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Zero-, one- and two-dimensional hydrogen-bonded structures in the 1:1 proton-transfer compounds of 4,5-dichlorophthalic acid with the monocyclic heteroaromatic Lewis bases 2-aminopyrimidine, nicotinamide and isonicotinamide

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The structures of the anhydrous 1:1 proton-transfer compounds of 4,5-dichlorophthalic acid (DCPA) with the monocyclic heteroaromatic Lewis bases 2-aminopyrimidine, 3-(aminocarbonyl)pyridine (nicotinamide) and 4-(aminocarbonyl)pyridine (isonicotinamide), namely 2-aminopyrimidinium 2-carboxy-4,5-dichlorobenzoate, $C_4H_6N_3^+\cdot C_8H_3Cl_2O_4^-$, (I), 3-(aminocarbonyl)pyridinium 2-carboxy-4,5-dichlorobenzoate, $C_6H_7N_2O^+\cdot C_8H_3Cl_2O_4^-$, (II), and the unusual salt adduct 4-(aminocarbonyl)pyridinium 2-carboxy-4,5-dichlorobenzoate–methyl 2-carboxy-4,5-dichlorobenzoate (1/1), $C_6H_7N_2O^+\cdot C_8H_3Cl_2O_4^-\cdot C_9H_6Cl_2O_4$, (III), have been determined at 130 K. Compound (I) forms discrete centrosymmetric hydrogen-bonded cyclic bis(cation–anion) units having both $R_2^2(8)$ and $R_1^2(4)$ N—H···O interactions. In (II), the primary N—H···O-linked cation–anion units are extended into a two-dimensional sheet structure *via* amide–carboxyl and amide–carbonyl N—H···O interactions. The structure of (III) reveals the presence of an unusual and unexpected self-synthesized methyl monoester of the acid as an adduct molecule, giving one-dimensional hydrogen-bonded chains. In all three structures, the hydrogen phthalate anions are essentially planar with short intramolecular carboxyl–carboxylate O—H···O hydrogen bonds [O···O = 2.393 (8)–2.410 (2) Å]. This work provides examples of low-dimensional 1:1 hydrogen-bonded DCPA structure types, and includes the first example of a discrete cyclic 'heterotetramer.' This low dimensionality in the structures of the 1:1 aromatic Lewis base salts of the parent acid is generally associated with the planar DCPA anion species.

Comment

The 1:1 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*), with the occurrence of three-dimensional structures limited to the compounds with the bifunctional examples 3- and 4-aminobenzoic acid (Smith *et al.*, 2008*b*). In these two examples, the primary hydrogen-bonded cation–anion 'heterodimer' (Etter & Adsmond, 1990) is extended into sheet substructures through further anion–cation interactions, then into a three-dimensional framework *via* cyclic $R_2^2(8)$ cation carboxylic acid hydrogen bonds (Etter *et al.*, 1990). In these examples, the DCPA anions are nonplanar, whereas in the low-dimensional structure types, the DCPA anion species are essentially planar with the planarity achieved through short intramolecular carboxyl–carboxylate O—H···O hydrogen bonds [typically 2.441 (3) Å in the brucinium DCPA compound (Smith *et al.*, 2007)]. There is also a low incidence of hydrates among the structures of the 1:1 proton-transfer compounds of DCPA when prepared in aqueous alcohol solution, with the only three known examples limited to 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 *et al.*, 2009) and the drug quinacrine (a tetrahydrate) (Smith & Wermuth, 2009).

The 1:1 stoichiometric reaction of DCPA with the substituted monocyclic heteroaromatic bases 2-aminopyrimidine, 3-(aminocarbonyl)pyridine (nicotinamide) and 4-(aminocarbonyl)pyridine (isonicotinamide) in methanol gave the anhydrous compounds 2-aminopyrimidinium 2-carboxy-4,5-dichlorobenzoate, (I), 3-(aminocarbonyl)pyridinium 2-carboxy-4,5-dichlorobenzoate, (II), and the unusual adduct 4-(aminocarbonyl)pyridinium 2-carboxy-4,5-dichlorobenzoate–methyl 2-carboxy-4,5-dichlorobenzoate (1/1), (III). This set of compounds shows examples of zero-, one- and two-dimensional hydrogen-bonded structures.

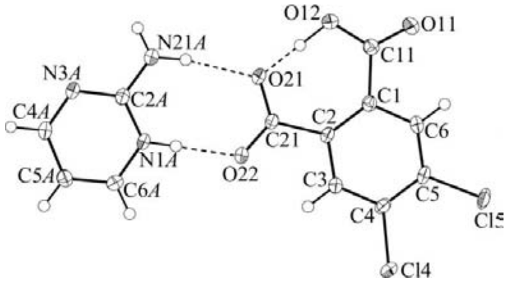

Figure 1
The molecular conformation and atom-numbering scheme for the 2-aminopyrimidinium cation and the 2-carboxy-4,5-dichlorobenzoate anion in (I), showing the cyclic $R_2^2(8)$ inter-species hydrogen-bonding associations as dashed lines. Non-H atoms are shown as 50% probability displacement ellipsoids.

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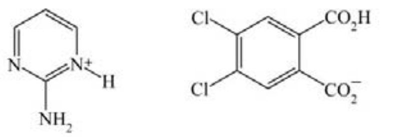
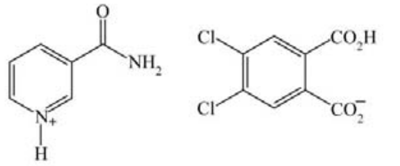
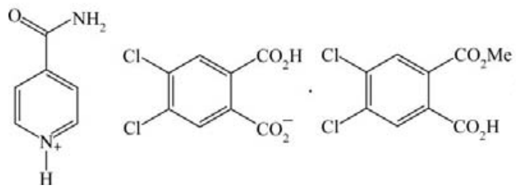
All three compounds have at least one direct hetero-ring $N^+{-}H\cdots O_{carboxyl}$ hydrogen-bonding interaction (Figs. 1–3 and Tables 1–3), and all show low-dimensional hydrogen-bonded overall structures, *viz.* two-dimensional in (II), one-dimensional in (III) and the first example of a cyclic zero-dimensional bis(cation–anion) species in (I) (Figs. 4–6). Associated with all of these DCPA structure types is the essentially planar monoanion species, which is found in *ca* 50% of the known 1:1 acid salts of DCPA with aromatic Lewis bases (Smith *et al.*, 2008*a*). However, structures (I)–(III) are sufficiently different as to be described separately.



(I)



(II)



(III)

With compound (I), the primary cation–anion association is an asymmetric cyclic $R_2^2(8)$ pyrimidinium–carboxyl $N\cdots O,O'$ association (Fig. 1). This is the high-probability type 4 hydrogen-bonding structural motif described by Allen *et al.* (1998). The cation–anion pairs so formed repeat across inversion centres *via* cyclic three-centre $R_1^2(4)$ amine–carboxyl $N^+{-}H\cdots O,O'$ associations, enclosing $R_6^6(12)$ rings, giving discrete four-molecule 'heterotetramer' structural units (Fig. 4). Although other zero-dimensional structures are known among the DCPA proton-transfer compounds [others being discrete cation–anion 'heterodimers' (Etter & Adsmond, 1990), with brucine (Smith *et al.*, 2007), hexamethylenetetramine and 1,10-phenanthroline (Smith *et al.*, 2009)], the formation of this bis(cation–anion) structure type is driven more by the interactive features of the 2-aminopyrimidine molecular synthon and finds a small incidence among its 1:1 salts with the aromatic acids, *e.g.* (3,4-dichlorophenoxy)acetic acid (Lynch *et al.*, 1994) and phthalic acid (Smith *et al.*, 1995).

With (II), the nicotinamide cations form chain structures through homomeric amide–carbonyl $N31{-}H\cdots O$ interactions. These chains are linked along the *b* cell direction by associations involving H-atom donors of both the amide N and the primary pyridinium groups to carboxyl O-atom acceptors of the anions (Table 2), giving a sheet parallel to (100) (Fig. 5).

Compound (III) is an example of a 1:1:1 cation–anion adduct structure with the adduct molecule an unexpected methyl monoester of DCPA, arising from self-synthesis in the methanol solvent under the conditions of the reaction. This phenomenon has no precedence among the proton-transfer compounds prepared under similar conditions in our labora-

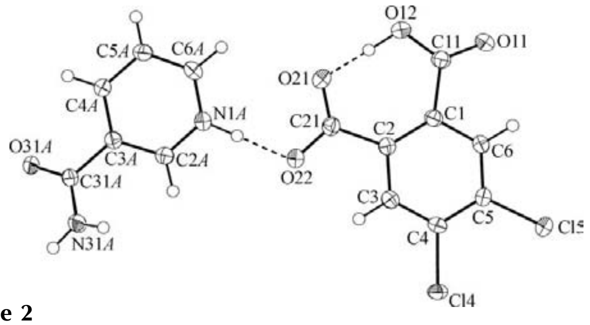


Figure 2

The molecular conformation and atom-numbering scheme for the 3-(aminocarbonyl)pyridinium cation and the 2-carboxy-4,5-dichlorobenzoate anion in (II). The dashed lines indicate the inter-species hydrogen bonds, while non-H atoms are shown as 50% probability displacement ellipsoids.

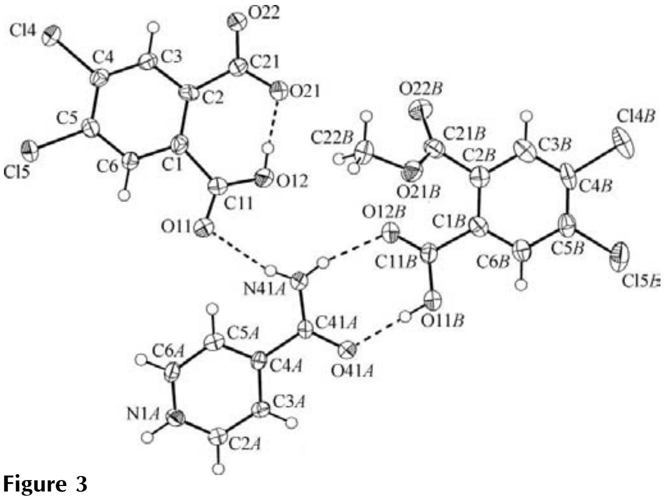


Figure 3

The molecular conformation and atom-numbering scheme for the 4-(aminocarbonyl)pyridinium cation, the 2-carboxy-4,5-dichlorobenzoate anion and the methyl 2-carboxy-4,5-dichlorobenzoate adduct molecule in (III). The dashed lines indicate the inter-species hydrogen bonds, while non-H atoms are shown as 50% probability displacement ellipsoids.

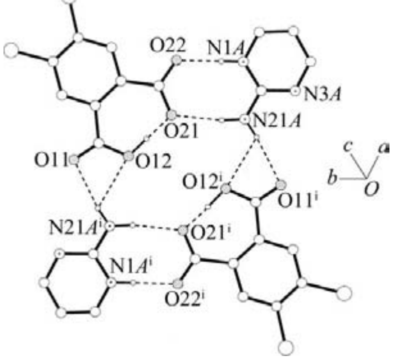


Figure 4

Hydrogen-bonding in the discrete cyclic centrosymmetric bis(cation–anion) 'heterotetramer' structural units in (I), shown as dashed lines. Non-interacting H atoms have been omitted. See Table 1 for symmetry code.

tory. In (III), the primary pyridinium–carboxyl $N^+—H\cdots O$ hydrogen-bonded unit is extended into a zigzag chain along $[10\overline{1}]$ *via* an amide–carboxyl $N—H\cdots O$ association (Fig. 6). The second amide N atom, together with the amide carbonyl O atom, is involved in an asymmetric cyclic $R_2^2(8)$ association with the peripherally linked DCPA methyl monoester adduct molecule (*B*).

There is an absence in (I)–(III) of short intermolecular $Cl\cdots Cl$ interactions such as has been found in the DCPA compounds with 3- and 4-aminobenzoic acids (Smith *et al.*, 2008*a*). The occurrence of this phenomenon, particularly in dichloro-substituted aromatic compounds, has previously been described (Sarma & Desiraju, 1986). However, in all three structures there are short $Cl\cdots O_{carboxyl}$ associations [for (I): $Cl4\cdots O22^{ii}$ = 3.0683 (14) Å; symmetry code: (ii) $-x + 1, -y + 2, -z + 1$; for (II): $Cl4\cdots O11^{ii}$ = 3.1583 (15) Å; symmetry code: (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{5}{2}$; for (III): $Cl4\cdots O22^{iii}$ = 2.983 (5) Å; symmetry code: (iii) $x, -y + 1, z - \frac{1}{2}$].

With the DCPA anions in this series, the essential planarity is the result of the presence of short intramolecular hydrogen bonds between the carboxyl groups [$O\cdots O$ distances range from 2.393 (8) Å in (III) to 2.410 (2) Å in (II)]. The torsion angles associated with these groups (C2—C1—C11—O11 and C1—C2—C21—O22) are −170.16 (16) and −179.70 (16)°, respectively, for (I), −178.73 (19) and 172.53 (18)° for (II), and 173.0 (7) and −178.5 (7)° for (III). The planarity also means that there are short intramolecular aromatic ring $C—H\cdots O_{carboxyl}$ contacts [typically, the $C\cdots O$ distances are $C6—H6\cdots O11$ = 2.676 (2) Å and $C3—H3\cdots O22$ = 2.643 (2) Å in (I)]. With the methyl ester adduct molecule in (III), the carboxylic acid group provides hydrogen-bonding links to the cation–anion chain structure rather than forming an intramolecular hydrogen bond and is therefore rotated out of the molecular plane [C2*B*—C1*B*—C11*B*—O11*B* = −151.6 (6)°].

This present series provides a set of low-dimensional hydrogen-bonded structure types in the series of 1:1 proton-transfer compounds of 4,5-dichlorophthalic acid with aromatic Lewis bases. This low dimensionality is largely associated with planarity in the internally hydrogen-bonded hydrogen phthalate anion species.

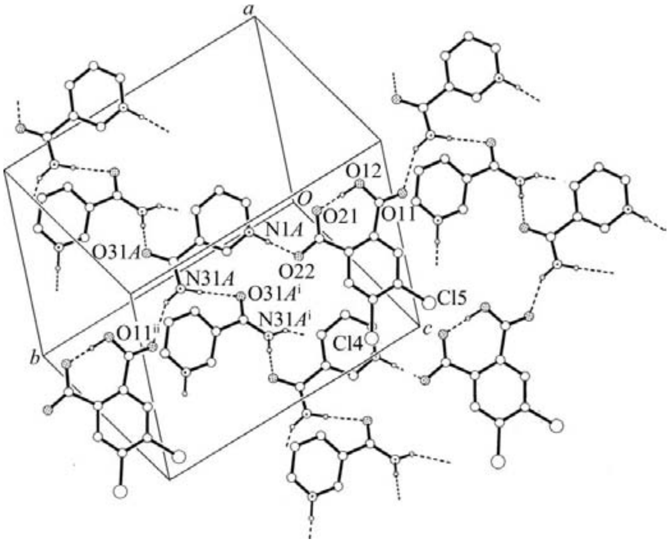


Figure 5

Hydrogen-bonding in the homomeric cation chains and the peripheral cation–anion extensions in the sheet structure in a perspective view of the unit cell of (II). Non-interacting H atoms have been omitted, and hydrogen bonds are shown as dashed lines. See Table 2 for symmetry codes.

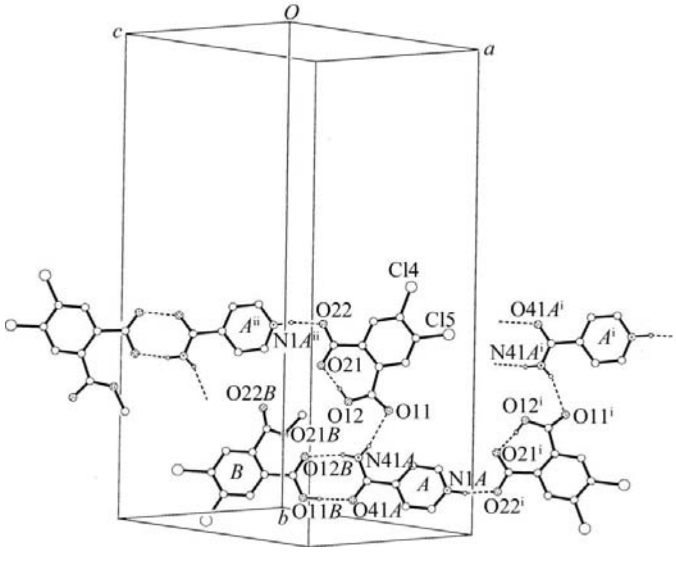


Figure 6

The zigzag hydrogen-bonded chains formed by extension of the cation–anion pairs and the peripherally attached methyl monoester adduct *B* molecules in the structure of (III), in a perspective view of the unit cell. Non-interacting H atoms have been omitted. [Symmetry code: (ii) $x - \frac{1}{2}, y + \frac{3}{2}, z - \frac{1}{2}$; see Table 3 for symmetry code (i).]

Experimental

Compounds (I)–(III) were synthesized by heating together, for 10 min under reflux, 1 mmol quantities of 4,5-dichlorophthalic acid and, respectively, 2-aminopyrimidine, nicotinic acid and isonicotinic acid in methanol (50 ml). All compounds were obtained as small colourless plates or needles [m.p. (I) 334 K; (II) 455–457 K; (III) 433–434 K] after partial room-temperature evaporation of the solvent.

Compound (I)

Crystal data

$C_4H_6N_3^+\cdot C_8H_3Cl_2O_4^-$
M_r = 330.12
Triclinic, $P\overline{1}$
a = 6.9738 (4) Å
b = 9.4413 (4) Å
c = 10.8900 (7) Å
α = 97.420 (4)°
β = 100.527 (5)°
γ = 109.473 (5)°
V = 650.50 (7) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 4.70 mm^{-1}
T = 180 K
0.40 × 0.25 × 0.06 mm

Data collection

Oxford Diffraction Gemini-S Ultra CCD-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.263, T_{max} = 0.750
4955 measured reflections
2542 independent reflections
2300 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

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Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.095$
$S = 1.09$
2542 reflections
206 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12···O21	1.02 (4)	1.38 (3)	2.4037 (19)	177 (3)
N1*A*—H1*A*···O22	0.87 (2)	1.79 (2)	2.6609 (19)	178.8 (19)
N21*A*—H21*A*···O11^{i}	0.86 (2)	2.18 (3)	3.038 (2)	173 (3)
N21*A*—H21*A*···O12^{i}	0.86 (2)	2.47 (3)	2.971 (2)	117 (2)
N21*A*—H22*A*···O21	0.92 (3)	2.02 (3)	2.929 (2)	169.4 (19)

Symmetry code: (i) $-x-1, -y+1, -z$.

Compound (II)

Crystal data

$C_6H_7N_2O^+ \cdot C_8H_3Cl_2O_4^-$
$M_r = 357.14$
Monoclinic, $P2_1/c$
$a = 11.4303$ (3) Å
$b = 13.7933$ (3) Å
$c = 9.2082$ (2) Å
$\beta = 99.454$ (2)°
$V = 1432.06$ (6) Å^3
$Z = 4$
Cu $K\alpha$ radiation
$\mu = 4.36$ mm^{-1}
$T = 130$ K
0.50 × 0.25 × 0.07 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.340$, $T_{\max} = 0.740$
6939 measured reflections
2798 independent reflections
2237 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.095$
$S = 0.96$
2798 reflections
224 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12···O21	0.99 (4)	1.43 (4)	2.410 (2)	180 (6)
N1*A*—H1*A*···O22	0.96 (2)	1.62 (2)	2.571 (2)	178 (3)
N31*A*—H31*A*···O31*A*^{i}	0.88 (3)	2.04 (3)	2.908 (2)	171 (2)
N31*A*—H32*A*···O11^{ii}	0.89 (3)	2.06 (3)	2.869 (2)	151 (2)

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

Compound (III)

Crystal data

$C_6H_7N_2O^+ \cdot C_8H_3Cl_2O_4^- \cdot C_9H_6Cl_2O_4$
$M_r = 606.18$
Monoclinic, Cc
$a = 11.9645$ (4) Å
$b = 26.1393$ (6) Å
$c = 9.3213$ (3) Å
$\beta = 122.509$ (3)°
$V = 2458.39$ (15) Å^3
$Z = 4$
Cu $K\alpha$ radiation
$\mu = 4.90$ mm^{-1}
$T = 130$ K
0.56 × 0.14 × 0.07 mm

Data collection

Oxford Diffraction Gemini-S Ultra CCD-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.454$, $T_{\max} = 0.710$
6097 measured reflections
3034 independent reflections
2530 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.128$
$S = 0.97$
3034 reflections
363 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Absolute structure: Flack (1983), 576 Friedel pairs
Flack parameter: 0.03 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12···O21	0.81 (8)	1.60 (9)	2.394 (10)	166 (11)
N1*A*—H1*A*···O22^{i}	0.93 (8)	1.70 (7)	2.620 (8)	169 (5)
N41*A*—H41*A*···O12*B*	0.83 (7)	2.05 (8)	2.866 (9)	166 (5)
N41*A*—H42*A*···O11	0.82 (8)	2.14 (8)	2.935 (6)	167 (10)
O11*B*—H11*B*···O41*A*	0.85 (9)	1.81 (8)	2.661 (7)	174 (8)

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

H atoms potentially involved in hydrogen-bonding interactions in all compounds were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included at calculated positions (C—H = 0.93–0.96 Å) and treated as riding [with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $1.5U_{\rm eq}$(methyl C)]. For compound (III), the correct orientation of the structure with respect to the polar-axis directions was established by means of the Flack (1983) x parameter.

For all compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); 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: GD3270). Services for accessing these data are described at the back of the journal.

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