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Anhydrous 1:1 proton-transfer compounds of isonipecotamide with picric acid and 3,5-dinitrosalicylic acid: 4-carbamoylpiperidinium 2,4,6-trinitrophenolate and two polymorphs of 4-carbamoylpiperidinium 2-carboxy-4,6-dinitrophenolate

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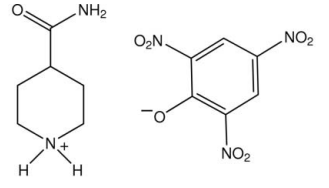
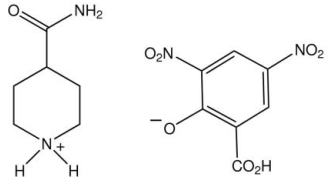
The structures of the anhydrous 1:1 proton-transfer compounds of isonipecotamide (piperidine-4-carboxamide) with picric acid and 3,5-dinitrosalicylic acid, namely 4-carbamoylpiperidinium 2,4,6-trinitrophenolate, $C_6H_{13}N_2O^+\cdot C_6H_2N_3O_7^-$, (I), and 4-carbamoylpiperidinium 2-carboxy-4,6-dinitrophenolate [two forms of which were found, the monoclinic α-polymorph, (II), and the triclinic β-polymorph, (III)], $C_6H_{13}N_2O^+\cdot C_7H_3N_2O_7^-$, have been determined at 200 K. All three compounds form hydrogen-bonded structures, *viz.* one-dimensional in (II), two-dimensional in (I) and three-dimensional in (III). In (I), the cations form centrosymmetric cyclic head-to-tail hydrogen-bonded homodimers [graph set $R_2^2(14)$] through lateral duplex piperidinium–amide N—H···O interactions. These dimers are extended into a two-dimensional network structure through further interactions with phenolate and nitro O-atom acceptors, including a direct symmetric piperidinium–phenol/nitro N—H···O,O cation–anion association [graph set $R_1^2(6)$]. The monoclinic polymorph, (II), has a similar $R_1^2(6)$ cation–anion hydrogen-bonding interaction to (I) but with an additional conjoint symmetrical $R_2^1(4)$ interaction as well as head-to-tail piperidinium–amide N—H···O,O hydrogen bonds and amide–carboxyl N—H···O hydrogen bonds, giving a network structure which includes large $R_4^3(20)$ rings. The hydrogen bonding in the triclinic polymorph, (III), is markedly different from that of monoclinic (II). The asymmetric unit contains two independent cation–anion pairs which associate through cyclic piperidinium–carboxyl N—H···O,O′ interactions [graph set $R_1^2(4)$]. The cations also show the zigzag head-to-tail piperidinium–amide N—H···O hydrogen-bonded chain substructures found in (II), but in addition feature amide–nitro and amide–phenolate N—H···O associations. As well, there is a centrosymmetric double-amide N—H···$O_{carboxyl}$ bridged bis(cation–anion) ring system [graph set $R_4^2(8)$] in the three-dimensional framework. The structures reported here demonstrate the utility of the isonipecotamide cation as a synthon with previously unrecognized potential for structure assembly applications. Furthermore, the structures of the two polymorphic 3,5-dinitrosalicylic acid salts show an unusual dissimilarity in hydrogen-bonding characteristics, considering that both were obtained from identical solvent systems.

Comment

The structures of piperidine-4-carboxylic acid (isonipecotic acid) (O'Neil, 2001) and its derivatives are uncommon in the crystallographic literature. Both anhydrous isonipecotic acid (Mora *et al.*, 2005) and its monohydrate (Delgado *et al.*, 2001) show the presence of piperidinium–carboxylate zwitterions while the structure of the hydrochloride is also known (Ma & Li, 2006; Adams *et al.*, 2006; Szafran *et al.*, 2007). However, neither the structures of its amide (isonipecotamide, INIPA) nor any of its derivatives have been reported, although the structures of the acetate (Smith & Wermuth, 2010) and the bipyridine-4,4′-disulfonate (Smith *et al.*, 2010) are now known. Picric acid has been used to produce stable crystalline Lewis base salts suitable for X-ray analysis and the number of picrate structures in the literature reflects this. Similarly, 3,5-dinitrosalicylic acid (DNSA) has proved to be a versatile synthon for crystal engineering usage (Kumar *et al.*, 1999) and a large number of structures of proton-transfer compounds with this acid have also been reported (Smith *et al.*, 2002, 2003, 2007). With these, the majority (*circa* 70%) are phenolates rather than carboxylates, the H atom being *anti*-located on the carboxyl O within an intramolecular hydrogen bond.


(I)


(II), (III)

We therefore carried out 1:1 stoichiometric reactions of isonipecotamide with a number of aromatic acids including picric acid and 3,5-dinitrosalicylic acid in 50% aqueous ethanol, with a view to obtaining crystals suitable for X-ray analysis, hence allowing description of the hydrogen-bonding present in these compounds. We obtained good crystals of the anhydrous picrate salt 4-carbamoylpiperidinium picrate, (I), as well as two anhydrous polymorphic salts with DNSA, namely

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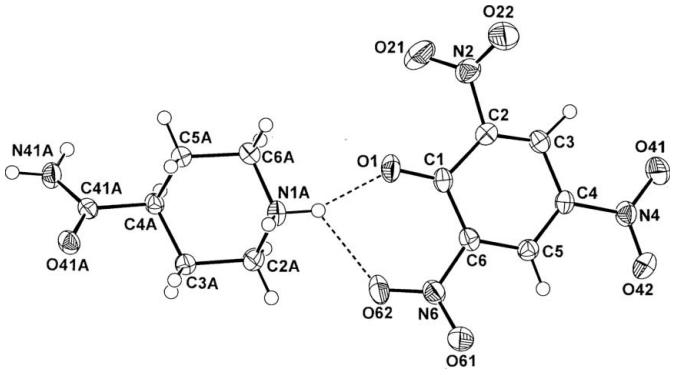

Figure 1
The molecular configuration and atom-naming scheme for the isonipecotamide cation and the picrate anion in (I). Displacement ellipsoids are drawn at the 50% probability level. Intermolecular hydrogen bonds are shown as dashed lines.

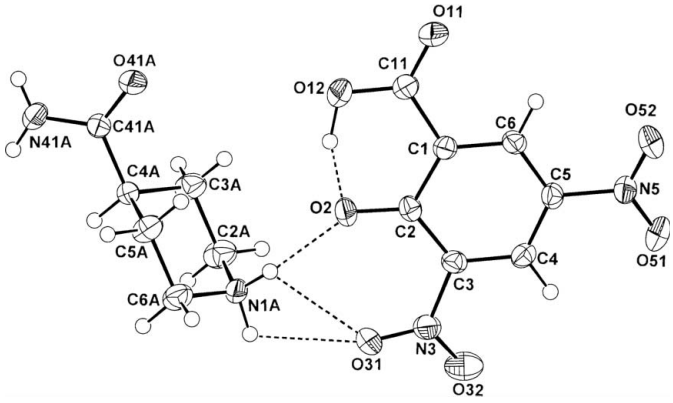

Figure 2
The molecular configuration and atom-naming scheme for the isonipecotamide cation and the DNSA anion in (II). Displacement ellipsoids are drawn at the 50% probability level. Inter- and intramolecular hydrogen bonds and short molecular contacts are shown as dashed lines.

4-carbamoylpiperidinium 2-carboxy-4,6-dinitrophenolate, *i.e.* the monoclinic (α) polymorph, (II), and the triclinic (β) polymorph, (III). The crystals of (II) were obtained after partial room-temperature evaporation of solvent whereas with the identical parallel reaction in which the solution was taken to dryness, the second anhydrous triclinic polymorph, (III), was obtained. The structures of (I)–(III) are described here, representing the first reported aromatic organic acid salts of the Lewis base isonipecotamide (excluding the biphenyl-4,4′-disulfonate salt; Smith & Wermuth, 2010). It was of particular interest to determine what differences, if any, might be found in the hydrogen bonding in the two polymorphic salts (II) and (III).

With salts (I)–(III) (Figs. 1–3), proton transfer occurs to the hetero-N atom of the piperidine ring and, in each, the resulting group, along with the amine substituent group, are subsequently involved in hydrogen-bonding interactions (Tables 1–3). All three salts are phenolates and form hydrogen-bonded structures, *viz.* one-dimensional in (II), two-dimensional in (I) and three-dimensional in (III). A feature of the hydrogen-bonding motifs in (II) and (III) is the presence

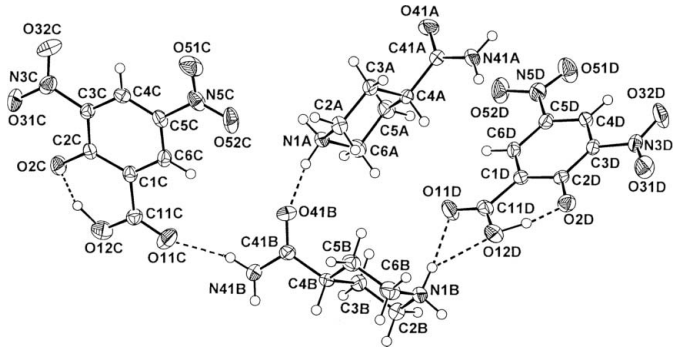

Figure 3
The molecular configuration and atom-naming scheme for the two isonipecotamide cations (*A* and *B*) and the two DNSA anions (*C* and *D*) in the asymmetric unit of (III). Displacement ellipsoids are drawn at the 50% probability level. Inter-species hydrogen bonds are shown as dashed lines.

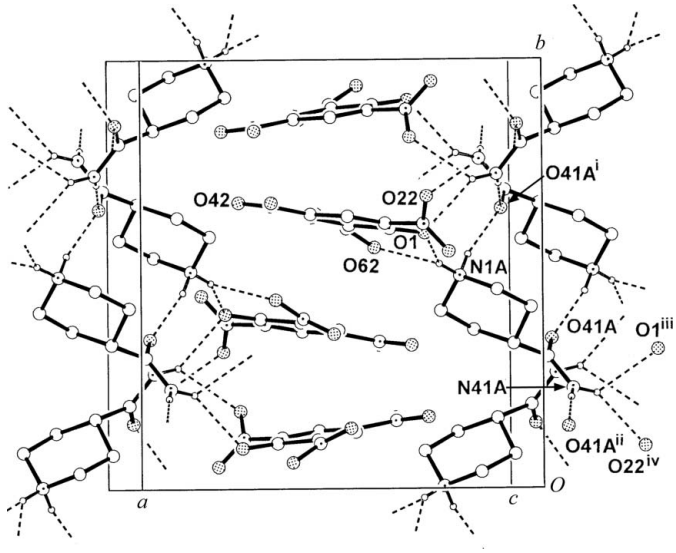

Figure 4
The two-dimensional hydrogen-bonded network structure of (I) extending across the (010) plane of the unit cell, showing hydrogen-bonding associations as dashed lines. Non-associative H atoms have been omitted. For symmetry codes, see Table 1.

of homomolecular head-to-tail piperidinium–amide N—H···O interactions giving infinite zigzag chain structures.

In (I), the two piperidinium H-atom donors give three hydrogen-bonding interactions. One of the H atoms gives a symmetric cyclic $R_1^2(6)$ association (Etter *et al.*, 1990) with phenolate and nitro O-atom acceptors of the anion (Fig. 1). The second H atom forms a hydrogen bond with an amide O-atom acceptor giving a centrosymmetric cyclic head-to-tail homodimer [graph set $R_2^2(14)$] (Table 1 and Fig. 4). This ring is conjoint with a piperidine–amide N—H···O cyclic $R_4^2(8)$ association and the previously mentioned $R_1^2(6)$ association. These rings are linked by other amide–nitro N—H···O interactions into a two-dimensional network structure which lies in the (011) plane with the picrate ring systems layering down the *b* axis of the unit cell. The *ortho*-related nitro-substituent groups of the picrate anion are significantly

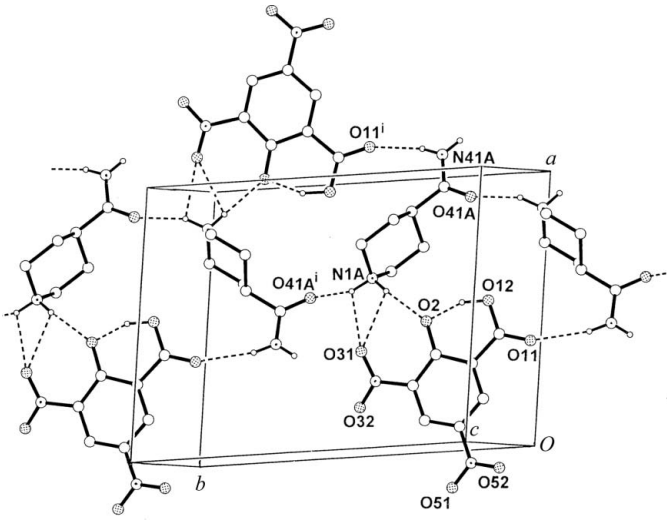

Figure 5
The one-dimensional hydrogen-bonded ribbon structure of (II) extending along the *b* cell direction, showing hydrogen-bonding associations and short inter-ion associations as dashed lines. Non-associative H atoms have been omitted. For symmetry codes, see Table 2.

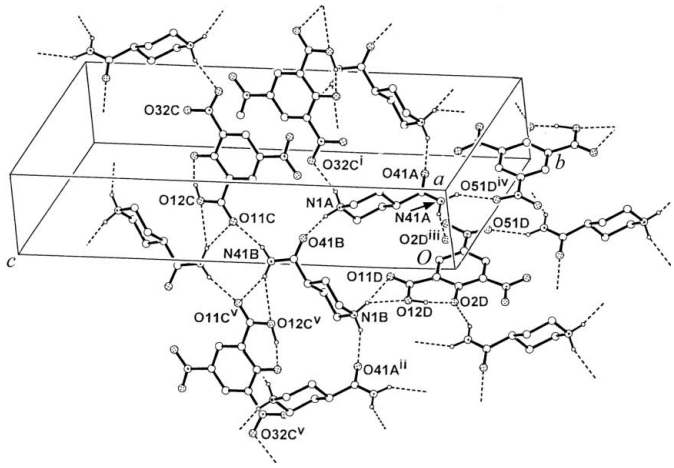

Figure 6
The three-dimensional hydrogen-bonded framework structure of (III) in a perspective view of the unit cell, showing hydrogen-bonding associations as dashed lines. Non-associative H atoms have been omitted. For symmetry codes, see Table 3.

rotated out of the benzene plane [torsion angles: C1—C2—N2—O22 = 134.13 (16)° and C5—C6—N6—O62 = −157.57 (16)°], compared with the *para*-nitro group [C3—C4—N4—O42 = 176.78 (14)°].

In the monoclinic α-polymorph of the 3,5-dinitrosalicylic acid salt, (II), a cyclic $R_1^2(6)$ proximal piperidinium–phenol/nitro N—H···O,O cation–anion association similar to that in (I) is present (Fig. 2). This is also similar to the association found in a number of DNSA proton-transfer compounds (Smith *et al.*, 2007), but in (II) there is an additional conjoint symmetrical $R_1^2(4)$ piperidinium N—H···O,O′ interaction (Fig. 2). Head-to-tail piperidinium–amide N—H···O hydrogen bonds (Table 2) give ribbon structures which extend along the *b* cell direction and enclose $R_4^3(20)$ ring systems (Fig. 5). The short intramolecular hydrogen bond which is characteristic of the DNSA anion is found in (II) as well as in the triclinic polymorph, (III). In both structures, the *anti*-related H atom is located on the carboxyl group rather than on the phenolic O atom, but this is the majority case with the DNSA anions in the known structures of the proton-transfer salts of this acid (Smith *et al.*, 2002, 2003, 2007).

The triclinic modification (the β-polymorph) of the isonipecotamide–DNSA compound, (III), has two INIPA cations (*A* and *B*) and two anions (*C* and *D*) in the asymmetric unit (Fig. 3). Although there is no major difference in the amide side-chain conformations of the two independent cations in (III) [as indicated by the torsion angle C3—C4—C41—N41 of 93.6 (2)° for cation *A* and 86.5 (2)° for cation *B*], these differ significantly from that found in (II) [122.29 (16)°]. With the DNSA anions the differences are less obvious. As expected, because of the presence of the intramolecular hydrogen bond, the carboxyl group is essentially coplanar with the benzene ring in all three anions [C2—C1—C11—O11 = −179.15 (16)° for (II), −178.18 (18)° for (III*C*) and −179.09 (16)° for (III*D*)]. Both nitro groups in the two polymorphs are slightly rotated out of the plane [C2—C3—N3—O32 = 165.64 (17)° for (II), −170.75 (16)° for (III*C*), −177.65 (15)° for (III*D*); C4—C5—N5—O52 = −166.78 (16)° for (II), −175.98 (17)° for (III*C*) and −170.94 (18)° for (III*D*)]. However, the hydrogen-bonding differences between (II) and (III) are very significant (Table 3). There is an absence of the proximal piperidinium–phenolate/nitro N—H···O,O interaction with either of the DNSA anions. Instead, one of the cations (*B*) gives an N—H···O,$O''_{\rm carboxyl}$ interaction with a *D* anion [graph set $R_1^2(4)$], the other (*A*) acting as a bridge between cation *B* amide O and anion nitro O-atom acceptors. The anions also form the zigzag head-to-tail piperidinium–amide N—H···O-bridged hydrogen-bonded chain substructures also found in (II) (Fig. 6). In addition, the hydrogen bonding in the overall three-dimensional framework structure features a centrosymmetric duplex amide H—N—H-bridged bis(cation–anion) $R_4^2(8)$ ring system (Fig. 6).

The structures reported here demonstrate the utility of the isonipecotamide cation as a synthon with previously unrecognized potential for structure assembly applications. Furthermore, the structures of the two polymorphic 3,5-dinitrosalicylic acid salts, (II) and (III), show unusually diverse hydrogen-bonding characteristics with only slight molecular conformational differences. In the absence of any additive induced effects during crystallization, the observed polymorphism can be seen as an artefact of solvent gradient effects, considering that the parallel crystallizations occurred from identical ethanol–water solvent mixtures.

Experimental

The title compounds were synthesized by heating together for 10 min under reflux 1 mmol quantities of piperidine-4-carboxamide (isonipecotamide) and 2,4,6-trinitrophenol (picric acid) [for (I)] or 3,5-dinitrosalicylic acid [for (II) and (III)] in 50 ml of 50% ethanol–water. After concentration to *ca* 30 ml, partial room-temperature evaporation [(I) and (III)] or evaporation to dryness [(II)] of the hot-filtered

solutions gave yellow prisms of (I) (m.p. 452 K) or yellow plates of (II) and (III) (m.p. 475 K for both).

Compound (I)

Crystal data

$C_6H_{13}N_2O^+\cdot C_6H_2N_3O_7^-$
M_r = 357.29
Monoclinic, $P2_1/c$
a = 13.4426 (11) Å
b = 13.7495 (13) Å
c = 8.3662 (15) Å
β = 100.752 (13)°
V = 1519.2 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 200 K
0.25 × 0.20 × 0.15 mm

Data collection

Oxford Diffraction Gemini-S Ultra CCD-detector diffractometer
Absorption correction: multi-scan (*CrysAlis Pro*; Oxford Diffraction, 2009)
T_{min} = 0.950, T_{max} = 0.981
10181 measured reflections
2994 independent reflections
2279 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.107
S = 0.93
3422 reflections
238 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Compound (II)

Crystal data

$C_6H_{13}N_2O^+\cdot C_7H_3N_2O_7^-$
M_r = 356.30
Monoclinic, $P2_1/n$
a = 11.7131 (12) Å
b = 12.6450 (11) Å
c = 11.8521 (14) Å
β = 118.196 (14)°
V = 1547.1 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 200 K
0.40 × 0.40 × 0.20 mm

Data collection

Oxford Diffraction Gemini-S Ultra CCD-detector diffractometer
Absorption correction: multi-scan (*CrysAlis Pro*; Oxford Diffraction, 2009)
T_{min} = 0.93, T_{max} = 0.98
19733 measured reflections
3048 independent reflections
2456 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.098
S = 1.06
3048 reflections
242 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Compound (III)

Crystal data

$C_6H_{13}N_2O^+\cdot C_7H_3N_2O_7^-$
M_r = 356.30
Triclinic, $P\overline{1}$
a = 6.4628 (4) Å
b = 10.2375 (5) Å
c = 23.8964 (12) Å
α = 98.644 (4)°
β = 96.905 (5)°
γ = 100.753 (5)°
V = 1517.65 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 200 K
0.40 × 0.30 × 0.18 mm

Data collection

Oxford Diffraction Gemini S Ultra CCD-detector diffractometer
Absorption correction: multi-scan (*CrysAlis Pro*; Oxford Diffraction, 2009)
T_{min} = 0.96, T_{max} = 0.98
19052 measured reflections
5940 independent reflections
4477 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.095
S = 0.82
5940 reflections
475 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H11A···O1	0.934 (18)	1.901 (17)	2.7545 (19)	150.8 (15)
N1A—H11A···O62	0.934 (18)	2.227 (17)	2.859 (2)	124.3 (13)
N1A—H12A···O41A^{i}	0.912 (18)	2.012 (18)	2.8932 (19)	162.0 (16)
N41A—H43A···O41A^{ii}	0.866 (17)	2.029 (17)	2.894 (2)	177 (2)
N41A—H44A···O1^{iii}	0.910 (19)	2.316 (19)	3.072 (2)	140.3 (15)
N41A—H44A···O22^{iv}	0.910 (19)	2.437 (19)	3.017 (2)	121.8 (14)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H11A···O2	0.86 (2)	1.98 (2)	2.817 (2)	164 (2)
N1A—H11A···O31	0.86 (2)	2.43 (2)	2.835 (3)	109.7 (17)
N1A—H12A···O31	0.93 (2)	2.43 (2)	2.835 (3)	106.1 (15)
N1A—H12A···O41A^{i}	0.93 (2)	1.844 (19)	2.6964 (19)	151 (2)
N41A—H41A···O11^{i}	0.88 (2)	2.19 (2)	3.053 (2)	168 (2)
O12—H12···O2	1.01	1.52	2.4829 (17)	157

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H11A···O32C^{i}	0.91 (2)	2.113 (19)	2.980 (2)	160.1 (17)
N1A—H12A···O41B	0.93 (2)	1.86 (2)	2.759 (2)	159.7 (19)
N1B—H11B···O41A^{ii}	0.92 (2)	1.91 (2)	2.757 (2)	153 (2)
N1B—H12B···O11D	0.97 (3)	2.09 (3)	3.039 (2)	167 (2)
N1B—H12B···O12D	0.97 (3)	2.26 (2)	2.980 (2)	131 (2)
N41A—H41A···O2D^{iii}	0.86 (2)	2.18 (2)	2.954 (2)	148.8 (19)
N41A—H42A···O51D^{iv}	0.91 (2)	2.18 (2)	2.999 (2)	149.0 (18)
N41B—H41B···O11C^{v}	0.90 (2)	2.34 (2)	3.176 (2)	154.9 (18)
N41B—H41B···O12C^{v}	0.90 (2)	2.58 (2)	3.388 (2)	149.5 (18)
N41B—H42B···O11C	0.89 (2)	2.09 (2)	2.950 (2)	164.3 (19)
O12C—H12C···O2C	1.12	1.38	2.460 (2)	157
O12D—H12D···O2D	1.10	1.37	2.4422 (18)	163

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

H atoms involved in hydrogen-bonding interactions were located by difference methods and, with the exception of the carboxyl H atoms in both (II) and (III) which were allowed to ride, their positional and isotropic displacement parameters were refined. The other H atoms were included in the refinements at calculated positions (aliphatic C—H = 0.99 or 1.00 Å and aromatic C—H = 0.95 Å), while using a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(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); *SIR92* (Altomare *et al.*, 1994) for (II) and (III). For all compounds, program(s) used to refine structure: *SHELXL97* 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: FG3206). Services for accessing these data are described at the back of the journal.

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