *z*) are 3.36 (3) and 3.43 (3) Å, respectively, indicative of a possible  $\pi$ – $\pi$  charge-transfer interaction between the component species along the stack (Goldberg, 1975; Goldberg & Shmueli, 1973). Specific overlapping contacts occur between the central ring of the phenazinium ion (C20/N21/C22/C27/N28/C29) and the benzene ring of BFDC<sup>-</sup> (C4–C9), and between the peripheral phenazinium (C22–C27) and furan (O1/C2–C4/C9) fragments. The corresponding ring-centroid distances, the dihedral angles between the planes concerned and the interplanar spacings are 3.855 (2) Å, 1.58 (16)° and 3.3439 (13) Å, and 3.838 (2) Å, 1.56 (18)° and 3.3282 (15) Å, respectively. Optimization of the stacking interactions may affect the utilization of the less expected mode of intermolecular hydrogen bonding in this structure. It is also noted that the second N-atom site of phenazine is involved in a weak C–H...N interaction (Table 3), which operates between units of neighbouring stacks along with the C–H...O contacts.

Structure (IV) also represents a hydrogen-bonded adduct of BFDC<sup>-</sup> with a diamine, but here both N-atom sites are involved in conventional hydrogen bonds with neighbouring species. This is facilitated by the fact that the terminal amine groups of the 1-ammonium-4-aminophenylene moiety act not only as H-atom acceptors from but also as H-atom donors to the surrounding molecules. As in (II), single H-atom transfer occurs from the more acidic function of the dicarboxylic acid to the N-containing ligand, while preserving the intramolecular hydrogen bonding in the resulting BFDC<sup>-</sup> ion (Fig. 1*d*); the respective graph-set descriptors are *D* and *S*(7). The ion pair thus formed bears five H-atom donors (the H



**Figure 5**

Ball-and-stick illustration of the crystal structure of (IV), showing the helical arrangement of the alternating constituent moieties around the 2<sub>1</sub> screw axis, and the extended intermolecular hydrogen bonding (dashed lines) along it. Additional hydrogen bonds which operate between neighbouring helices (Table 4) are not shown.

atoms on N16 and N23) and potentially five H-atom acceptors (O11, O12, O14, O15 and N23), facilitating the formation of an extended intermolecular hydrogen-bonding network between the two multidentate components in three dimensions (Table 4; the C–H...O contacts are of minor significance in this structure and have been omitted from this table). The various chain segments of this network in the different directions are denoted by C<sub>2</sub><sup>2</sup>(6), C<sub>2</sub><sup>2</sup>(7), C<sub>2</sub><sup>2</sup>(13) and C<sub>2</sub><sup>2</sup>(14) graph-set descriptors.

A partial illustration of the intermolecular networking is given in Fig. 5. While it is somewhat problematic to exhibit a three-dimensional connectivity scheme in a two-dimensional projection, we prefer to emphasize a different point in this figure. BFDC and 1,4-phenylenediamine are nonchiral species, and yet, upon ion-pair formation, they crystallize in a chiral architecture of space-group symmetry *P*2<sub>1</sub>, as a result of the extended supramolecular hydrogen bonding. This is an interesting manifestation of the induction of supramolecular chirality, occasionally observed in crystals of achiral salts (Goldberg, 2009; Tanaka *et al.*, 2006). Fig. 5 shows that the two ionic components in (IV) are arranged along the hydrogen-bonded chains in an alternating manner, and that optimization of the hydrogen bonding imparts 2<sub>1</sub> helicity to the hydrogen-bonded arrays. No rigorous explanation of the occurrence of the supramolecular chirality phenomenon can be provided at this point, apart from indicating that in the earlier observed examples it was also induced by the presence of extended arrays of hydrogen bonds between the interacting components (Goldberg, 2008; Vinodu & Goldberg, 2005).

In summary, this study characterizes the molecular structure of pure benzofurandicarboxylic acid. It confirms its tendency to deprotonate into a monoanionic form in mild basic environments, transferring the H atom to one of the N-atom sites of the Lewis base present in the reaction/crystallization mixture. The proximal positions of the two carboxylic acid functions promote the formation of an intramolecular hydrogen bond. Evidently, the BFDC<sup>-</sup> entity is an excellent H-atom acceptor in hydrogen bonding, facilitating its supramolecular association with a variety of mono- or polydentate H-atom donors.

## Experimental

All the reactants and solvents were obtained commercially. Compounds (I)–(IV) were obtained unintentionally while attempting to prepare coordination polymers of BFDC with various oxophilic lanthanide ions in basic environments. The title compounds thus represent by-products of these efforts.

Compound (I) was obtained by dissolving a mixture of BFDC (0.1 mmol, 0.021 g) and gadolinium oxalate hydrate (0.1 mmol, 0.055 g) in water (5 ml) and HCl (32%, 2 drops). The resulting solution was sealed in a bath reactor for 3 d at 373 K. It was then left to evaporate slowly at room temperature, yielding crystals after 12 d. For (II), BFDC (0.1 mmol, 0.021 g) was reacted with Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.1 mmol, 0.055 g) in a 1:1 mixture of water and pyridine (5 ml), and sealed in a bath reactor at 373 K for 3 d. The product was filtered and left to evaporate slowly at room temperature, yielding BFDC–pyridine cocrystals after about one month. For (III), a mixture of BFDC (0.4 mmol, 0.082 g), phenazine (0.4 mmol, 0.073 g) and PrCl<sub>3</sub>·7H<sub>2</sub>O (0.8 mmol, 0.198 g) was dissolved in a 1:1 mixture of methanol and tetrahydrofuran (20 ml). The resulting solution was refluxed for 3 h, filtered and left to evaporate slowly. Yellow crystals appeared after two weeks. Compound (IV) was obtained by mixing BFDC (0.4 mmol, 0.082 g), PrCl<sub>3</sub>·7H<sub>2</sub>O (0.8 mmol, 0.197 g) and 1,4-phenylenediamine (0.4 mmol, 0.042 g) in a 3:1 mixture of tetrahydrofuran and water (20 ml). The resulting solution was refluxed overnight and then filtered, and the liquid was left to evaporate slowly at room temperature. Crystals of (IV) suitable for X-ray diffraction studies were obtained after 4 d.

## Compound (I)

## Crystal data

C <sub>10</sub> H <sub>6</sub> O <sub>5</sub>	$V = 847.28 (6) \text{ \AA}^3$
$M_r = 206.15$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.9614 (3) \text{ \AA}$	$\mu = 0.13 \text{ mm}^{-1}$
$b = 18.2529 (7) \text{ \AA}$	$T = 110 \text{ K}$
$c = 7.4731 (3) \text{ \AA}$	$0.45 \times 0.35 \times 0.20 \text{ mm}$
$\beta = 116.840 (2)^\circ$	

## Data collection

Nonius KappaCCD area-detector diffractometer	1517 reflections with $I > 2\sigma(I)$
7021 measured reflections	$R_{\text{int}} = 0.035$
1982 independent reflections	

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.141$	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
1982 reflections	
142 parameters	

Table 1

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11–H11 $\cdots$ O15	0.99 (2)	1.52 (2)	2.4990 (16)	168.6 (19)
O14–H14 $\cdots$ O12 <sup>i</sup>	0.96 (2)	1.66 (2)	2.6143 (17)	172.7 (19)
C7–H7 $\cdots$ O12 <sup>ii</sup>	0.95	2.52	3.468 (2)	173

Symmetry codes: (i)  $x, y, z - 1$ ; (ii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ .

## Compound (II)

## Crystal data

C <sub>5</sub> H <sub>6</sub> N <sup>+</sup> ·C <sub>10</sub> H <sub>5</sub> O <sub>5</sub> <sup>−</sup>	$V = 1240.21 (7) \text{ \AA}^3$
$M_r = 285.25$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 3.75760 (10) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 18.3933 (6) \text{ \AA}$	$T = 110 \text{ K}$
$c = 17.9788 (7) \text{ \AA}$	$0.50 \times 0.10 \times 0.10 \text{ mm}$
$\beta = 93.5522 (11)^\circ$	

## Data collection

Nonius KappaCCD area-detector diffractometer	2897 independent reflections
10181 measured reflections	1675 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.067$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.139$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
$S = 0.97$	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$
2897 reflections	
196 parameters	

## Compound (III)

## Crystal data

C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> <sup>+</sup> ·C <sub>10</sub> H <sub>5</sub> O <sub>5</sub> <sup>−</sup>	$V = 836.38 (7) \text{ \AA}^3$
$M_r = 386.35$	$Z = 2$
Monoclinic, $Pn$	Mo $K\alpha$ radiation
$a = 5.3881 (2) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$b = 8.3227 (4) \text{ \AA}$	$T = 110 \text{ K}$
$c = 18.6514 (11) \text{ \AA}$	$0.50 \times 0.40 \times 0.20 \text{ mm}$
$\beta = 90.3794 (18)^\circ$	

## Data collection

Nonius KappaCCD area-detector diffractometer	1970 independent reflections
7323 measured reflections	1352 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.105$	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
$S = 1.02$	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
1970 reflections	
269 parameters	
2 restraints	

## Compound (IV)

## Crystal data

C <sub>6</sub> H <sub>9</sub> N <sub>2</sub> <sup>+</sup> ·C <sub>10</sub> H <sub>5</sub> O <sub>5</sub> <sup>−</sup>	$V = 708.99 (5) \text{ \AA}^3$
$M_r = 314.29$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 5.8427 (2) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$b = 17.5893 (7) \text{ \AA}$	$T = 110 \text{ K}$
$c = 7.1302 (3) \text{ \AA}$	$0.50 \times 0.50 \times 0.10 \text{ mm}$
$\beta = 104.6337 (16)^\circ$	

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O14–H14 $\cdots$ O12	0.98 (2)	1.53 (3)	2.516 (2)	178 (2)
N16–H16 $\cdots$ O11	1.08 (2)	1.55 (2)	2.628 (2)	179 (2)
C17–H17 $\cdots$ O11 <sup>i</sup>	0.95	2.60	3.400 (3)	142
C18–H18 $\cdots$ O11 <sup>ii</sup>	0.95	2.51	3.366 (3)	150
C19–H19 $\cdots$ O14 <sup>iii</sup>	0.95	2.64	3.562 (3)	165

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (ii)  $-x + 2, -y, -z + 1$ ; (iii)  $x + \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .

**Table 3**  
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O11—H11...O15	0.99 (5)	1.52 (5)	2.503 (3)	171 (4)
N28—H28...O14	1.03 (4)	1.57 (4)	2.553 (4)	158 (3)
C6—H6...O12 <sup>i</sup>	0.95	2.51	3.328 (4)	144
C8—H8...N21 <sup>ii</sup>	0.95	2.50	3.427 (4)	165
C26—H26...O15	0.95	2.48	3.395 (4)	161

Symmetry codes: (i)  $x + \frac{1}{2}, -y, z - \frac{1}{2}$ ; (ii)  $x - 2, y - 1, z$ .

**Table 4**  
Hydrogen-bond geometry (Å, °) for (IV).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O14—H14...O11	0.97 (5)	1.53 (5)	2.464 (3)	160 (4)
N16—H16A...O11	0.93 (4)	1.91 (4)	2.817 (3)	164 (3)
N16—H16B...O12 <sup>i</sup>	0.90 (4)	1.98 (4)	2.808 (3)	153 (3)
N16—H16C...N23 <sup>ii</sup>	1.05 (4)	1.80 (4)	2.842 (4)	173 (3)
N23—H23A...O14 <sup>iii</sup>	0.83 (4)	2.30 (4)	3.110 (3)	166 (3)
N23—H23B...O15 <sup>iv</sup>	0.92 (4)	2.16 (4)	3.047 (3)	162 (3)

Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $x, y, z + 1$ ; (iii)  $-x + 1, y + \frac{1}{2}, -z + 1$ ; (iv)  $-x, y + \frac{1}{2}, -z + 1$ .

#### Data collection

Nonius KappaCCD area-detector diffractometer  
5908 measured reflections  
1729 independent reflections  
1422 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.036$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.110$   
 $S = 1.02$   
1729 reflections  
227 parameters  
1 restraint  
H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{Å}^{-3}$

H atoms bound to C atoms were located in calculated positions and constrained to ride on their parent atoms, with  $C-H = 0.95 \text{ Å}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . H atoms bound to N and O atoms were located in difference Fourier maps and their coordinates were refined freely, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{O})$  in (I)–(III) and  $1.5U_{\text{eq}}(\text{N}, \text{O})$  in (IV).

In all cases but one, the distribution of the C—O bond distances within the carboxyl/carboxylate groups was consistent with their being in either a protonated or a deprotonated delocalized state. The only exception is exhibited by the bonds  $C10-O11 = 1.290 (3) \text{ Å}$  and  $C10-O12 = 1.216 (4) \text{ Å}$  in (IV), which seem to better represent a carboxylic acid rather than a carboxylate functionality. However, a prominent residual electron-density peak was located near atom N16 rather than O11, and remained there after a few cycles of least-

squares refinement of its coordinates (as an H atom), which thus suggests that proton transfer has occurred at least partially from atom O11 to N16.

Notably, the electron-deficient N—H bonds involved in hydrogen bonding to the anionic BFDC<sup>−</sup> species in (II) and (III) were refined to be slightly longer than in neutral amines, as expected (Tables 2 and 3). As the absolute structure could not be determined reliably in the noncentrosymmetric light-atom structures of (III) and (IV), the Friedel pairs were merged in the crystallographic refinements of the corresponding structural models using the MERG3 parameter in *SHELXL97* (Sheldrick, 2008), which reduced the data-to-parameter ratio to about 8.

For all compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3317). Services for accessing these data are described at the back of the journal.

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