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Supramolecular association in proton-transfer adducts containing benzamidinium cations. II. Concomitant polymorphs of the molecular salt of 2,6-dimethoxybenzoic acid with benzamidine[1]

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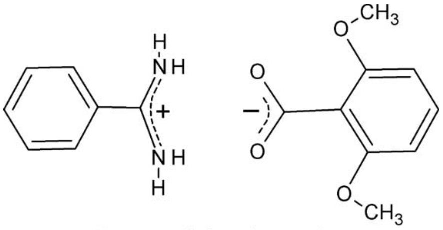
Two concomitant polymorphs of the molecular salt formed by 2,6-dimethoxybenzoic acid, $C_9H_{10}O_4$ (Dmb), with benzamidine, $C_7H_8N_2$ (benzenecarboximidamide, Benzam) from water solution have been identified. Benzamidinium 2,6-dimethoxybenzoate, $C_7H_9N_2^+\cdot C_9H_9O_4^-$ (BenzamH$^+$·Dmb$^-$), was obtained through protonation at the imino N atom of Benzam as a result of proton transfer from the acidic hydroxy group of Dmb. In the monoclinic polymorph, (I) (space group $P2_1/n$), the asymmetric unit consists of two Dmb$^-$ anions and two monoprotonated BenzamH$^+$ cations. In the orthorhombic polymorph, (II) (space group $P2_12_12_1$), one Dmb$^-$ anion and one BenzamH$^+$ cation constitute the asymmetric unit. In both polymorphic salts, the amidinium fragments and carboxylate groups are completely delocalized. This delocalization favours the aggregation of the molecular components of these acid–base complexes into nonplanar dimers with an $R_2^2(8)$ graph-set motif *via* $N^+-H\cdots O^-$ charge-assisted hydrogen bonding. Both the monoclinic and orthorhombic forms exhibit one-dimensional isostructurality, as the crystal structures feature identical hydrogen-bonding motifs consisting of dimers and catemers.

Comment

The present study is a continuation of work carried out in our laboratory on the design and synthesis of hydrogen-bonding systems formed by benzamidine with benzoic acid derivatives. The protonated analogue of benzamidine is a multiple hydrogen-bond donor, and its amidinium group exhibits ideal requirements to couple with carboxylate groups in crystal structures. These acid–base complexes are usually arranged in a dimeric motif similar to that found in carboxylic acid dimers *via* $N^+-H\cdots O^-$ (±)-CAHB (charge-assisted hydrogen bonds with both plus and minus charges on the donor and acceptor atoms, respectively; Gilli & Gilli, 2009), provided that ΔpK_a is sufficiently large [ΔpK_a = pK_a(conjugate acid of the base) − pK_a(acid), where the pK_a values are for aqueous solutions at 298 K]. It is generally accepted that for large ΔpK_a values (*i.e.* greater than 3), salts of the type $B^+\cdots A^-$ are formed, while with smaller ΔpK_a values, $B\cdots H-A$ compounds (cocrystals) can be expected, but this parameter seems inappropriate for accurately predicting salt or cocrystal formation in the solid state when ΔpK_a is between 0 and 3 (Portalone & Colapietro, 2009; Portalone, 2011*a*; Delori *et al.*, 2012). This dimeric motif is commonly observed in biological systems between arginine and aspartic and glutamic acids (Saenger, 1984).



(I) Monoclinic polymorph
(II) Orthorhombic polymorph

In this study, we report the molecular and supramolecular structures of two concomitant polymorphs, *i.e.* two different polymorphs simultaneously crystallized from the same solvent (Bernstein *et al.*, 1999), of the acid–base complex formed by benzamidine (Benzam) with 2,6-dimethoxybenzoic acid (Dmb). Interestingly, Dmb has two polymorphic modifications, *viz.* the orthorhombic form (Portalone, 2009) and the tetragonal form (Portalone, 2011*b*). In the former polymorph, the carboxyl group is twisted away from the plane of the aromatic ring by 56.1 (1)° and the OH group adopts an antiplanar conformation, while in the latter the twist angle is 65.7 (2)° and the OH group is synplanar. The molecular components of the orthorhombic polymorph do not form the conventional $R_2^2(8)$ dimeric units [see Etter *et al.* (1990), Bernstein *et al.* (1995) and Motherwell *et al.* (1999) for graph-set nomenclature of hydrogen bonds] as they do in the tetragonal polymorph, but are associated in the crystal structure as catemers through single $O-H\cdots O$(carbonyl) hydrogen bonds between adjacent molecules. As the observation of polymorphism in multicomponent systems such as cocrystals and molecular salts is scant, although of topical interest given the growing relevance of pharmaceutical cocrystals (Tiekink & Vittal, 2006), we have been attracted by the planned synthesis of polymorphic molecular salts resulting from the combination of two conformationally flexible molecules, such as Dmb and benzamidine. For BenzamH$^+$·Dmb$^-$, since ΔpK_a = 7.5, the salt is expected. Indeed, in this proton-transfer compound protonation occurs at the imino N atom attached to Benzam as a result of proton transfer from the acidic hydroxy group of Dmb.

Polymorph (I) crystallizes in the monoclinic space group $P2_1/n$, with two crystallographically independent dimers of monoprotonated benzamidinium cations (BenzamH$^+$) and

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[1] Part I: Portalone (2010).

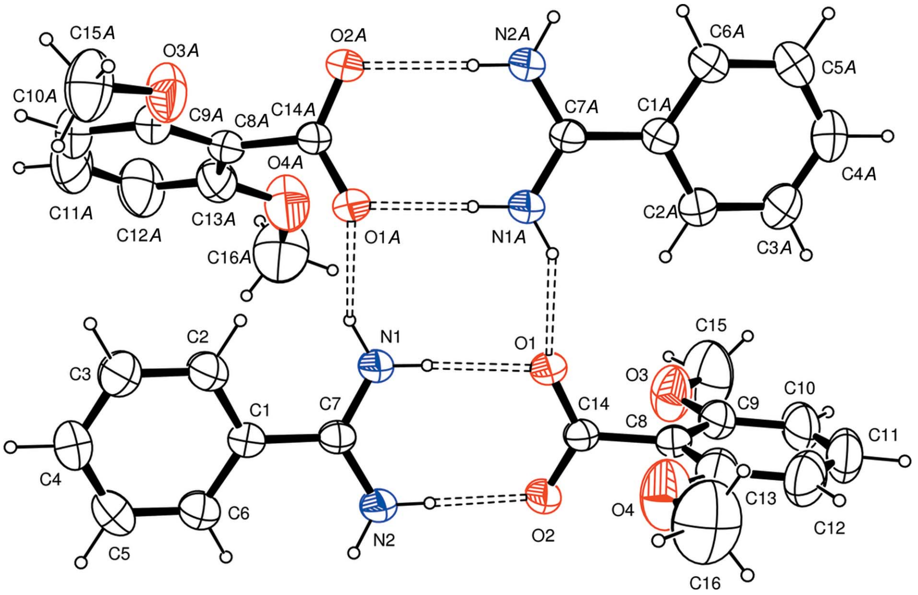

Figure 1
The asymmetric unit of polymorph (I), showing the atom-labelling scheme and hydrogen bonding (dashed lines). The asymmetric unit was selected so that the four ions are linked by N$^+$—H···O$^-$ (±)-CAHB hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level.

benzoate anions (Dmb$^-$) in the asymmetric unit (Fig. 1). Polymorph (II) crystallizes in the orthorhombic space group $P2_12_12_1$, with one BenzamH$^+$ cation and one Dmb$^-$ anion in the asymmetric unit (Fig. 2).

The molecular structures of polymorphs (I) and (II) are very similar. In both polymorphic forms, the BenzamH$^+$ cations are not planar. The dihedral angles between the mean plane of the benzene ring and the amidinium group [20.2 (1) and 14.4 (1)° for polymorph (I), and 23.6 (1)° for polymorph (II)] are close to the values observed in benzamidine [22.7 (1)°; Barker *et al.*, 1996], benzamidinium (2-acetamidobenzoyl)formate [16 (3)°; Joshi *et al.*, 1994] and benzamidinium acetylsalicylate [15.2 (2)°; Kolev *et al.*, 2009]. For both polymorphs this disposition is a consequence of an overcrowding effect, *i.e.* steric hindrance between the NH$_2$ group and the benzene ring, as indicated by the N—C(*ortho*) contacts in the range 2.859 (2)–2.893 (2) Å, and prevents conjugation between the N—C—N system and the benzene ring. Indeed, the C—C(amidine) distances are in the range 1.479 (3)–1.481 (3) Å and compare well with the expected C*sp*^{2}—C*sp*^{2} single-bond length of 1.482 (1) Å (Allen *et al.*, 1987). Interestingly, only the nonplanar conformation has been observed in small-molecule crystal structures, whereas in structures containing benzamidinium in the Protein Data Bank (PDB; Berman *et al.*, 2000), the most frequently encountered one is the planar conformation (Li *et al.*, 2009). The C—N bond lengths are in the range 1.305 (2)–1.317 (2) Å, evidencing the delocalization of the π electrons and double-bond character compared with the corresponding bond lengths found in benzamidine [1.294 (3) and 1.344 (3) Å; Barker *et al.*, 1996] and benzdiamidine [1.283 (2) and 1.349 (2) Å; Jokić *et al.*, 2001].

The benzene rings in the Dmb$^-$ anions of polymorphs (I) and (II) are essentially planar, and the methoxy substituents force the carboxylate groups to be almost orthogonal to the plane of the aromatic fragment [the twist angles between the aromatic ring and the carboxylate group are 88.7 (1) and 72.3 (1)° for polymorph (I), and 78.9 (1)° for polymorph (II)]. In these anions, the bond lengths and angles of the benzene ring are in accord with the corresponding values obtained for both the orthorhombic and tetragonal forms of 2,6-dimethoxybenzoic acid (Portalone, 2009, 2011*b*) and for 4-methoxybenzamidinium 2,6-dimethoxybenzoate (Portalone, 2012). The C—O distances of the carboxylate group range from 1.246 (2) to 1.255 (2) Å, indicating delocalization of the negative charge.

The molecular components of both polymorphs are joined by two N$^+$—H···O$^-$ (±)-CAHB hydrogen bonds to form ionic dimers with graph-set motif $R_2^2(8)$. Remarkably, at variance with the well known carboxylic acid dimer $R_2^2(8)$ motif, in both polymorphs the carboxylate–amidinium pairs are not planar, as the dihedral angles for the planes defined by

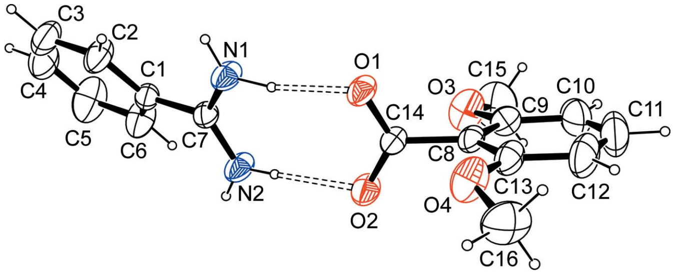

Figure 2
The asymmetric unit of polymorph (II), showing the atom-labelling scheme and hydrogen bonding (dashed lines). The asymmetric unit was selected so that the two ions are linked by N$^+$—H···O$^-$ (±)-CAHB hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level.

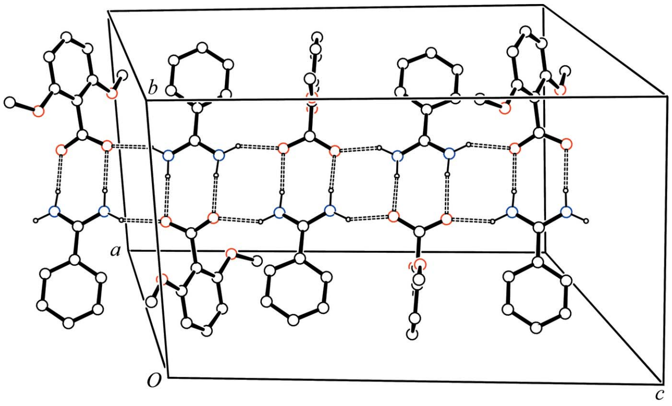

Figure 3
The supramolecular structure of polymorph (I), viewed approximately down *a*. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted. Hydrogen bonding is indicated by dashed lines.

the CN_2^+ and CO_2^- atoms are in the range 26.8–29.5°. Nonetheless, the interface is very stable, as indicated by the $N^+—H\cdots O^-$ parameters: $N^+\cdots O^-$ distances in the range 2.785 (2)–2.868 (2) Å) and $N^+—H\cdots O^-$ angles in the range 148 (2)–177 (2)°. This deviation from planarity of carboxylate–amidinium pairs has previously been observed in the crystal structure of 3-amidinium benzoate (Papoutsakis *et al.*, 1999).

Due to the protonated base, supramolecular aggregations in (I) and (II) are dominated by an extensive series of $N^+—H\cdots O^-$ (±)-CAHB hydrogen bonds (Tables 1 and 2). In the supramolecular structures of polymorphs (I) and (II) (Figs. 3 and 4), eight and four hydrogen bonds, respectively, link the molecular components into a one-dimensional structure. As mentioned previously, each subunit, built from the ion pairs of the asymmetric unit, forms $R_2^2(8)$ dimers *via* the interaction of the N—H and C=O groups. These subunits are then joined into linear chains through hydrogen bonding to adjacent antiparallel dimers. Such a disposition of dimers and catemers has frequently been observed in the solid-state structures of amides (Meléndez & Hamilton, 1998).

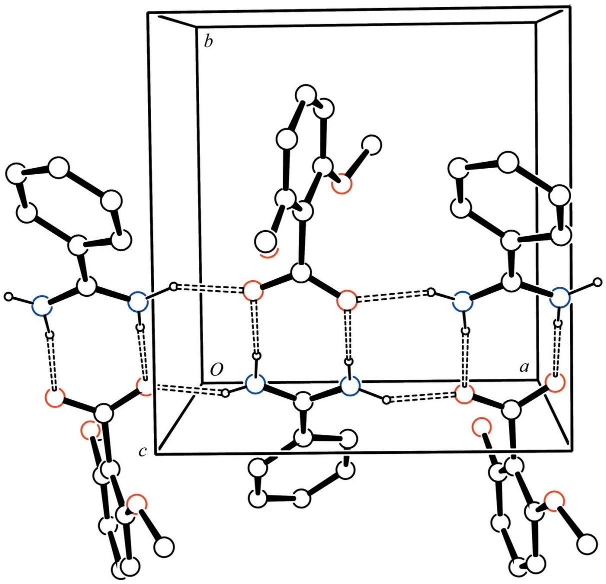

Figure 4
The supramolecular structure of polymorph (II), viewed approximately down *c*. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted. Hydrogen bonding is indicated by dashed lines.

From a supramolecular retrosynthesis perspective, only those synthons that occur repeatedly in crystal structures, namely robust synthons of a particular set of functional groups, are useful in crystal design (Nangia & Desiraju, 1998). Moreover, hydrogen bonds are often formed in a hierarchical fashion (Etter, 1990; Allen *et al.*, 1999; Bis *et al.*, 2007; Shattock *et al.*, 2008) and there is a need to ascertain the prevalence of a particular heterosynthon over another in a competitive environment. From the results reported herein, the crystal structures of polymorphs (I) and (II) are both consistent with the $R_2^2(8)$ supramolecular heterosynthon persistence exhibited by the benzamidinium adducts that have been archived in the Cambridge Structural Database (CSD, Version 5.33, November 2011; Allen, 2002). Consequently, the existence of polymorphism in these molecular salts should be related to the conformational flexibility of the carboxylate and amidinium groups. Polymorphs (I) and (II) therefore represent examples of conformational polymorphism. To the best of our knowledge, the only exception to the complementarity of amidinium and carboxylate groups has been reported for benzamidinium isoorotate (Portalone, 2010).

Experimental

Equimolar amounts of benzamidine (Fluka, 95%) and 2,6-dimethoxybenzoic acid (Sigma Aldrich, 99%), dissolved in ethanol (20 ml), were refluxed for 8 h at 323 K. The mixture was cooled to room temperature and the solvent evaporated under vacuum. The product was then recrystallized from water to give, after one week, colourless crystals suitable for X-ray analysis. Careful examination of the batch under a microscope showed crystals in the form of tablets of (I) and small prisms of (II). The majority of the crystals were (II), with a small quantity of (I). Unfortunately, any attempts to produce more crystals of polymorph (I) by repeating the crystallization conditions were unsuccessful. Crystallization of the molecular salt carried out under a wide range of different sets of conditions (different solvents, different molar ratios *etc.*) led systematically to the orthorhombic polymorph, (II).

Polymorph (I)

Crystal data

$C_7H_9N_2^+\cdot C_9H_9O_4^-$
$M_r = 302.32$
Monoclinic, $P2_1/n$
$a = 14.7103$ (2) Å
$b = 11.7174$ (1) Å
$c = 19.7281$ (3) Å
$\beta = 109.145$ (2)°
$V = 3212.39$ (8) $Å^3$
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 298$ K
0.20 × 0.15 × 0.14 mm

Data collection

Oxford Xcalibur S CCD area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{min} = 0.982$, $T_{max} = 0.987$
248320 measured reflections
5682 independent reflections
4978 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	0.92 (2)	1.89 (3)	2.799 (2)	171 (2)
N1—H1B···O1A	0.90 (3)	2.03 (3)	2.827 (2)	148 (2)
N2—H2A···O2	0.95 (2)	1.85 (2)	2.796 (2)	176.3 (19)
N2—H2B···O2^{i}	0.93 (2)	1.93 (2)	2.763 (2)	148.7 (19)
N1A—H1A1···O1A	0.92 (2)	1.87 (3)	2.785 (2)	175 (2)
N1A—H1A2···O1	0.91 (3)	1.95 (3)	2.773 (2)	150 (2)
N2A—H2A1···O2A	0.92 (2)	1.95 (2)	2.868 (2)	173.0 (19)
N2A—H2A2···O2A^{ii}	0.92 (3)	1.94 (3)	2.789 (2)	153 (2)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.129$
$S = 1.18$
5682 reflections
437 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}

Polymorph (II)

Crystal data

$C_7H_9N_2^+ \cdot C_9H_9O_4^-$
$M_r = 302.32$
Orthorhombic, $P2_12_12_1$
$a = 9.8921$ (1) Å
$b = 10.4471$ (1) Å
$c = 15.1403$ (2) Å
$V = 1564.65$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 298$ K
0.20 × 0.15 × 0.12 mm

Data collection

Oxford Xcalibur S CCD area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
$T_{\rm min} = 0.935$, $T_{\rm max} = 0.986$
327892 measured reflections
3175 independent reflections
2872 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.156$
$S = 1.19$
3175 reflections
219 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

In both polymorphs, all H atoms were found in a difference map, but for the final refinements all benzene-bound H atoms were positioned with idealized geometry and included in the calculations as riding on their parent atoms, with C—H = 0.97 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Methyl-bound H atoms were located from idealized local difference electron-density calculations and their C—H distances were allowed to vary during refinement, while being kept equivalent in any one methyl group, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C). The positional and displacement parameters of the H atoms of the amidine groups were refined freely, giving N—H distances in the range 0.84 (3)–1.00 (3) Å. In the absence of significant anomalous scattering in this light-atom study of polymorph (II), Friedel pairs were merged.

For both polymorphs, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	1.00 (3)	1.82 (3)	2.802 (2)	166 (2)
N1—H1B···O2^{i}	0.84 (3)	2.00 (3)	2.792 (2)	157 (3)
N2—H2B···O1^{ii}	0.96 (3)	1.90 (3)	2.794 (2)	154 (3)
N2—H2A···O2	0.86 (3)	1.97 (3)	2.821 (2)	177 (3)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: UK3051). Services for accessing these data are described at the back of the journal.

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supplementary materials

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Supramolecular association in proton-transfer adducts containing benzamidinium cations. II. Concomitant polymorphs of the molecular salt of 2,6-dimethoxybenzoic acid with benzamidine

Simona Irrera, Giancarlo Ortaggi and Gustavo Portalone

(I) Benzamidinidium 2,6-dimethoxybenzoate

Crystal data

$C_7H_9N_2^+\cdot C_9H_9O_4^-$
$M_r = 302.32$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 14.7103$ (2) Å
$b = 11.7174$ (1) Å
$c = 19.7281$ (3) Å
$\beta = 109.145$ (2)°
$V = 3212.39$ (8) Å^3
$Z = 8$
$F(000) = 1280$
$D_x = 1.250$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cell parameters from 71996 reflections
$\theta = 2.7$–32.5°
$\mu = 0.09$ mm^{-1}
$T = 298$ K
Tablet, colourless
0.20 × 0.15 × 0.14 mm

Data collection

Oxford Xcalibur S CCD area-detector diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.0696 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{min} = 0.982$, $T_{max} = 0.987$
248320 measured reflections
5682 independent reflections
4978 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 25.1$°, $\theta_{min} = 2.7$°
$h = -17 \rightarrow 17$
$k = -13 \rightarrow 13$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.129$
$S = 1.18$
5682 reflections
437 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 1.0275P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
N1	0.03204 (13)	−0.09912 (16)	0.19097 (9)	0.0442 (4)
H1A	−0.0078 (16)	−0.037 (2)	0.1779 (12)	0.058 (6)*
H1B	0.0478 (17)	−0.127 (2)	0.2356 (14)	0.064 (7)*
N2	0.05603 (13)	−0.08038 (15)	0.08423 (8)	0.0434 (4)
H2A	0.0065 (15)	−0.0247 (19)	0.0728 (11)	0.051 (6)*
H2B	0.0836 (16)	−0.1015 (19)	0.0499 (12)	0.057 (6)*
C1	0.15214 (13)	−0.22020 (16)	0.16763 (9)	0.0375 (4)
C2	0.19618 (18)	−0.2465 (2)	0.23911 (12)	0.0658 (7)
H2	0.1780	−0.2063	0.2757	0.079*
C3	0.2663 (2)	−0.3302 (3)	0.25849 (14)	0.0894 (10)
H3	0.2971	−0.3487	0.3087	0.107*
C4	0.29260 (19)	−0.3871 (2)	0.20706 (14)	0.0726 (8)
H4	0.3416	−0.4460	0.2210	0.087*
C5	0.24997 (19)	−0.3609 (2)	0.13663 (14)	0.0661 (7)
H5	0.2692	−0.4007	0.1004	0.079*
C6	0.17957 (16)	−0.27801 (19)	0.11630 (11)	0.0539 (6)
H6	0.1492	−0.2602	0.0659	0.065*
C7	0.07768 (12)	−0.13012 (15)	0.14702 (9)	0.0337 (4)
O1	−0.07302 (11)	0.10458 (12)	0.16122 (7)	0.0517 (4)
O2	−0.08607 (10)	0.08850 (11)	0.04679 (6)	0.0468 (3)
O3	−0.28794 (11)	0.17659 (14)	0.06376 (10)	0.0719 (5)
O4	0.01547 (13)	0.33083 (15)	0.10538 (12)	0.0840 (6)
C8	−0.13889 (14)	0.26004 (16)	0.08429 (9)	0.0397 (4)
C9	−0.23748 (15)	0.27510 (18)	0.06566 (11)	0.0491 (5)
C10	−0.27836 (19)	0.3830 (2)	0.05061 (13)	0.0647 (7)
H10	−0.3474	0.3930	0.0377	0.078*
C11	−0.2192 (2)	0.4750 (2)	0.05443 (14)	0.0752 (8)
H11	−0.2473	0.5504	0.0436	0.090*
C12	−0.1210 (2)	0.4630 (2)	0.07318 (14)	0.0722 (7)
H12	−0.0804	0.5293	0.0761	0.087*
C13	−0.08068 (17)	0.35450 (19)	0.08794 (12)	0.0552 (6)
C14	−0.09559 (13)	0.14224 (16)	0.09883 (9)	0.0352 (4)
C15	−0.39002 (19)	0.1817 (3)	0.0417 (2)	0.1092 (13)
H15A	−0.4099 (5)	0.237 (2)	0.0725 (11)	0.164*
H15B	−0.4160 (6)	0.1048 (17)	0.0464 (14)	0.164*
H15C	−0.4156 (6)	0.207 (2)	−0.0092 (11)	0.164*
C16	0.0817 (3)	0.4227 (3)	0.1170 (2)	0.1181 (14)

H16A	0.0782 (15)	0.4693 (18)	0.1579 (13)	0.177*
H16B	0.0656 (13)	0.4706 (18)	0.0734 (11)	0.177*
H16C	0.1476 (15)	0.3922 (7)	0.1279 (16)	0.177*
N1A	−0.03060 (14)	0.09627 (16)	0.30888 (9)	0.0496 (5)
H1A1	0.0110 (17)	0.036 (2)	0.3226 (12)	0.061 (7)*
H1A2	−0.0469 (17)	0.125 (2)	0.2637 (14)	0.063 (7)*
N2A	−0.04005 (13)	0.09148 (15)	0.42044 (9)	0.0440 (4)
H2A1	−0.0029 (15)	0.0266 (19)	0.4282 (11)	0.051 (6)*
H2A2	−0.0631 (16)	0.115 (2)	0.4560 (13)	0.064 (7)*
C1A	−0.12632 (13)	0.24195 (15)	0.34031 (9)	0.0377 (4)
C2A	−0.16792 (17)	0.27778 (18)	0.27002 (11)	0.0550 (6)
H2A3	−0.1555	0.2362	0.2315	0.066*
C3A	−0.2270 (2)	0.3725 (2)	0.25458 (13)	0.0727 (8)
H3A	−0.2562	0.3968	0.2052	0.087*
C4A	−0.24465 (19)	0.4325 (2)	0.30864 (14)	0.0695 (7)
H4A	−0.2862	0.4990	0.2975	0.083*
C5A	−0.20335 (18)	0.3982 (2)	0.37838 (13)	0.0620 (6)
H5A	−0.2153	0.4412	0.4166	0.074*
C6A	−0.14501 (15)	0.30321 (18)	0.39470 (11)	0.0495 (5)
H6A	−0.1169	0.2790	0.4442	0.059*
C7A	−0.06351 (13)	0.13984 (15)	0.35715 (9)	0.0344 (4)
O1A	0.08851 (11)	−0.09474 (11)	0.34245 (7)	0.0477 (4)
O2A	0.06223 (10)	−0.12115 (11)	0.44559 (7)	0.0459 (3)
O3A	0.25262 (11)	−0.25549 (13)	0.47826 (9)	0.0638 (4)
O4A	−0.04000 (12)	−0.29495 (15)	0.29483 (9)	0.0738 (5)
C8A	0.10499 (14)	−0.28187 (16)	0.38908 (10)	0.0390 (4)
C9A	0.19058 (15)	−0.33014 (17)	0.43287 (11)	0.0461 (5)
C10A	0.20891 (19)	−0.4456 (2)	0.42869 (14)	0.0643 (6)
H10A	0.2683	−0.4790	0.4597	0.077*
C11A	0.1415 (2)	−0.5118 (2)	0.37979 (16)	0.0798 (8)
H11A	0.1535	−0.5929	0.3774	0.096*
C12A	0.0574 (2)	−0.4663 (2)	0.33399 (15)	0.0762 (8)
H12A	0.0111	−0.5141	0.2993	0.091*
C13A	0.04010 (16)	−0.35059 (18)	0.33850 (12)	0.0540 (5)
C14A	0.08406 (12)	−0.15605 (15)	0.39317 (9)	0.0340 (4)
C15A	0.34956 (18)	−0.2927 (2)	0.51199 (17)	0.0819 (8)
H15D	0.3773 (7)	−0.3192 (17)	0.4742 (6)	0.123*
H15E	0.3505 (2)	−0.3577 (16)	0.5457 (10)	0.123*
H15F	0.3892 (8)	−0.2275 (12)	0.5398 (10)	0.123*
C16A	−0.0970 (2)	−0.3497 (3)	0.23207 (17)	0.0950 (10)
H16D	−0.1438 (14)	−0.2944 (11)	0.2015 (8)	0.143*
H16E	−0.1323 (14)	−0.4139 (17)	0.2448 (3)	0.143*
H16F	−0.0553 (8)	−0.3794 (18)	0.2055 (8)	0.143*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0567 (11)	0.0485 (10)	0.0307 (9)	0.0184 (9)	0.0186 (8)	0.0060 (8)
N2	0.0488 (10)	0.0528 (10)	0.0309 (8)	0.0144 (8)	0.0164 (8)	0.0074 (8)
C1	0.0415 (10)	0.0392 (10)	0.0343 (10)	0.0026 (8)	0.0157 (8)	0.0010 (8)

C2	0.0752 (16)	0.0860 (17)	0.0402 (12)	0.0412 (14)	0.0243 (11)	0.0112 (12)
C3	0.099 (2)	0.120 (2)	0.0519 (14)	0.0678 (19)	0.0286 (15)	0.0290 (15)
C4	0.0754 (17)	0.0763 (17)	0.0750 (17)	0.0401 (14)	0.0369 (14)	0.0194 (14)
C5	0.0802 (17)	0.0654 (15)	0.0630 (15)	0.0240 (13)	0.0376 (13)	−0.0042 (12)
C6	0.0672 (14)	0.0586 (13)	0.0387 (11)	0.0166 (11)	0.0211 (10)	0.0006 (10)
C7	0.0364 (9)	0.0368 (9)	0.0277 (9)	−0.0015 (8)	0.0101 (7)	−0.0026 (7)
O1	0.0754 (10)	0.0533 (8)	0.0298 (7)	0.0258 (7)	0.0218 (7)	0.0097 (6)
O2	0.0641 (9)	0.0474 (8)	0.0301 (7)	0.0174 (7)	0.0172 (6)	0.0016 (6)
O3	0.0472 (9)	0.0626 (10)	0.1058 (14)	0.0119 (8)	0.0250 (9)	0.0152 (10)
O4	0.0628 (11)	0.0574 (10)	0.1257 (16)	−0.0100 (9)	0.0227 (11)	−0.0006 (10)
C8	0.0550 (12)	0.0392 (10)	0.0258 (9)	0.0085 (9)	0.0144 (8)	0.0022 (8)
C9	0.0556 (13)	0.0502 (12)	0.0414 (11)	0.0154 (10)	0.0159 (10)	0.0049 (9)
C10	0.0701 (16)	0.0607 (15)	0.0587 (14)	0.0304 (13)	0.0149 (12)	0.0070 (12)
C11	0.106 (2)	0.0473 (14)	0.0655 (16)	0.0296 (15)	0.0194 (15)	0.0064 (12)
C12	0.101 (2)	0.0397 (13)	0.0734 (17)	0.0017 (13)	0.0243 (15)	0.0010 (12)
C13	0.0663 (15)	0.0472 (12)	0.0495 (12)	0.0051 (11)	0.0154 (11)	0.0010 (10)
C14	0.0382 (10)	0.0400 (10)	0.0285 (9)	0.0060 (8)	0.0126 (8)	0.0030 (8)
C15	0.0492 (16)	0.104 (2)	0.174 (4)	0.0153 (16)	0.0370 (19)	0.022 (2)
C16	0.092 (2)	0.090 (2)	0.161 (4)	−0.033 (2)	0.026 (2)	−0.008 (2)
N1A	0.0699 (12)	0.0519 (10)	0.0312 (9)	0.0242 (10)	0.0223 (8)	0.0069 (8)
N2A	0.0607 (11)	0.0437 (10)	0.0306 (9)	0.0151 (9)	0.0191 (8)	0.0038 (7)
C1A	0.0441 (10)	0.0356 (10)	0.0348 (10)	0.0009 (8)	0.0150 (8)	−0.0009 (8)
C2A	0.0788 (15)	0.0495 (12)	0.0382 (11)	0.0196 (11)	0.0210 (11)	0.0047 (9)
C3A	0.101 (2)	0.0633 (15)	0.0506 (13)	0.0349 (14)	0.0212 (13)	0.0172 (12)
C4A	0.0853 (18)	0.0506 (13)	0.0767 (17)	0.0307 (13)	0.0321 (14)	0.0128 (12)
C5A	0.0806 (17)	0.0519 (13)	0.0614 (14)	0.0179 (12)	0.0342 (13)	−0.0037 (11)
C6A	0.0618 (13)	0.0488 (12)	0.0408 (11)	0.0124 (10)	0.0207 (10)	−0.0009 (9)
C7A	0.0397 (10)	0.0357 (9)	0.0282 (9)	0.0002 (8)	0.0115 (8)	−0.0022 (7)
O1A	0.0716 (10)	0.0423 (7)	0.0379 (7)	0.0150 (7)	0.0299 (7)	0.0098 (6)
O2A	0.0665 (9)	0.0450 (8)	0.0323 (7)	0.0154 (7)	0.0246 (6)	0.0035 (6)
O3A	0.0533 (9)	0.0563 (9)	0.0671 (10)	0.0168 (7)	−0.0003 (8)	−0.0038 (8)
O4A	0.0683 (11)	0.0666 (10)	0.0649 (10)	0.0100 (9)	−0.0074 (8)	−0.0177 (9)
C8A	0.0499 (11)	0.0384 (10)	0.0334 (9)	0.0065 (9)	0.0202 (9)	0.0019 (8)
C9A	0.0544 (12)	0.0431 (11)	0.0428 (11)	0.0127 (10)	0.0186 (10)	0.0050 (9)
C10A	0.0732 (16)	0.0490 (13)	0.0703 (15)	0.0239 (12)	0.0232 (13)	0.0100 (12)
C11A	0.103 (2)	0.0378 (13)	0.097 (2)	0.0138 (14)	0.0305 (18)	−0.0053 (13)
C12A	0.0861 (19)	0.0474 (14)	0.0850 (18)	−0.0016 (13)	0.0141 (15)	−0.0186 (13)
C13A	0.0612 (14)	0.0479 (12)	0.0516 (12)	0.0063 (10)	0.0165 (11)	−0.0063 (10)
C14A	0.0377 (10)	0.0381 (10)	0.0268 (9)	0.0066 (8)	0.0114 (7)	0.0010 (8)
C15A	0.0538 (15)	0.0728 (17)	0.103 (2)	0.0125 (13)	0.0030 (14)	0.0060 (16)
C16A	0.086 (2)	0.088 (2)	0.084 (2)	−0.0080 (17)	−0.0094 (16)	−0.0218 (17)

Geometric parameters (Å, º)

N1—C7	1.310 (2)	N1A—C7A	1.305 (2)
N1—H1A	0.92 (2)	N1A—H1A1	0.92 (2)
N1—H1B	0.90 (3)	N1A—H1A2	0.91 (3)
N2—C7	1.310 (2)	N2A—C7A	1.310 (2)
N2—H2A	0.95 (2)	N2A—H2A1	0.92 (2)
N2—H2B	0.93 (2)	N2A—H2A2	0.92 (3)

C1—C2	1.380 (3)	C1A—C2A	1.385 (3)
C1—C6	1.384 (3)	C1A—C6A	1.391 (3)
C1—C7	1.479 (3)	C1A—C7A	1.481 (3)
C2—C3	1.383 (3)	C2A—C3A	1.381 (3)
C2—H2	0.9700	C2A—H2A3	0.9700
C3—C4	1.372 (4)	C3A—C4A	1.371 (3)
C3—H3	0.9700	C3A—H3A	0.9700
C4—C5	1.359 (3)	C4A—C5A	1.370 (3)
C4—H4	0.9700	C4A—H4A	0.9700
C5—C6	1.380 (3)	C5A—C6A	1.378 (3)
C5—H5	0.9700	C5A—H5A	0.9700
C6—H6	0.9700	C6A—H6A	0.9700
O1—C14	1.246 (2)	O1A—C14A	1.251 (2)
O2—C14	1.251 (2)	O2A—C14A	1.248 (2)
O3—C9	1.366 (3)	O3A—C9A	1.365 (3)
O3—C15	1.421 (3)	O3A—C15A	1.430 (3)
O4—C13	1.370 (3)	O4A—C13A	1.375 (3)
O4—C16	1.419 (3)	O4A—C16A	1.402 (3)
C8—C9	1.386 (3)	C8A—C13A	1.389 (3)
C8—C13	1.387 (3)	C8A—C9A	1.392 (3)
C8—C14	1.508 (3)	C8A—C14A	1.514 (3)
C9—C10	1.389 (3)	C9A—C10A	1.387 (3)
C10—C11	1.372 (4)	C10A—C11A	1.374 (4)
C10—H10	0.9700	C10A—H10A	0.9700
C11—C12	1.375 (4)	C11A—C12A	1.378 (4)
C11—H11	0.9700	C11A—H11A	0.9700
C12—C13	1.393 (3)	C12A—C13A	1.387 (3)
C12—H12	0.9700	C12A—H12A	0.9700
C15—H15A	0.9946	C15A—H15D	1.0080
C15—H15B	0.9946	C15A—H15E	1.0080
C15—H15C	0.9946	C15A—H15F	1.0080
C16—H16A	0.9886	C16A—H16D	0.9925
C16—H16B	0.9886	C16A—H16E	0.9925
C16—H16C	0.9886	C16A—H16F	0.9925

C7—N1—H1A	117.0 (14)	C7A—N1A—H1A1	117.3 (14)
C7—N1—H1B	121.7 (15)	C7A—N1A—H1A2	121.7 (15)
H1A—N1—H1B	120 (2)	H1A1—N1A—H1A2	121 (2)
C7—N2—H2A	117.5 (12)	C7A—N2A—H2A1	118.2 (13)
C7—N2—H2B	122.8 (14)	C7A—N2A—H2A2	123.3 (15)
H2A—N2—H2B	119.6 (19)	H2A1—N2A—H2A2	118 (2)
C2—C1—C6	119.12 (18)	C2A—C1A—C6A	118.80 (18)
C2—C1—C7	119.83 (16)	C2A—C1A—C7A	120.53 (16)
C6—C1—C7	121.04 (17)	C6A—C1A—C7A	120.68 (16)
C1—C2—C3	119.9 (2)	C3A—C2A—C1A	120.3 (2)
C1—C2—H2	120.1	C3A—C2A—H2A3	119.9
C3—C2—H2	120.1	C1A—C2A—H2A3	119.9
C4—C3—C2	120.4 (2)	C4A—C3A—C2A	120.4 (2)
C4—C3—H3	119.8	C4A—C3A—H3A	119.8

C2—C3—H3	119.8	C2A—C3A—H3A	119.8
C5—C4—C3	119.9 (2)	C5A—C4A—C3A	119.7 (2)
C5—C4—H4	120.0	C5A—C4A—H4A	120.1
C3—C4—H4	120.0	C3A—C4A—H4A	120.1
C4—C5—C6	120.5 (2)	C4A—C5A—C6A	120.6 (2)
C4—C5—H5	119.8	C4A—C5A—H5A	119.7
C6—C5—H5	119.8	C6A—C5A—H5A	119.7
C5—C6—C1	120.2 (2)	C5A—C6A—C1A	120.14 (19)
C5—C6—H6	119.9	C5A—C6A—H6A	119.9
C1—C6—H6	119.9	C1A—C6A—H6A	119.9
N1—C7—N2	118.95 (18)	N1A—C7A—N2A	118.76 (18)
N1—C7—C1	120.66 (16)	N1A—C7A—C1A	120.36 (16)
N2—C7—C1	120.39 (16)	N2A—C7A—C1A	120.88 (16)
C9—O3—C15	118.9 (2)	C9A—O3A—C15A	117.38 (18)
C13—O4—C16	119.0 (2)	C13A—O4A—C16A	118.5 (2)
C9—C8—C13	119.14 (18)	C13A—C8A—C9A	118.60 (18)
C9—C8—C14	120.48 (18)	C13A—C8A—C14A	119.93 (17)
C13—C8—C14	120.37 (18)	C9A—C8A—C14A	121.40 (17)
O3—C9—C8	114.31 (17)	O3A—C9A—C10A	124.2 (2)
O3—C9—C10	124.7 (2)	O3A—C9A—C8A	114.88 (17)
C8—C9—C10	121.0 (2)	C10A—C9A—C8A	120.9 (2)
C11—C10—C9	118.7 (2)	C11A—C10A—C9A	118.9 (2)
C11—C10—H10	120.6	C11A—C10A—H10A	120.6
C9—C10—H10	120.6	C9A—C10A—H10A	120.6
C10—C11—C12	121.7 (2)	C10A—C11A—C12A	121.8 (2)
C10—C11—H11	119.1	C10A—C11A—H11A	119.1
C12—C11—H11	119.1	C12A—C11A—H11A	119.1
C11—C12—C13	119.1 (2)	C11A—C12A—C13A	118.7 (2)
C11—C12—H12	120.4	C11A—C12A—H12A	120.7
C13—C12—H12	120.4	C13A—C12A—H12A	120.7
O4—C13—C8	114.87 (19)	O4A—C13A—C12A	124.1 (2)
O4—C13—C12	124.8 (2)	O4A—C13A—C8A	114.90 (18)
C8—C13—C12	120.3 (2)	C12A—C13A—C8A	121.0 (2)
O1—C14—O2	124.56 (17)	O2A—C14A—O1A	124.75 (16)
O1—C14—C8	118.12 (15)	O2A—C14A—C8A	118.39 (15)
O2—C14—C8	117.31 (15)	O1A—C14A—C8A	116.85 (15)
O3—C15—H15A	109.5	O3A—C15A—H15D	109.5
O3—C15—H15B	109.5	O3A—C15A—H15E	109.5
H15A—C15—H15B	109.5	H15D—C15A—H15E	109.5
O3—C15—H15C	109.5	O3A—C15A—H15F	109.5
H15A—C15—H15C	109.5	H15D—C15A—H15F	109.5
H15B—C15—H15C	109.5	H15E—C15A—H15F	109.5
O4—C16—H16A	109.5	O4A—C16A—H16D	109.5
O4—C16—H16B	109.5	O4A—C16A—H16E	109.5
H16A—C16—H16B	109.5	H16D—C16A—H16E	109.5
O4—C16—H16C	109.5	O4A—C16A—H16F	109.5
H16A—C16—H16C	109.5	H16D—C16A—H16F	109.5
H16B—C16—H16C	109.5	H16E—C16A—H16F	109.5

C6—C1—C2—C3	−0.4 (4)	C6A—C1A—C2A—C3A	−0.1 (3)
C7—C1—C2—C3	−179.6 (2)	C7A—C1A—C2A—C3A	179.5 (2)
C1—C2—C3—C4	0.2 (5)	C1A—C2A—C3A—C4A	0.4 (4)
C2—C3—C4—C5	0.3 (5)	C2A—C3A—C4A—C5A	0.0 (4)
C3—C4—C5—C6	−0.6 (5)	C3A—C4A—C5A—C6A	−0.7 (4)
C4—C5—C6—C1	0.4 (4)	C4A—C5A—C6A—C1A	0.9 (4)
C2—C1—C6—C5	0.1 (3)	C2A—C1A—C6A—C5A	−0.5 (3)
C7—C1—C6—C5	179.3 (2)	C7A—C1A—C6A—C5A	179.8 (2)
C2—C1—C7—N1	−20.8 (3)	C2A—C1A—C7A—N1A	14.1 (3)
C6—C1—C7—N1	160.0 (2)	C6A—C1A—C7A—N1A	−166.25 (19)
C2—C1—C7—N2	159.5 (2)	C2A—C1A—C7A—N2A	−165.8 (2)
C6—C1—C7—N2	−19.7 (3)	C6A—C1A—C7A—N2A	13.9 (3)
C15—O3—C9—C8	−176.9 (2)	C15A—O3A—C9A—C10A	14.0 (3)
C15—O3—C9—C10	3.1 (4)	C15A—O3A—C9A—C8A	−165.6 (2)
C13—C8—C9—O3	−179.92 (18)	C13A—C8A—C9A—O3A	176.49 (18)
C14—C8—C9—O3	1.4 (3)	C14A—C8A—C9A—O3A	−0.5 (3)
C13—C8—C9—C10	0.1 (3)	C13A—C8A—C9A—C10A	−3.1 (3)
C14—C8—C9—C10	−178.58 (18)	C14A—C8A—C9A—C10A	179.93 (19)
O3—C9—C10—C11	−179.9 (2)	O3A—C9A—C10A—C11A	−178.8 (2)
C8—C9—C10—C11	0.1 (3)	C8A—C9A—C10A—C11A	0.8 (3)
C9—C10—C11—C12	−0.5 (4)	C9A—C10A—C11A—C12A	1.3 (4)
C10—C11—C12—C13	0.7 (4)	C10A—C11A—C12A—C13A	−1.0 (5)
C16—O4—C13—C8	−174.1 (3)	C16A—O4A—C13A—C12A	−15.1 (4)
C16—O4—C13—C12	7.0 (4)	C16A—O4A—C13A—C8A	164.8 (2)
C9—C8—C13—O4	−178.76 (19)	C11A—C12A—C13A—O4A	178.6 (3)
C14—C8—C13—O4	−0.1 (3)	C11A—C12A—C13A—C8A	−1.4 (4)
C9—C8—C13—C12	0.1 (3)	C9A—C8A—C13A—O4A	−176.55 (18)
C14—C8—C13—C12	178.79 (19)	C14A—C8A—C13A—O4A	0.5 (3)
C11—C12—C13—O4	178.3 (2)	C9A—C8A—C13A—C12A	3.4 (3)
C11—C12—C13—C8	−0.5 (4)	C14A—C8A—C13A—C12A	−179.6 (2)
C9—C8—C14—O1	−88.9 (2)	C13A—C8A—C14A—O2A	108.7 (2)
C13—C8—C14—O1	92.5 (2)	C9A—C8A—C14A—O2A	−74.3 (2)
C9—C8—C14—O2	90.2 (2)	C13A—C8A—C14A—O1A	−70.1 (2)
C13—C8—C14—O2	−88.4 (2)	C9A—C8A—C14A—O1A	106.8 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	0.92 (2)	1.89 (3)	2.799 (2)	171 (2)
N1—H1*B*···O1*A*	0.90 (3)	2.03 (3)	2.827 (2)	148 (2)
N2—H2*A*···O2	0.95 (2)	1.85 (2)	2.796 (2)	176.3 (19)
N2—H2*B*···O2^{i}	0.93 (2)	1.93 (2)	2.763 (2)	148.7 (19)
N1*A*—H1*A*1···O1*A*	0.92 (2)	1.87 (3)	2.785 (2)	175 (2)
N1*A*—H1*A*2···O1	0.91 (3)	1.95 (3)	2.773 (2)	150 (2)
N2*A*—H2*A*1···O2*A*	0.92 (2)	1.95 (2)	2.868 (2)	173.0 (19)
N2*A*—H2*A*2···O2*A*^{ii}	0.92 (3)	1.94 (3)	2.789 (2)	153 (2)

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

(II) Benzamidinidium 2,6-dimethoxybenzoate

Crystal data

$C_7H_9N_2^+\cdot C_9H_9O_4^-$
M_r = 302.32
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 9.8921 (1) Å
b = 10.4471 (1) Å
c = 15.1403 (2) Å
V = 1564.65 (3) Å^3
Z = 4

$F(000)$ = 640
D_x = 1.283 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 116123 reflections
θ = 2.8–32.6°
μ = 0.09 mm^{-1}
T = 298 K
Small prism, colourless
0.20 × 0.15 × 0.12 mm

Data collection

Oxford Xcalibur S CCD area-detector diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.0696 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
$T_{\min}$ = 0.935, $T_{\max}$ = 0.986

327892 measured reflections
3175 independent reflections
2872 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
$\theta_{\max}$ = 32.6°, $\theta_{\min}$ = 2.8°
$h = -15\rightarrow14$
$k = -15\rightarrow15$
$l = -22\rightarrow22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.156
S = 1.19
3175 reflections
219 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0886P)^2 + 0.1272P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.30 e Å^{-3}
$\Delta\rho_{\min}$ = −0.18 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.24030 (16)	0.15399 (19)	−0.03437 (12)	0.0400 (4)
H1A	0.248 (2)	0.225 (2)	0.0091 (16)	0.034 (6)*
H1B	0.165 (3)	0.130 (3)	−0.0539 (19)	0.043 (7)*
N2	0.46956 (16)	0.1472 (2)	−0.03504 (13)	0.0420 (4)

H2A	0.468 (3)	0.209 (3)	0.002 (2)	0.051 (8)*
H2B	0.557 (3)	0.112 (3)	−0.048 (2)	0.051 (8)*
C1	0.34893 (17)	0.00992 (15)	−0.13753 (11)	0.0301 (3)
C2	0.2336 (2)	−0.0641 (2)	−0.14905 (17)	0.0479 (5)
H2	0.1576	−0.0543	−0.1091	0.058*
C3	0.2269 (3)	−0.1521 (3)	−0.21747 (19)	0.0569 (6)
H3	0.1463	−0.2038	−0.2253	0.068*
C4	0.3339 (3)	−0.1663 (3)	−0.27409 (18)	0.0577 (6)
H4	0.3286	−0.2270	−0.3224	0.069*
C5	0.4486 (3)	−0.0945 (3)	−0.26236 (19)	0.0663 (8)
H5	0.5244	−0.1057	−0.3023	0.080*
C6	0.4578 (2)	−0.0058 (2)	−0.19409 (16)	0.0501 (6)
H6	0.5394	0.0444	−0.1862	0.060*
C7	0.35372 (17)	0.10679 (16)	−0.06615 (12)	0.0299 (3)
O1	0.24645 (12)	0.37862 (14)	0.06668 (10)	0.0377 (3)
O2	0.46808 (13)	0.35660 (15)	0.08260 (12)	0.0438 (4)
O3	0.4554 (2)	0.6099 (2)	−0.02050 (12)	0.0595 (5)
O4	0.2968 (2)	0.4922 (2)	0.25686 (10)	0.0552 (5)
C8	0.36935 (16)	0.55819 (17)	0.11803 (12)	0.0318 (3)
C9	0.4143 (2)	0.6527 (2)	0.06053 (15)	0.0420 (4)
C10	0.4192 (3)	0.7809 (2)	0.0872 (2)	0.0575 (6)
H10	0.4480	0.8471	0.0464	0.069*
C11	0.3826 (3)	0.8113 (2)	0.1723 (3)	0.0680 (8)
H11	0.3857	0.9000	0.1910	0.082*
C12	0.3416 (3)	0.7191 (3)	0.23192 (19)	0.0595 (7)
H12	0.3179	0.7424	0.2920	0.071*
C13	0.3349 (2)	0.5912 (2)	0.20401 (15)	0.0410 (4)
C14	0.36127 (16)	0.42050 (16)	0.08702 (10)	0.0286 (3)
C15	0.5270 (4)	0.6947 (4)	−0.0758 (3)	0.0815 (10)
H15A	0.466 (2)	0.767 (3)	−0.094 (2)	0.122*
H15B	0.559 (3)	0.6477 (16)	−0.1298 (18)	0.122*
H15C	0.607 (3)	0.730 (3)	−0.0430 (12)	0.122*
C16	0.2997 (3)	0.5119 (4)	0.35037 (17)	0.0696 (8)
H16A	0.227 (2)	0.572 (3)	0.3672 (5)	0.104*
H16B	0.388 (3)	0.548 (2)	0.3676 (5)	0.104*
H16C	0.285 (3)	0.430 (2)	0.3808 (8)	0.104*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0227 (6)	0.0471 (9)	0.0502 (9)	0.0013 (6)	−0.0006 (6)	−0.0191 (8)
N2	0.0240 (7)	0.0473 (9)	0.0546 (10)	0.0006 (6)	−0.0022 (6)	−0.0209 (9)
C1	0.0274 (7)	0.0274 (6)	0.0354 (7)	−0.0009 (6)	0.0000 (6)	−0.0047 (6)
C2	0.0304 (8)	0.0466 (11)	0.0668 (13)	−0.0078 (8)	0.0030 (9)	−0.0205 (11)
C3	0.0455 (11)	0.0490 (12)	0.0762 (16)	−0.0064 (10)	−0.0115 (11)	−0.0253 (13)
C4	0.0728 (16)	0.0485 (12)	0.0518 (12)	−0.0024 (12)	−0.0034 (12)	−0.0192 (10)
C5	0.0710 (16)	0.0700 (17)	0.0579 (14)	−0.0136 (15)	0.0275 (13)	−0.0268 (13)
C6	0.0439 (10)	0.0511 (12)	0.0552 (12)	−0.0135 (10)	0.0188 (10)	−0.0166 (10)
C7	0.0247 (6)	0.0285 (7)	0.0366 (7)	−0.0007 (6)	0.0010 (6)	−0.0042 (6)
O1	0.0240 (5)	0.0409 (7)	0.0481 (7)	−0.0046 (5)	−0.0001 (5)	−0.0131 (6)

O2	0.0260 (6)	0.0437 (7)	0.0617 (9)	0.0014 (5)	−0.0011 (6)	−0.0191 (7)
O3	0.0740 (12)	0.0593 (10)	0.0451 (8)	−0.0179 (10)	0.0083 (8)	0.0012 (7)
O4	0.0642 (11)	0.0634 (10)	0.0380 (7)	−0.0107 (9)	0.0119 (7)	−0.0117 (7)
C8	0.0225 (6)	0.0339 (7)	0.0392 (8)	−0.0014 (6)	−0.0016 (6)	−0.0094 (7)
C9	0.0365 (9)	0.0407 (9)	0.0486 (10)	−0.0029 (8)	−0.0056 (8)	−0.0022 (8)
C10	0.0570 (14)	0.0361 (10)	0.0795 (17)	−0.0045 (10)	−0.0055 (13)	−0.0004 (11)
C11	0.0660 (17)	0.0393 (11)	0.099 (2)	0.0001 (12)	0.0005 (16)	−0.0243 (13)
C12	0.0561 (14)	0.0564 (13)	0.0662 (14)	0.0015 (11)	0.0068 (12)	−0.0340 (12)
C13	0.0323 (8)	0.0453 (10)	0.0454 (9)	−0.0015 (7)	0.0034 (7)	−0.0175 (8)
C14	0.0242 (6)	0.0333 (7)	0.0283 (6)	−0.0026 (6)	0.0034 (6)	−0.0067 (6)
C15	0.096 (2)	0.077 (2)	0.0720 (19)	−0.017 (2)	0.0219 (19)	0.0166 (17)
C16	0.0728 (18)	0.097 (2)	0.0388 (11)	0.0119 (18)	0.0022 (11)	−0.0101 (13)

Geometric parameters (Å, º)

N1—C7	1.317 (2)	O3—C9	1.368 (3)
N1—H1A	1.00 (3)	O3—C15	1.410 (4)
N1—H1B	0.84 (3)	O4—C13	1.361 (3)
N2—C7	1.309 (2)	O4—C16	1.431 (3)
N2—H2A	0.86 (3)	C8—C13	1.389 (3)
N2—H2B	0.96 (3)	C8—C9	1.389 (3)
C1—C6	1.386 (3)	C8—C14	1.515 (2)
C1—C2	1.389 (3)	C9—C10	1.400 (3)
C1—C7	1.481 (2)	C10—C11	1.376 (5)
C2—C3	1.387 (3)	C10—H10	0.9700
C2—H2	0.9700	C11—C12	1.380 (5)
C3—C4	1.370 (4)	C11—H11	0.9700
C3—H3	0.9700	C12—C13	1.403 (3)
C4—C5	1.371 (4)	C12—H12	0.9700
C4—H4	0.9700	C15—H15A	1.0051
C5—C6	1.391 (3)	C15—H15B	1.0051
C5—H5	0.9700	C15—H15C	1.0051
C6—H6	0.9700	C16—H16A	0.9863
O1—C14	1.255 (2)	C16—H16B	0.9863
O2—C14	1.252 (2)	C16—H16C	0.9863
C7—N1—H1A	117.3 (14)	C9—C8—C14	119.81 (16)
C7—N1—H1B	121 (2)	O3—C9—C8	115.16 (19)
H1A—N1—H1B	121 (2)	O3—C9—C10	124.1 (2)
C7—N2—H2A	117 (2)	C8—C9—C10	120.7 (2)
C7—N2—H2B	126.0 (19)	C11—C10—C9	118.8 (3)
H2A—N2—H2B	116 (3)	C11—C10—H10	120.6
C6—C1—C2	119.64 (17)	C9—C10—H10	120.6
C6—C1—C7	120.47 (16)	C10—C11—C12	121.9 (2)
C2—C1—C7	119.88 (16)	C10—C11—H11	119.0
C3—C2—C1	120.1 (2)	C12—C11—H11	119.0
C3—C2—H2	119.9	C11—C12—C13	118.8 (2)
C1—C2—H2	119.9	C11—C12—H12	120.6
C4—C3—C2	120.1 (2)	C13—C12—H12	120.6
C4—C3—H3	119.9	O4—C13—C8	115.48 (18)

C2—C3—H3	119.9	O4—C13—C12	124.0 (2)
C3—C4—C5	119.9 (2)	C8—C13—C12	120.5 (2)
C3—C4—H4	120.0	O2—C14—O1	124.38 (15)
C5—C4—H4	120.0	O2—C14—C8	118.58 (15)
C4—C5—C6	121.0 (2)	O1—C14—C8	117.03 (15)
C4—C5—H5	119.5	O3—C15—H15A	109.5
C6—C5—H5	119.5	O3—C15—H15B	109.5
C1—C6—C5	119.2 (2)	H15A—C15—H15B	109.5
C1—C6—H6	120.4	O3—C15—H15C	109.5
C5—C6—H6	120.4	H15A—C15—H15C	109.5
N2—C7—N1	119.58 (15)	H15B—C15—H15C	109.5
N2—C7—C1	120.72 (15)	O4—C16—H16A	109.5
N1—C7—C1	119.69 (15)	O4—C16—H16B	109.5
C9—O3—C15	118.4 (2)	H16A—C16—H16B	109.5
C13—O4—C16	117.9 (2)	O4—C16—H16C	109.5
C13—C8—C9	119.29 (18)	H16A—C16—H16C	109.5
C13—C8—C14	120.88 (17)	H16B—C16—H16C	109.5

C6—C1—C2—C3	−0.8 (4)	C14—C8—C9—C10	178.4 (2)
C7—C1—C2—C3	178.0 (2)	O3—C9—C10—C11	−176.1 (3)
C1—C2—C3—C4	−0.1 (4)	C8—C9—C10—C11	1.9 (4)
C2—C3—C4—C5	0.9 (5)	C9—C10—C11—C12	0.1 (5)
C3—C4—C5—C6	−0.7 (5)	C10—C11—C12—C13	−1.2 (5)
C2—C1—C6—C5	0.9 (4)	C16—O4—C13—C8	161.5 (2)
C7—C1—C6—C5	−177.8 (2)	C16—O4—C13—C12	−17.9 (4)
C4—C5—C6—C1	−0.2 (5)	C9—C8—C13—O4	−177.59 (18)
C6—C1—C7—N2	−23.6 (3)	C14—C8—C13—O4	1.1 (3)
C2—C1—C7—N2	157.6 (2)	C9—C8—C13—C12	1.8 (3)
C6—C1—C7—N1	155.5 (2)	C14—C8—C13—C12	−179.5 (2)
C2—C1—C7—N1	−23.3 (3)	C11—C12—C13—O4	179.6 (3)
C15—O3—C9—C8	−167.5 (3)	C11—C12—C13—C8	0.2 (4)
C15—O3—C9—C10	10.7 (4)	C13—C8—C14—O2	−101.0 (2)
C13—C8—C9—O3	175.32 (18)	C9—C8—C14—O2	77.7 (2)
C14—C8—C9—O3	−3.4 (3)	C13—C8—C14—O1	79.5 (2)
C13—C8—C9—C10	−2.9 (3)	C9—C8—C14—O1	−101.8 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	1.00 (3)	1.82 (3)	2.802 (2)	166 (2)
N1—H1*B*···O2$^{\text{i}}$	0.84 (3)	2.00 (3)	2.792 (2)	157 (3)
N2—H2*B*···O1$^{\text{ii}}$	0.96 (3)	1.90 (3)	2.794 (2)	154 (3)
N2—H2*A*···O2	0.86 (3)	1.97 (3)	2.821 (2)	177 (3)

Symmetry codes: (i) *x*−1/2, −*y*+1/2, −*z*; (ii) *x*+1/2, −*y*+1/2, −*z*.