

Low-dimensional hydrogen-bonded structures in the 1:1 and 1:2 proton-transfer compounds of 4,5-dichlorophthalic acid with the aliphatic Lewis bases triethylamine, diethylamine, *n*-butylamine and piperidine

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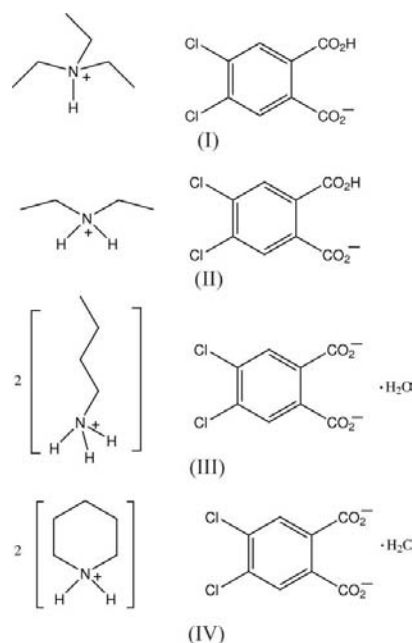
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The structures of the proton-transfer compounds of 4,5-dichlorophthalic acid (DCPA) with the aliphatic Lewis bases triethylamine, diethylamine, *n*-butylamine and piperidine, namely triethylaminium 2-carboxy-4,5-dichlorobenzoate, $C_6H_{16}N^+ \cdot C_8H_3Cl_2O_4^-$, (I), diethylaminium 2-carboxy-4,5-dichlorobenzoate, $C_4H_{12}N^+ \cdot C_8H_3Cl_2O_4^-$, (II), bis(butanaminium) 4,5-dichlorobenzene-1,2-dicarboxylate monohydrate, $2C_4H_{12}N^+ \cdot C_8H_2Cl_2O_4^{2-} \cdot H_2O$, (III), and bis(piperidinium) 4,5-dichlorobenzene-1,2-dicarboxylate monohydrate, $2C_5H_{12}N^+ \cdot C_8H_2Cl_2O_4^{2-} \cdot H_2O$, (IV), have been determined at 200 K. All compounds have hydrogen-bonding associations, giving discrete cation–anion units in (I) and linear chains in (II), while (III) and (IV) both have two-dimensional structures. In (I), a discrete cation–anion unit is formed through an asymmetric $R_1^2(4)$ $N^+ - H \cdots O_2$ hydrogen-bonding association, whereas in (II), chains are formed through linear $N - H \cdots O$ associations involving both aminium H-atom donors. In compounds (III) and (IV), the primary $N - H \cdots O$ -linked cation–anion units are extended into a two-dimensional sheet structure *via* amide–carboxyl $N - H \cdots O$ and amide–carbonyl $N - H \cdots O$ interactions. In the 1:1 salts (I) and (II), the hydrogen 4,5-dichlorophthalate anions are essentially planar with short intramolecular carboxyl–carboxyl $O - H \cdots O$ hydrogen bonds [$O \cdots O = 2.4223$ (14) and 2.388 (2) Å, respectively]. This work provides a further example of the uncommon zero-dimensional hydrogen-bonded DCPA–Lewis base salt and the one-dimensional chain structure type, while even with the hydrate structures of the 1:2 salts with the primary and secondary amines, the low dimensionality generally associated with 1:1 DCPA salts is also found.

Comment

The proton-transfer compounds of the acid salts of 4,5-dichlorophthalic acid (DCPA) with aromatic and heteroaromatic nitrogen Lewis bases generally show low-dimensional hydrogen-bonded structure types (Smith *et al.*, 2008*a*, 2009*a*), with the occurrence of three-dimensional structures limited to the salts with the bifunctional associative-group-substituted compounds 3- and 4-aminobenzoic acid (Smith *et al.*, 2008*b*) and 4-chloroaniline (Smith *et al.*, 2009*b*). In two of these examples (with the aminocarboxylic acids), the primary hydrogen-bonded cation–anion ‘heterodimers’ (Etter & Adson, 1990) are extended into sheet substructures then into three-dimensional framework structures through cation associative-substituent-group interactions. In these three-dimensional structures, the DCPA anions are nonplanar (the ‘nonplanar’ conformation), whereas in the low-dimensional structure types the DCPA anion species are essentially planar (the ‘planar’ conformation) with the planarity a consequence of the short intramolecular carboxyl–carboxyl $O - H \cdots O$ hydrogen bond [typically 2.4054 (19) Å in the 1:1 1,10-phenanthroline–DCPA salt (Smith *et al.*, 2009*c*)].



The 1:1 examples with the secondary aliphatic amine diisopropylamine and the tertiary amine hexamethylenetetramine (Smith & Wermuth, 2010*a*) show simple one-dimensional hydrogen-bonded chain structures. Hydrates are also uncommon among the structures of the 1:1 proton-transfer compounds of DCPA, which is unusual considering that their common preparation is in aqueous alcoholic solution, or they are recrystallized from water, as is the case with the four compounds reported here. The only five known hydrated examples are the ammonium salt (Mattes & Dorau, 1986) (a monohydrate) and the salts with quinaldic acid (a monohydrate; Smith *et al.*, 2008*a*), 2-aminobenzoic acid (a dihydrate; Smith *et al.*, 2008*b*), hexamethylenetetramine (a monohydrate; Smith & Wermuth, 2010*a*) and the salt of the

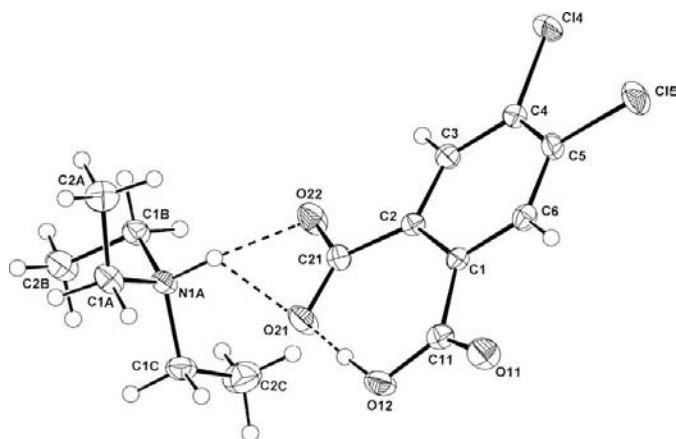


Figure 1

The molecular configuration and atom-numbering scheme for the triethylammonium cation and the 2-carboxy-4,5-dichlorobenzoate anion in (I). Non-H atoms are shown as 40% probability displacement ellipsoids.

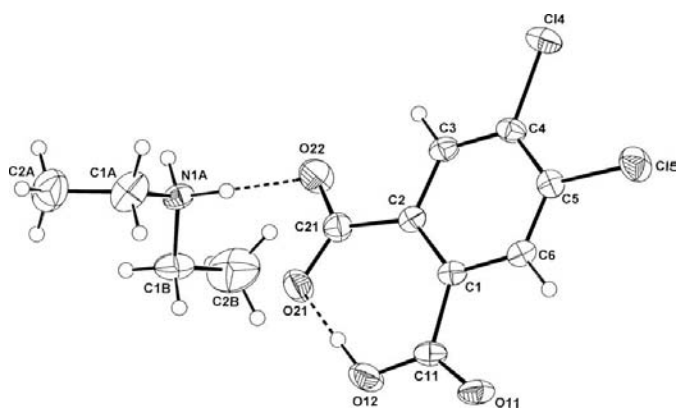


Figure 2

The molecular configuration and atom-numbering scheme for the isopropylammonium cation and the 2-carboxy-4,5-dichlorobenzoate anion in (II). Non-H atoms are shown as 40% probability displacement ellipsoids.

drug quinacrine (a tetrahydrate; Smith *et al.*, 2009). The dianionic DCPA anion is similarly uncommon among the known structures, examples being the salts with 4-ethylaniline (Odabaşoğlu & Büyükgüngör, 2007) and ethylenediamine (Smith & Wermuth, 2010c). It has been previously noted (Smith *et al.*, 2009c) in the structure of the 1,10-phenanthroline salt that with the 'planar' DCPA cations, there is a common set of abnormal bond parameters associated with the intramolecular hydrogen-bonded unit which typically evoke level C alerts in *checkCIF* (Spek, 2009), *viz.* significant bond lengthening of the *exo*-C1–C_{carboxyl} and *exo*-C2–C_{carboxyl} bonds, together with distortion of the external aromatic ring C to carboxyl C bond angles. It was intended in this work that, together with a description of the hydrogen-bonding features of four new DCPA salts, we would examine the complete set of known 'planar' hydrogen DCPA structures and compare these abnormal but interrelated features.

Because the known structures of the 1:1 aliphatic Lewis base salts with DCPA, with the exception of the ammonium salt (Mattes & Dorau, 1986), invariably have the 'planar'

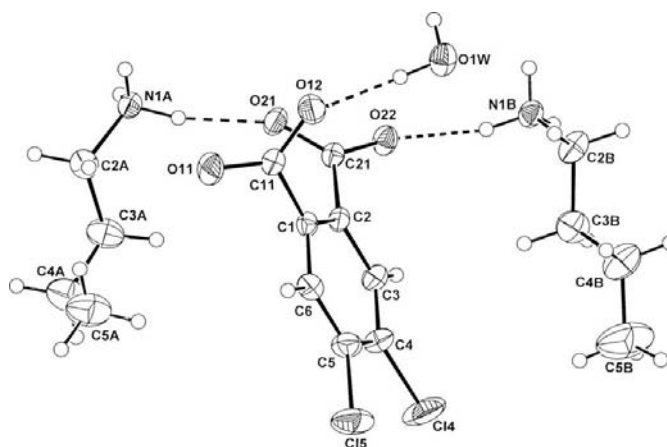


Figure 3

The molecular configuration and atom-numbering scheme for the two *n*-butylammonium cations (*A* and *B*), the 4,5-dichlorophthalate dianion and the water molecule of solvation (O1W) in (III). Inter- and intra-species hydrogen bonds are shown as dashed lines and non-H atoms are shown as 40% probability displacement ellipsoids.

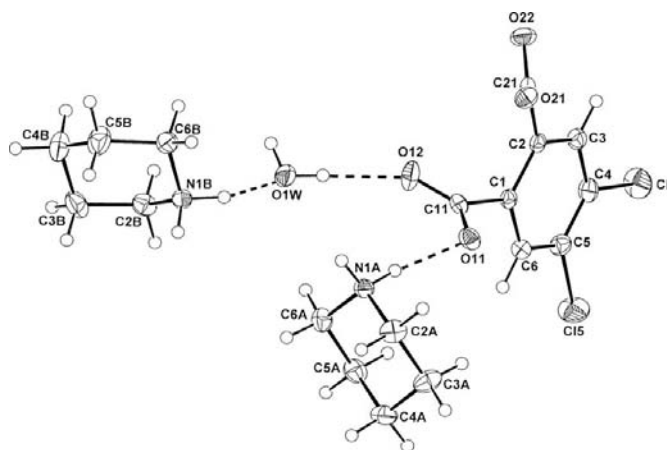


Figure 4

The molecular configuration and atom-numbering scheme for the two piperidinium cations (*A* and *B*), the 4,5-dichlorophthalate dianion and the water molecule of solvation (O1W) in (IV). Non-H atoms are shown as 40% probability displacement ellipsoids.

anion and since the number of characterized aliphatic examples is not great, we carried out the 1:1 stoichiometric reaction of DCPA with a series of aliphatic amines. Our experience indicated that such preparations generally yielded noncrystalline powders from methanol solution (a solvent of choice for the aromatic salts), but if recrystallized from water, they often gave crystals suitable for X-ray analysis. Using this technique, small quantities were obtained of quality crystals of the DCPA salts of the primary amine *n*-butylamine, the secondary amines diethylamine and piperidine and the tertiary amine triethylamine. These compounds are anhydrous triethylammonium 2-carboxy-4,5-dichlorobenzoate, (I), diethylammonium 2-carboxy-4,5-dichlorobenzoate, (II), and the hydrated salts bis(butanaminium) 4,5-dichlorobenzene-1,2-dicarboxylate monohydrate, (III), and bis(piperidinium) 4,5-dichlorobenzene-1,2-dicarboxylate monohydrate, (IV), and the structures are reported here (Figs. 1–4).

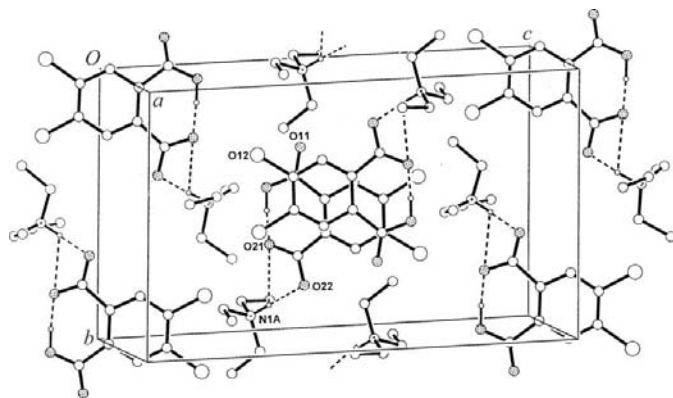


Figure 5
A perspective view of the zero-dimensional structure of the unit cell of (I), showing the partial anion–aromatic ring overlap down *a*. Non-associative H atoms have been omitted.

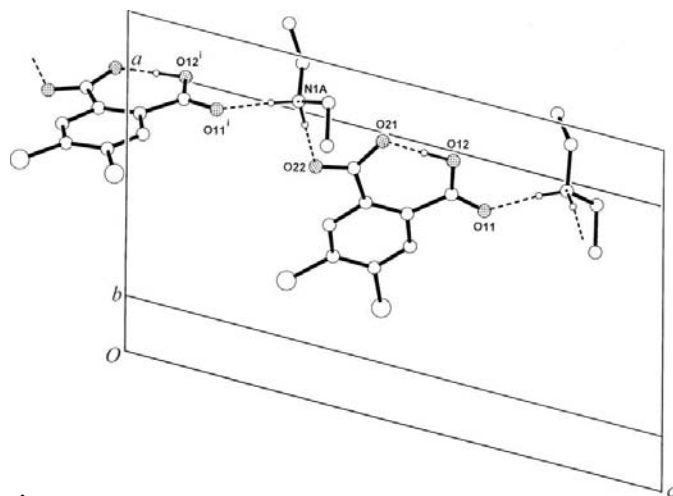


Figure 6
The hydrogen-bonding chain extension of the cation–anion pair along the *c* axial direction of the unit cell of (II). Non-associative H atoms have been omitted and hydrogen bonds are shown as dashed lines. For symmetry code (i), see Table 2.

Considering the 1:1 stoichiometric reaction conditions employed in the preparation of all four compounds, which should have resulted in 1:1 salts, compounds (III) and (IV) are unusual, giving dianionic phthalate salts as well as being hydrates, whereas (I) and (II) are the expected and more common anhydrous 1:1 hydrogen phthalate salts. All members of this set of compounds show low-dimensional hydrogen-bonded structures: zero- in (I), one- in (II) and two-dimensional in (III) and (IV) (Figs. 5–8). Also, all have at least one $N^+ - H \cdots O_{\text{carboxyl}}$ hydrogen-bonding interaction (Figs. 1–4), (II) having two such interactions, but in compounds (III) and (IV), the water O atom acts as an acceptor in an $N^+ - H \cdots O$ hydrogen bond (Tables 1–4). A listing of significant structural parameters for the DCPA anions of (I) and (II), as well as those for the complete set of ‘planar’ DCPA salts, is also made (Table 5).

With compound (I) the only cation–anion hydrogen-bonding association is asymmetric cyclic, involving both carboxyl O-atom acceptors [graph set $R_1^2(4)$; Etter *et al.*, 1990]

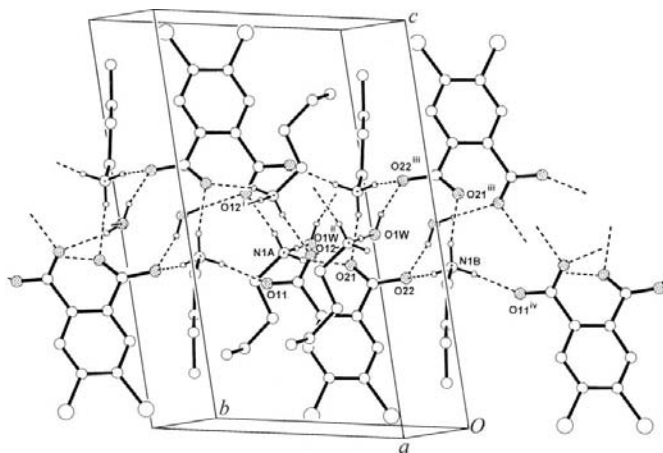


Figure 7
The two-dimensional hydrogen-bonded zigzag chains formed by extension of the cation–anion pairs, in the structure of (III), in a perspective view of the unit cell. Non-associative H atoms have been omitted. For symmetry codes, see Table 3.

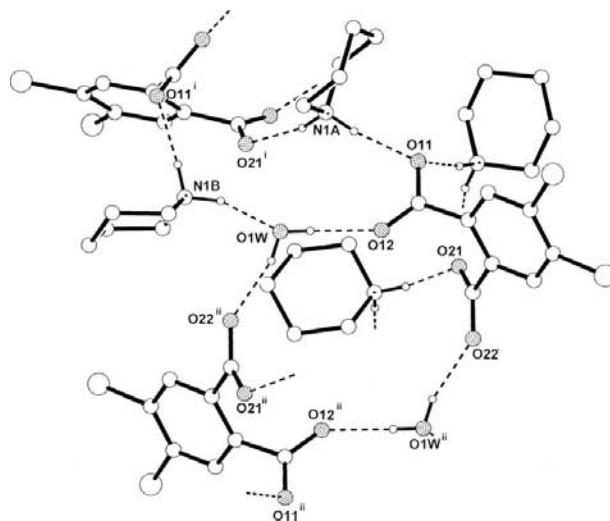


Figure 8
Hydrogen-bonding expansion of the asymmetric unit of (IV), showing the cyclic $R_1^2(18)$ and $R_5^2(17)$ associations. Non-associative H atoms have been omitted. For symmetry codes, see Table 4.

(Table 1). This results in discrete cation–anion units (‘heterodimers’; Etter & Adson, 1990), giving a zero-dimensional structure (Fig. 1). This structure therefore represents only the fifth of its type among the known series of 1:1 DCPA salts, the others being the tetra-*n*-butylammonium salt (Mattes & Dorau, 1986), the 1,8-bis(dimethylamino)-naphthalene salt (Mallinson *et al.*, 2003; Parkin *et al.*, 2007), the brucinium salt (Smith *et al.*, 2007) and the 1,10-phenanthroline salt (Smith *et al.*, 2009c), although the tetramethylammonium salt of DCPA (Bozkurt *et al.*, 2006) may also be considered discrete on the basis of formal intermolecular $N - H \cdots O$ hydrogen bonds. A unique discrete ‘heterotetramer’ (Etter & Adson, 1990) is found in the 1:1 compound with 2-aminopyrimidine (Smith *et al.*, 2009a). The only intermolecular associations in the structure of (I) are weak anion–anion $\pi - \pi$ interactions [ring centroid separation = 3.6494 (8) Å] due to partial aromatic ring overlap down the *a*

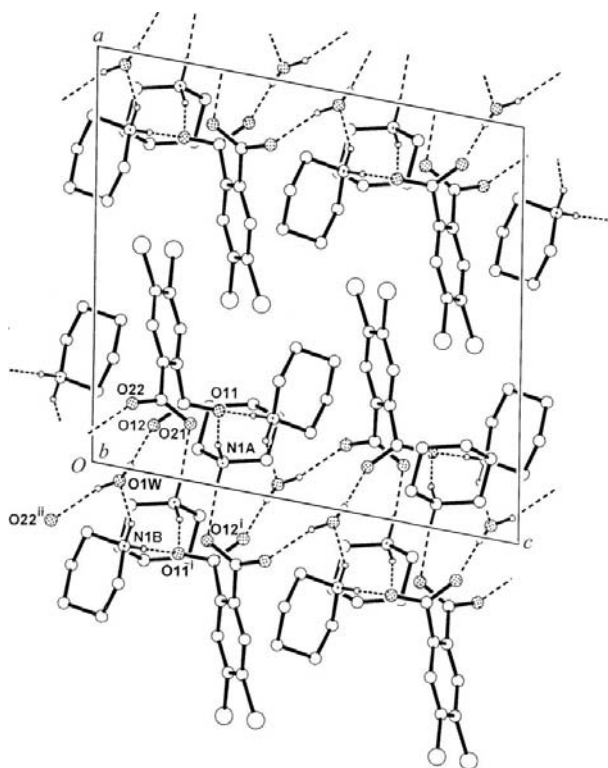


Figure 9

The two-dimensional hydrogen-bonded structure formed of (IV), viewed down the *b* axis of the unit cell. Non-associative H atoms have been omitted. For symmetry codes, see Table 4.

axis of the unit cell (Fig. 5). With (I), the 'planar' DCPA monoanion with the short intramolecular carboxyl–carboxyl O–H...O hydrogen bond is found (Tables 1 and 5).

With the diethylammonium salt, (II), the hydrogen-bonded cation–anion 'heterodimer' (Fig. 2) is extended through the second aminium H atom (Table 2) into a simple one-dimensional chain structure which lies along the *c* axial direction in the unit cell (Fig. 6). This structural motif is similar to that of the diisopropylammonium salt (Smith & Wermuth, 2010*a*). The DCPA anion in (II) also has the 'planar' conformation (Tables 2 and 5).

In the 2:1 monohydrate salt of *n*-butylamine with DCPA, (III), the two cations (*A* and *B*) provide hydrogen-bonding links between the DCPA 'nonplanar' dianions forming duplex chain structures which extend along the *b* direction in the unit cell (Fig. 7). The *A* and *B* aminium groups have different interactive environments (Table 3), with *B* linking only DCPA anions, while *A* links two anions and acts also as a donor to the water molecule which bridges carboxyl groups. Within the duplex chain structures are a series of cyclic conjoint hydrogen-bonding interactions [graph sets $R_4^4(12)$ and $R_4^3(10)$]. The N–H...O_{water} links expand the chains into sheets extending down the *a* cell direction in the two-dimensional structure.

With the 2:1 monohydrate salt with piperidine, (IV), the hydrogen-bonding expansion of the basic asymmetric unit (Fig. 8) is similar to that in (III), involving the two cations *A* and *B* in different environments, with *A* bridging carboxyl

groups and *B* bridging a carboxyl group and a water O-atom acceptor. The water also bridges carboxyl groups giving much larger conjoint cyclic interactions [graph sets $R_4^4(18)$ and $R_5^5(17)$] (Table 4). Duplex chains which lie along the *c* cell direction are extended down the *b* direction giving a two-dimensional sheet structure (Fig. 9). The conformations of the two carboxyl groups in the 'nonplanar' DCPA dianions in (III) and (IV) differ but not significantly [torsion angles C1–C2–C21–O22 and C2–C1–C11–O11 are, respectively, 147.29 (15) and 125.00 (17)° for (III), and –141.41 (13) and –118.74 (15)° for (IV)] since these values would be expected to be affected by hydrogen-bonding environments.

There is an absence in (I)–(IV) of short intermolecular Cl...Cl interactions such as has been found in the 1:1 DCPA compounds with the 3- and 4-aminobenzoic acids (Smith *et al.*, 2008*a*). However, in one of the 'planar' structures, (II), there are short intermolecular Cl...O_{carboxyl} associations [Cl4...O22ⁱⁱ = 2.9769 (17) Å; symmetry code: (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$].

With the 'planar' DCPA monoanions which comprise 19 of the total of 26 known examples within the series of known 1:1 compounds with both aromatic and aliphatic amines, there are also other inherent structural features which are present, including some which evoke *checkCIF* C alerts, as follows: (i) long sp^2 – sp^2 C_{ring}–C_{carboxyl} bond distances; (ii) distortion of the external bond angles associated with the C–C_{carboxyl} bonds; (iii) short aromatic C3–H...O_{carboxyl} and C6–H...O_{carboxyl} interactions. However, with point (iii), these short C...O contacts [2.6714 (16) and 2.6602 (17) Å for (I), and 2.663 (3) and 2.662 (2) Å for (II)] are an artefact of the 'planar' anion conformation. Table 5 lists the values relating to points (i) and (ii) for (I) and (II), as well as the comparative values for the intramolecular O–H...O carboxyl hydrogen bonds and the associated C2–C1–C11–O11 and C1–C2–C21–O22 torsion angles for the full set of known 1:1 'planar' DCPA compounds, and a remarkable consistency is observed. Regarding point (i), the lengthening of the C1–C11 and C2–C21 bonds [1.5366 (19) and 1.5344 (19) Å in (I), and 1.530 (3) and 1.521 (3) Å in (II)] compares with the series bond-length range: 1.511 (6) Å in the quinacrine salt (Smith *et al.*, 2009) to 1.538 (3) Å in the 1,10-phenanthroline salt (Smith *et al.*, 2009*c*). A typical value for this bond in a 'nonplanar' example is 1.500 (2) Å in the 2-carboxyanilinium–DCPA salt (Smith *et al.*, 2008*b*). Regarding point (ii), the *exo*-C1 and C2 ring angles (C1–C2–C21 and C2–C1–C11) [128.16 (11) and 129.73 (11)° for (I), and 128.33 (17) and 128.49 (16)° in (II)] compare with the range of 127.88 (16)° in the nicotinamide salt (Smith *et al.*, 2008*a*) to 129.73 (11)° in compound (I). The distances for the intramolecular hydrogen bond range from 2.34 (1) Å in the tetra-*n*-butylammonium salt (Mattes & Dorau, 1986) to 2.4507 (16) Å in the isopropylamine salt (Smith & Wermuth, 2010*b*), the latter being associated with the maximum deviation from planarity in the series, indicated by the C2–C1–C11–O11 torsion angle of –156.69 (13)°. Considering the high incidence of the 'planar' monoanionic DCPA species among this set of salts, it is apparent that the structural distortions invariably present in the anion, which

are a consequence of the internal carboxyl hydrogen bond, are accommodated internally rather than by assuming the 'nonplanar' conformation.

This present series of salts provides further examples of low-dimensional hydrogen-bonded structure types in the series of both 1:1 and 1:2 proton-transfer compounds of 4,5-dichlorophthalic acid with aliphatic Lewis bases. The dimensionality of the structure should be largely dictated by the type of amine involved (primary, secondary or tertiary), but with the 1:1 examples, the 'planar' internally hydrogen-bonded hydrogen phthalate anion species is found and with it low-dimensional hydrogen-bonded structures. This is also the case with the 'nonplanar' 1:2 dianionic DCPA examples, (III) and (IV). Furthermore, there is little variation in the conformational features of the monoanionic 'planar' DCPA anion species.

Experimental

Compounds (I)–(IV) were synthesized by heating together for 10 min under reflux 1 mmol quantities of 4,5-dichlorophthalic acid and, respectively, triethylamine, diethylamine, *n*-butylamine and piperidine in methanol (50 ml). All preparations gave colourless powders on complete evaporation of solvent but subsequent recrystallization from water gave, in all cases, small quantities of colourless crystals suitable for X-ray analysis [m.p.: 353 K in (I), 443 K in (II), 405 K in (III) and 447 K in (IV)].

Compound (I)

Crystal data

$C_6H_{16}N^+ \cdot C_8H_3Cl_2O_4^-$	$V = 1582.3 (2) \text{ \AA}^3$
$M_r = 336.20$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.3206 (7) \text{ \AA}$	$\mu = 0.42 \text{ mm}^{-1}$
$b = 11.2201 (7) \text{ \AA}$	$T = 200 \text{ K}$
$c = 19.4813 (12) \text{ \AA}$	$0.40 \times 0.40 \times 0.30 \text{ mm}$
$\beta = 98.576 (7)^\circ$	

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer	10740 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3098 independent reflections
$T_{\min} = 0.96, T_{\max} = 0.98$	2638 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.077$	$\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$
$S = 1.04$	$\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$
3098 reflections	
193 parameters	

Compound (II)

Crystal data

$C_4H_{12}N^+ \cdot C_8H_3Cl_2O_4^-$	$V = 1465.2 (3) \text{ \AA}^3$
$M_r = 308.14$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.9588 (13) \text{ \AA}$	$\mu = 0.45 \text{ mm}^{-1}$
$b = 9.9042 (11) \text{ \AA}$	$T = 200 \text{ K}$
$c = 17.062 (3) \text{ \AA}$	$0.35 \times 0.35 \times 0.15 \text{ mm}$
$\beta = 104.580 (14)^\circ$	

Table 1

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1A-H1A \cdots O21$	0.910 (15)	2.569 (16)	3.1614 (15)	123.3 (12)
$N1A-H1A \cdots O22$	0.910 (15)	1.837 (15)	2.7433 (16)	173.7 (14)
$O12-H12 \cdots O21$	0.99 (2)	1.44 (2)	2.4223 (14)	175 (2)

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1A-H1A \cdots O11^i$	0.89 (2)	1.89 (2)	2.772 (2)	169.6 (19)
$N1A-H2A \cdots O22$	0.94 (3)	1.83 (3)	2.765 (3)	173 (3)
$O12-H12 \cdots O21$	0.99 (3)	1.40 (3)	2.388 (2)	179 (4)

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

Table 3

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1A-H11A \cdots O12^i$	0.85 (2)	1.92 (2)	2.762 (2)	170 (2)
$N1A-H12A \cdots O1W^{ii}$	0.91 (2)	1.92 (2)	2.799 (2)	164 (2)
$N1A-H13A \cdots O21$	0.94 (2)	1.94 (2)	2.831 (2)	158.4 (17)
$N1B-H11B \cdots O22$	0.89 (2)	2.00 (3)	2.847 (2)	158.9 (19)
$N1B-H12B \cdots O21^{iii}$	0.89 (3)	1.90 (3)	2.7737 (19)	167.9 (17)
$N1B-H13B \cdots O11^{iv}$	0.89 (3)	1.86 (3)	2.7481 (19)	170 (2)
$O1W-H11W \cdots O12$	0.89 (3)	1.84 (3)	2.723 (2)	173 (2)
$O1W-H12W \cdots O22^{iii}$	0.91 (3)	1.87 (3)	2.7648 (18)	166 (3)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x + 1, -y, -z + 1$; (iv) $x, y - 1, z$.

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer	5638 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2802 independent reflections
$T_{\min} = 0.926, T_{\max} = 0.980$	2159 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.106$	$\Delta\rho_{\max} = 0.38 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$
2802 reflections	
184 parameters	

Compound (III)

Crystal data

$2C_4H_{12}N^+ \cdot C_8H_2Cl_2O_4^{2-} \cdot H_2O$	$\gamma = 67.777 (9)^\circ$
$M_r = 399.30$	$V = 1058.62 (18) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.1362 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.3043 (11) \text{ \AA}$	$\mu = 0.33 \text{ mm}^{-1}$
$c = 15.406 (1) \text{ \AA}$	$T = 200 \text{ K}$
$\alpha = 78.678 (7)^\circ$	$0.55 \times 0.30 \times 0.20 \text{ mm}$
$\beta = 85.846 (6)^\circ$	

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer	15869 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4851 independent reflections
$T_{\min} = 0.865, T_{\max} = 0.940$	3858 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.041$

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>
N1A—H11A...O21 ⁱ	0.90 (2)	1.80 (2)	2.6820 (17)	164.0 (17)
N1A—H12A...O11	0.914 (19)	1.907 (19)	2.8085 (17)	168.4 (16)
N1B—H11B...O11 ⁱ	0.896 (17)	1.917 (17)	2.8054 (16)	170.7 (16)
N1B—H12B...O1W	0.975 (19)	1.882 (19)	2.7866 (18)	153.1 (15)
O1W—H11W...O12	0.82 (2)	1.93 (2)	2.7490 (17)	176 (2)
O1W—H12W...O22 ⁱⁱ	0.84 (2)	1.96 (2)	2.7639 (17)	162 (2)

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

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.145$
 $S = 1.18$
 4851 reflections
 260 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.41 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{Å}^{-3}$

Compound (IV)**Crystal data**

$2\text{C}_5\text{H}_{12}\text{N}^+ \cdot \text{C}_8\text{H}_2\text{Cl}_2\text{O}_4^{2-} \cdot \text{H}_2\text{O}$
 $M_r = 423.32$
 Monoclinic, $P2_1/c$
 $a = 13.8481 (10) \text{ Å}$
 $b = 10.5937 (8) \text{ Å}$
 $c = 14.6129 (10) \text{ Å}$
 $\beta = 99.903 (7)^\circ$

$V = 2111.8 (3) \text{ Å}^3$
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.34 \text{ mm}^{-1}$
 $T = 200 \text{ K}$
 $0.35 \times 0.20 \times 0.18 \text{ mm}$

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.701, T_{\max} = 0.980$

26626 measured reflections
 4805 independent reflections
 3570 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$

Table 5

Comparative structural parameters (Å, °) and structural classification for the series of 'planar' 1:1 DCPA salts of the named Lewis base types.

Lewis base type	Structure type†	C1—C11	C2—C21	C1—C2—C21	C2—C1—C11	O12...O21	C1—C2—C21—O22	C2—C1—C11—O11
TEA ^a	0	1.5366 (19)	1.5344 (19)	128.16 (11)	129.73 (11)	2.4223 (14)	178.46 (13)	179.64 (13)
DEA ^a	2	1.530 (3)	1.521 (3)	128.33 (17)	128.49 (16)	2.388 (2)	-172.41 (19)	175.50 (19)
IPA ^b	1	1.5189 (18)	1.5297 (18)	128.32 (11)	128.14 (11)	2.4507 (16)	161.01 (13)	-156.69 (13)
DIPA ^c	1	1.523 (3)	1.516 (3)	128.5 (2)	128.2 (2)	2.381 (3)	-170.8 (2)	-176.7 (2)
HMT ^c	1	1.529 (9)	1.523 (8)	129.3 (5)	127.8 (5)	2.381 (8)	-173.7 (6)	173.6 (5)
INIPA ^d	1	1.522 (4)	1.534 (4)	128.8 (2)	128.2 (2)	2.392 (3)	-174.6 (3)	174.2 (3)
TMA ^e	1	1.528 (3)	1.529 (3)	128.9 (2)	128.9 (2)	2.380 (3)	180	180
TBA ^f	0	1.523 (13)	1.529 (14)	128.3 (9)	128.9 (8)	2.34 (1)	173 (1)	168 (1)
BRU ^g	0	1.523 (3)	1.535 (3)	128.9 (2)	128.4 (2)	2.441 (3)	-177.8 (2)	163.9 (2)
NICA ^h	0	1.531 (3)	1.528 (3)	127.88 (16)	128.93 (16)	2.410 (2)	172.58 (18)	-178.68 (19)
INICA ^h	1	1.521 (8)	1.515 (11)	128.3 (5)	128.0 (5)	2.393 (8)	-178.6 (7)	173.0 (7)
AMPM ^h	0	1.527 (2)	1.532 (2)	128.72 (14)	128.90 (14)	2.4037 (19)	-179.70 (16)	-170.16 (16)
PMPY ⁱ	1	1.527 (5)	1.531 (5)	128.9 (3)	128.8 (3)	2.376 (4)	169.9 (3)	-173.2 (3)
TFMAN ^j	2	1.5161 (19)	1.520 (2)	128.35 (13)	128.69 (12)	2.3908 (17)	-179.04 (16)	179.50 (16)
8-AQ ^k	1	1.525 (2)	1.534 (2)	129.27 (14)	128.36 (14)	2.3922 (18)	-175.88 (15)	174.38 (15)
8-HQ ^k	1	1.527 (3)	1.518 (3)	127.97 (19)	128.88 (19)	2.389 (2)	-176.6 (2)	171.3 (2)
BTMAP ^l	0	1.536 (2)	1.534 (2)	129.09 (15)	129.00 (14)	2.4004 (19)	172.41 (15)	179.32 (16)
PHEN ^m	0	1.538 (2)	1.536 (3)	128.55 (15)	129.18 (16)	2.4054 (19)	-179.53 (16)	-168.30 (16)
QAC ^{n‡}	2	1.527 (7)	1.527 (7)	129.6 (5)	128.4 (4)	2.366 (7)	177.0 (5)	-172.4 (5)
QAC ^{n‡}	2	1.522 (8)	1.511 (6)	128.2 (4)	129.0 (4)	2.377 (5)	178.5 (5)	-174.2 (5)

(a) This work (TEA is triethylamine and DEA is diethylamine); (b) Smith & Wermuth (2010b) (IPA is isopropylamine); (c) Smith & Wermuth (2010a) (DIPA is diisopropylamine and HMT is hexamethylenetetramine); (d) Smith & Wermuth (2010e) (INIPA is isonipecotamide); (e) Bozkurt *et al.* (2006) (TMA is the tetramethylammonium ion); (f) Mattes & Dorau (1986) (TBA is the tetra-*n*-butylammonium ion); (g) Smith *et al.* (2007) (BRU is brucine); (h) Smith *et al.* (2009a) (NICA is nicotinamide, INICA is isonicotinamide and AMPM is 2-aminopyrimidine); (i) Smith & Wermuth (2010d) (PMPY is 4-methylpyridine); (j) Odabaşoğlu & Büyükgüngör (2007) [TFMAN is 3-(trifluoromethyl)aniline]; (k) Smith *et al.* (2008b) (8-AQ is 8-aminoquinoline and 8-HQ is 8-hydroxyquinoline); (l) Mallinson *et al.* (2003); Parkin *et al.* (2007) [BTMAP is 1,8-bis(trimethylamino)naphthalene]; (m) Smith *et al.* (2009c) (PHEN is 1,10-phenanthroline); (n) Smith *et al.* (2009) (QAC is quinacrine). † 0 = zero-dimensional; 1 = one-dimensional; 2 = two-dimensional. ‡ For the quinacrine salt, there are two independent DCPA anions in the asymmetric unit.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.103$
 $S = 0.96$
 4805 reflections
 268 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{Å}^{-3}$

H atoms potentially involved in hydrogen-bonding interactions were all located in difference maps and their positional and isotropic displacement parameters were refined; the resulting O—H and N—H distances are given in Tables 1–4. Other H atoms were included at calculated positions [C—H = 0.95 (aromatic) or 0.98–0.99 Å (aliphatic)] and treated as riding atoms, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$.

For all compounds, data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for (I), (II) and (IV); *SIR92* (Altomare *et al.*, 1994) for (III). For all compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3347). Services for accessing these data are described at the back of the journal.

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