Crystal structures of three anhydrous salts of the Lewis base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with the ring-substituted benzoic acid analogues 4-aminobenzoic acid, 3,5-dinitrobenzoic acid and 3,5-dinitrosalicylic acid

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Crystal structures of three anhydrous salts of the Lewis base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with the ring-substituted benzoic acid analogues 4-aminobenzoic acid, 3,5-dinitrobenzoic acid and 3,5-dinitrosalicylic acid

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The anhydrous salts of the Lewis base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with 4-aminobenzoic acid [1-aza-8-azoniabicyclo[5.4.0]undec-7-ene 4-aminobenzoate, C9H17N2⁺·C7H6NO2⁻ (I)], 3,5-dinitrobenzoic acid [1-aza-8-azoniabicyclo[5.4.0]undec-7-ene 3,5-dinitrobenzoate, C9H17N2⁺·C7H3N2O6⁻ (II)] and 3,5-dinitrosalicylic acid (DNSA) [1-aza-8-azoniabicyclo[5.4.0]undec-7-ene 2-hydroxy-3,5-dinitrobenzoate, C9H17N2⁺·C7H3N2O7⁻ (III)] have been determined and their hydrogen-bonded structures are described. In both (II) and (III), the DBU cations have a common disorder in three of the C atoms of the six-membered ring moieties [site-occupancy factors (SOF) = 0.735 (3)/0.265 (3) and 0.686 (4)/0.314 (4), respectively], while in (III), there is additional rotational disorder in the DNSA anion, giving two sites (SOF = 0.72/0.28, values fixed) for the phenol group. In the crystals of (I) and (III), the cation–anion pairs are linked through a primary N—H···O carboxyl hydrogen bond [2.665 (2) and 2.869 (3) Å, respectively]. In (II), the ion pairs are linked through an asymmetric three-centre R1(2) N—H···O,O' chelate association. In (I), structure extension is through amine N—H···O carboxyl hydrogen bonds between the PABA anions, giving a three-dimensional structure. The crystal structures of (II) and (III) are very similar, the cation–anion pairs being associated only through weak C—H···O hydrogen bonds, giving in both overall two-dimensional layered structures lying parallel to (001). No π···π ring associations are present in any of the structures.

1. Chemical context and database survey

The Lewis base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is an alkaloid isolated from the sponge Niphates digitalis (Regalado et al., 2010) but is commonly synthesized. It finds use as a curing agent for epoxy resins, as a catalyst in organic syntheses, and as a counter-cation in metal complex chemistry, e.g. with the pentabromo(triphenylphosphane)platinum(IV) monoanion (Motevalli et al., 1989). It has also found use in binding organic liquids (BOLs), which usually comprise a mixture of amidines or guanidine and alcohol, and are used to reversibly capture and release gases such as CO2, CS2, SO2 or COS (Shannon et al., 2015; Pérez et al., 2004; Heldebrant et al., 2009). The structure of one of these formed from the absorption of CO2 is the bicarbonate (Pérez et al., 2004).

As a very strong base (pKa ca 14), protonation of the N8 group of the six-membered hetero-ring of DBU is readily achieved and results in the formation of salts with carboxylic
acids and phenols. The Cambridge Structural Database (2015 version) (Groom & Allen, 2014) contains 35 examples of organic salts of DBU, among them the benzyl dithiocarbonate (Heldebrant et al., 2009) and the phenolate from 2,6-di(tert-butyl)-4-nitrophenol (Lynch & McClenaghan, 2003). However, of the total there are surprisingly few carboxylate salts, e.g. with Kemp’s triacid (1,3,5-trimethylecyclohexane-1,3,5-tricarboxylic acid) (a monoanionic acetonitrile salt) (Huczynski et al., 2008) and the dianionic salt of the tetra(3-carboxyphenyl)-substituted porphyrin (Lipstman & Goldberg, 2013).

No reported crystal structures of salts with simple substituted benzoic acids are found, so in order to examine the hydrogen-bonding in crystals of the DBU salts with some common ring-substituted benzoic acids, a number of these were prepared. Suitable crystals were obtained with 4-aminobenzoic acid (PABA), (3,5-dinitrobenzoic acid (DNBA) and (3,5-dinitrosalicylic acid (DNSA), giving the anhydrous salts, C_9H_7N_2^+ C_7H_6NO_2^- (I), C_9H_7N_2^+ C_7H_3N_2O_6^- (II) and C_9H_7N_2^+ C_7H_3N_2O_7^- (III), respectively and their structures and hydrogen-bonding modes are reported herein.

2. Structural commentary

The asymmetric units of (I)–(III) comprise a DBU cation (A) and a 4-aminobenzoate anion (B), (I) (Fig. 1), a 3,5-dinitrobenzoate anion (B), (II) (Fig. 2), and a 3,5-dinitrosalicylic anion (B), (III) (Fig. 3). The cation–anion pairs in (I) and (III) are linked through a primary N8A—H···O_carboxyl hydrogen bond [2.665 (2) and 2.871 (3) Å, respectively; Tables 1 and 3]. In (II), the ion pairs are linked through an asymmetric three-centre R̃3(4), N8A—H···O,O′ chelate association [2.777 (2), 3.117 (2) Å; Table 2]. With (III), the corresponding longer contact with the second carboxyl O12B atom is 3.222 (3) Å (Fig. 3).
With the structures of (II) and (III), there is disorder in the six-membered ring system involving atoms C9A and C10A (with alternative minor occupancy sites C12A and C13A), giving similar site occupancy factors [SOF 0.735 (3)/0.265 (3) and 0.686 (4)/0.314 (4) for (II) and (III), respectively]. This feature is found in three other structures among the CSD set: the previously mentioned 2,6-di(tert-butyl)-4-nitrophenolate (SOF 0.60/0.40) (Lynch & McClenaghan, 2003); in the 8-bromoguanosine 8-bromoguanoside adduct salt (SOF = 0.63/0.37) (Saftić et al., 2012) and in the counter-cation of a bromocarbyne Mo complex (SOF = 0.83/0.17) (Cordiner et al., 2008).

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

| D—H—A       | D—H   | H···A  | D···A  | D—H···A |
|--------------|-------|--------|--------|---------|
| N8A—H8A···O11B | 0.89 (2) | 1.78 (2) | 2.665 (2) | 170 (2) |
| N4B—H11B···O11B' | 0.89 (2) | 2.05 (2) | 2.939 (2) | 176 (2) |
| N4B—H12B···O12B' | 0.92 (2) | 1.98 (2) | 2.891 (2) | 176 (2) |

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

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

| D—H—A       | D—H   | H···A  | D···A  | D—H···A |
|--------------|-------|--------|--------|---------|
| N8A—H8A···O11B | 0.90 (2) | 1.88 (2) | 2.777 (2) | 177 (2) |
| N8A—H8A···O12B | 0.90 (2) | 2.53 (2) | 3.117 (2) | 124 (1) |
| C10A—H11A···O32B' | 0.99 | 2.44 | 3.247 (3) | 138 |
| C2A—H21A···O31B' | 0.99 | 2.60 | 3.438 (2) | 143 |

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

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

| D—H—A       | D—H   | H···A  | D···A  | D—H···A |
|--------------|-------|--------|--------|---------|
| N8A—H8A···O11B | 0.88 (2) | 1.99 (2) | 2.871 (3) | 176 (2) |
| O2B—H2B···O12B | 0.84 | 1.72 | 2.473 (3) | 147 |
| C10A—H11A···O32B' | 0.99 | 2.45 | 3.251 (3) | 138 |
| C2A—H21A···O31B' | 0.99 | 2.48 | 3.281 (3) | 138 |

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

With the structures of (II) and (III), there is disorder in the six-membered ring system involving atoms C9A and C10A (with alternative minor occupancy sites C12A and C13A), giving similar site occupancy factors [SOF 0.735 (3)/0.265 (3) and 0.686 (4)/0.314 (4) for (II) and (III), respectively]. This feature is found in three other structures among the CSD set: the previously mentioned 2,6-di(tert-butyl)-4-nitrophenolate (SOF 0.60/0.40) (Lynch & McClenaghan, 2003); in the 8-bromoguanosine 8-bromoguanoside adduct salt (SOF = 0.63/0.37) (Saftić et al., 2012) and in the counter-cation of a bromocarbyne Mo complex (SOF = 0.83/0.17) (Cordiner et al., 2008).

Figure 4
The three-dimensional hydrogen-bonded framework structure of (I) viewed approximately along a. For symmetry codes, see Table 1.

Figure 5
The packing of the hydrogen-bonded cation-anion pairs in the unit cell of (II), viewed along a. The minor-component disordered atoms and the non-associative H atoms have been omitted.

Figure 6
The packing of the hydrogen-bonded cation-anion pairs in the unit cell of (III), viewed along a. The minor-component disordered atoms and the non-associative H atoms have been omitted.
Table 4
Experimental details.

| Crystal data | (I) | (II) | (III) |
|--------------|-----|------|-------|
| Chemical formula | C₂H₇N₂⁺·C₂H₅NO₂⁻ | C₂H₇N₂⁺·C₂H₅NO₂⁻ | C₂H₇N₂⁺·C₂H₅NO₂⁻ |
| Mᵣ | 289.37 | 364.36 | 380.36 |
| Crystal system, space group | Orthorhombic, P₂₁2₁2₁ | Monoclinic, P2₁/n | Monoclinic, P2₁/n |
| Temperature (K) | 200 | 200 | 200 |
| a, b, c (Å) | 8.0986 (4), 12.9213 (6), 13.7344 (7) | 6.0197 (4), 19.6228 (13), 14.3866 (8) | 6.1537 (3), 19.1541 (14), 14.5527 (11) |
| α, β, γ (°) | 90, 90, 90 | 90, 98.078 (5), 90 | 90, 98.343 (6), 90 |
| V (Å³) | 1437.23 (12) | 1682.53 (18) | 1697.2 (2) |
| Z | 4 | 4 | 4 |
| Crystal data | Mo Ka | Mo Ka | Mo Ka |
| µ (mm⁻¹) | 0.09 | 0.11 | 0.12 |
| Crystal size (mm) | 0.40 × 0.26 × 0.24 | 0.30 × 0.13 × 0.08 | 0.30 × 0.13 × 0.10 |
| Data collection | Oxford Diffraction Gemini-S CCD-detector | Oxford Diffraction Gemini-S CCD-detector | Oxford Diffraction Gemini-S CCD-detector |
| Diffractometer | | | |
| Absorption correction | Multi-scan (CrysAlis PRO; Agilent, 2014) | Multi-scan (CrysAlis PRO; Agilent, 2014) | Multi-scan (CrysAlis PRO; Agilent, 2014) |
| Tmin, Tmax | 0.93, 0.99 | 0.90, 0.99 | 0.920, 0.990 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 7372, 3324, 2847 | 7082, 3311, 2561 | 7800, 3339, 2347 |
| Rint | 0.031 | 0.024 | 0.034 |
| (sin θ/λ)max (Å⁻¹) | 0.687 | 0.617 | 0.617 |
| Refinement | | | |
| R[F² > 2σ(F²)], wR(F²), S | 0.044, 0.098, 1.07 | 0.045, 0.109, 1.02 | 0.058, 0.123, 1.03 |
| No. of reflections | 3324 | 3311 | 3339 |
| No. of parameters | 199 | 245 | 263 |
| No. of restraints | 3 | 3 | 3 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |
| Δρmax, Δρmin (e Å⁻³) | 0.20, −0.25 | 0.18, −0.22 | 0.29, −0.29 |

Computer programs: CrysAlis PRO (Agilent, 2014), SIR92 (Altomare et al., 1993), SHELXL97 (Sheldrick, 2008) within WinGX (Farrugia, 2012) and PLATON (Spek, 2009).

With the PABA anion in (I), the carboxylate group is essentially coplanar with the benzene ring [torsion angle C2B—C1B—C11B—O11B = 179.25 (15)°, a feature similar to those found in the parent acid (Gracin & Fischer, 2005) and its co-crystals, e.g. with 4-nitrobenzoic acid (Bowers et al., 2005). The carboxylate groups of the DNBA and DNSA anions in both (II) and (III) are also essentially coplanar with the benzene rings: torsion angles C2B—C1B—C11B—O11B = −176.60 (16)° and −179.4 (2)°, respectively. The 5- and 3-substituted nitro groups are also either in-plane or out-of-plane [torsion angles C4B—C5B—N5B—O52B = 179.61 (16)° in (II) and −177.5 (2)° in (III) and C2B—C3B—N3B—O32B = −166.31 (17)° in (II) and −155.2 (2)° in (III)]. Also, in (III), the phenolic substituent group (O2B) is disordered by rotation about the C1B···C4B ring vector giving a minor site-occupancy factor for the O21B—H21B group of 0.28 (SOF fixed in the final refinement cycles). This is similar to the disorder in three examples among the DNA proton-transfer salts with Lewis bases, e.g. with nicotinamide (SOF = 0.76/0.24) (Koman et al., 2003), with 2,6-diaminopyridine (0.90/0.10) (Smith et al., 2003) and with quinoline-2-carboxylic acid (0.51/0.49) (Smith et al., 2007). In (III), the usual short intramolecular phenol O···H···Ocarboxyl hydrogen bond is present (Table 3).

3. Supramolecular features

In the crystal of (I), the N8A···H···O11B hydrogen-bonded cation–anion pairs are extended through intermolecular N4B···H···O11B² and ···N12B³ hydrogen-bonding extensions (Table 1), giving an overall three-dimensional network structure (Fig. 4). The structure contains no inter-ring π···π interactions or C—H···O hydrogen bonds.

The unit-cell parameters, space group (Table 4), and the overall crystal packing of (II) and (III) are very similar (Figs. 5 and 6). Although no classical hydrogen-bonding interactions are present between the primary cation–anion pairs, with both structures there are two minor cation C···H···O hydrogen-bonding extensions to nitro O-atom acceptors, C2A—H···O31B² [3.309 (2) Å in (II) and 3.281 (3) Å in (III)] and C10A—H···O32B² [3.247 (3) Å in (II) and 3.251 (5) Å in (III)] (Tables 2 and 3). These give two-dimensional layered structures lying parallel to (001). There are no inter-ring π···π interactions in either (II) or (III).

4. Synthesis and crystallization

The title compounds (I)–(III) were prepared by first dissolving 100 mg of either PABA, DNBA, or DNSA in 5 mL of warm...
ethanol followed by the addition, with stirring, of 111 mg (I), 72 mg (II) or 67 mg (III) of BDU, respectively. Slow evaporation at room temperature gave colourless needles of (I), colourless prisms of (II), and fine yellow needles of (III), from which specimens were cleaved for the X-ray analyses.

5. Refinement details
Crystal data, data collection and structure refinement details are given in Table 4. Hydrogen atoms were placed in calculated positions [C—H aromatic = 0.95 Å or C—H methylene = 0.99 Å] and were allowed to ride in the refinements, with $U_{iso}(H) = 1.2U_{eq}(C)$. The amine and amonium H-atoms were located in difference-Fourier analyses and were allowed to refine with distance restraints [N—H = 0.90 (2) Å] and with $U_{iso}(H) = 1.2U_{eq}(N)$. Disorder involving atoms C9A and C10A of the six-membered ring systems of both (II) and (III) gave refined minor occupancy sites C12A and C13A, with site occupancy factors of 0.735 (3)/0.265 (3) and 0.686 (4)/0.314 (4), respectively. Also in (III), the phenol group of the DNSA anion was found to be disordered with the minor occupancy site (O21B) having a SOF = 0.28, which was fixed in the final cycles of refinement. In the structure of (I), although of no relevance in the achiral molecule, the Flack parameter (Flack, 1983) was determined as −0.1 (13) for 1668 Friedel pairs, which serves to indicate the lack of any usable anomalous scattering signal, as expected for an all-light-atom structure determined with Mo Kα X-rays.

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Crystal structures of three anhydrous salts of the Lewis base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with the ring-substituted benzoic acid analogues 4-aminobenzoic acid, 3,5-dinitrobenzoic acid and 3,5-dinitrosalicylic acid

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Computing details

For all compounds, data collection: CrysAlis PRO (Agilent, 2014); cell refinement: CrysAlis PRO (Agilent, 2014); data reduction: CrysAlis PRO (Agilent, 2014); program(s) used to solve structure: SIR92 (Altomare et al., 1993); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) within WinGX (Farrugia, 2012); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON (Spek, 2009).

(I) 1-Aza-8-azoniabicyclo[5.4.0]undec-7-ene 4-aminobenzoate

Crystal data

C₉H₁₇N₂⁺·C₇H₆NO₂⁻  

Mᵣ = 289.37  

Orthorhombic, P 2₁2₁2₁  

Hall symbol: P 2ac 2ab  
a = 8.0986 (4) Å  
b = 12.9213 (6) Å  
c = 13.7344 (7) Å  
V = 1437.23 (12) Å³  
Z = 4

Dᵣ = 1.337 Mg m⁻³  
Mo Kα radiation, λ = 0.71073 Å  
Cell parameters from 2097 reflections  
θ = 3.5–28.4°  
µ = 0.09 mm⁻¹  
T = 200 K  
Prism, colourless  
0.40 × 0.26 × 0.24 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer  
Radiation source: Enhance (Mo) X-ray source  
Graphite monochromator  
Detector resolution: 16.067 pixels mm⁻¹  
ω scans  
Absorption correction: multi-scan  
(CrysAlis PRO; Agilent, 2014)  
Tₘᵢₙ = 0.93, Tₘₐₓ = 0.99

7372 measured reflections  
3324 independent reflections  
2847 reflections with I > 2σ(I)  
Rₑₐₜ = 0.031  
θₑₐₜ = 29.2°, θₑₘᵢₙ = 3.3°  
h = −10→10  
k = −16→15  
l = −17→18

Refinement

Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.044  
wR(F²) = 0.098  
S = 1.07  
3324 reflections  
199 parameters

3 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

\[ \Delta \rho_{\text{max}} = 0.20 \text{ e Å}^{-3} \]

\[ \Delta \rho_{\text{min}} = -0.25 \text{ e Å}^{-3} \]

\[ w = 1/[\sigma(F_o^2) + (0.0438P)^2 + 0.0476P] \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

\( (\Delta \sigma)_{\text{max}} < 0.001 \)

\( \Delta \rho_{\text{max}} = 0.20 \text{ e Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.25 \text{ e Å}^{-3} \)

Absolute structure: Flack (1983), 1668 Friedel pairs

Absolute structure parameter: −0.1 (13)

**Special details**

**Geometry.** Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

**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 \( F^2 > 2\sigma(F^2) \) 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         | \( U_{iso}^*/U_{eq} \) |
|-----------|-----------|-----------|-------------------------|
| N1A 0.32105 (18) | 0.84571 (11) | 0.67893 (11) | 0.0229 (4) |
| N8A 0.36282 (18) | 0.67732 (12) | 0.62864 (11) | 0.0241 (5) |
| C2A 0.2390 (2)  | 0.94651 (14) | 0.66676 (13) | 0.0256 (5) |
| C3A 0.3174 (2)  | 1.01454 (14) | 0.58999 (14) | 0.0291 (6) |
| C4A 0.2728 (2)  | 0.98456 (14) | 0.48576 (14) | 0.0288 (6) |
| C5A 0.3145 (2)  | 0.87339 (14) | 0.45932 (13) | 0.0271 (5) |
| C6A 0.2207 (2)  | 0.79201 (14) | 0.51882 (13) | 0.0262 (5) |
| C7A 0.3028 (2)  | 0.77086 (13) | 0.61456 (13) | 0.0209 (5) |
| C9A 0.4591 (2)  | 0.64922 (14) | 0.71447 (13) | 0.0262 (5) |
| C10A 0.5429 (2) | 0.74497 (13) | 0.75333 (13) | 0.0280 (6) |
| C11A 0.4170 (2) | 0.82988 (15) | 0.76868 (13) | 0.0302 (6) |
| O11B 0.28719 (17) | 0.51621 (9)  | 0.51597 (9)  | 0.0320 (4) |
| O12B 0.29529 (19) | 0.56473 (11) | 0.36120 (11) | 0.0428 (5) |
| N4B 0.6170 (2)  | 0.11141 (13) | 0.33808 (12) | 0.0296 (5) |
| C1B 0.3958 (2)  | 0.37941 (13) | 0.40190 (12) | 0.0206 (5) |
| C2B 0.43611 (19) | 0.36990 (13) | 0.30648 (12) | 0.0212 (5) |
| C3B 0.5089 (2)  | 0.27615 (13) | 0.28504 (12) | 0.0220 (5) |
| C4B 0.5475 (2)  | 0.20495 (13) | 0.35867 (13) | 0.0220 (5) |
| C5B 0.5100 (2)  | 0.23253 (13) | 0.45489 (12) | 0.0243 (5) |
| C6B 0.4347 (2)  | 0.32664 (13) | 0.47496 (13) | 0.0227 (5) |
| C11B 0.3204 (2) | 0.50006 (14) | 0.42672 (14) | 0.0238 (5) |
| H8A 0.342 (2)   | 0.6279 (14)  | 0.5850 (13)  | 0.0290* |
| H10A 0.59810    | 0.72880     | 0.81580     | 0.0340* |
| H11A 0.34180    | 0.81070     | 0.82260     | 0.0360* |
| H12A 0.47390    | 0.89490     | 0.78670     | 0.0360* |
| H13A 0.62810    | 0.76860     | 0.70660     | 0.0340* |
| H21A 0.24080    | 0.98360     | 0.72980     | 0.0310* |
| H22A 0.12200    | 0.93460     | 0.64920     | 0.0310* |
| H31A 0.43890    | 1.01140     | 0.59740     | 0.0350* |
| H32A 0.28290    | 1.08700     | 0.60140     | 0.0350* |
| H41A 0.15290    | 0.99540     | 0.47620     | 0.0350* |
### Atomic displacement parameters (Å²)

|       | U¹¹  | U²²  | U³³  | U¹²  | U¹³  | U²³  |
|-------|------|------|------|------|------|------|
| N1A   | 0.0263 (7) | 0.0220 (8) | 0.0205 (7) | 0.0030 (6) | -0.0033 (6) | -0.0022 (6) |
| N8A   | 0.0294 (8) | 0.0197 (8) | 0.0233 (8) | -0.0004 (6) | -0.0008 (6) | -0.0024 (7) |
| C2A   | 0.0276 (9) | 0.0223 (9) | 0.0269 (10) | 0.0053 (7) | -0.0018 (7) | -0.0053 (8) |
| C3A   | 0.0311 (10) | 0.0218 (9) | 0.0343 (11) | -0.0005 (8) | -0.0031 (8) | -0.0024 (8) |
| C4A   | 0.0314 (10) | 0.0263 (9) | 0.0287 (10) | 0.0011 (8) | -0.0008 (8) | 0.0041 (8) |
| C5A   | 0.0295 (9) | 0.0292 (10) | 0.0225 (9) | 0.0039 (8) | -0.0010 (7) | -0.0007 (8) |
| C6A   | 0.0312 (9) | 0.0221 (9) | 0.0253 (9) | -0.0010 (7) | -0.0062 (8) | -0.0035 (8) |
| C7A   | 0.0202 (8) | 0.0203 (9) | 0.0223 (9) | -0.0013 (7) | 0.0013 (7) | -0.0012 (7) |
| C9A   | 0.0268 (9) | 0.0251 (9) | 0.0267 (10) | 0.0030 (8) | -0.0003 (7) | 0.0033 (8) |
| C10A  | 0.0269 (9) | 0.0301 (10) | 0.0269 (10) | 0.0034 (8) | -0.0065 (8) | -0.0010 (8) |
| C11A  | 0.0365 (11) | 0.0306 (10) | 0.0235 (9) | 0.0053 (8) | -0.0094 (8) | -0.0056 (8) |
| O11B  | 0.0520 (8) | 0.0207 (7) | 0.0233 (7) | -0.0025 (6) | 0.0074 (6) | -0.0035 (5) |
| O12B  | 0.0643 (9) | 0.0337 (8) | 0.0305 (8) | 0.0187 (7) | 0.0123 (7) | 0.0099 (7) |
| N4B   | 0.0406 (9) | 0.0260 (9) | 0.0223 (9) | 0.0072 (7) | 0.0000 (7) | -0.0008 (7) |
| C1B   | 0.0194 (8) | 0.0215 (9) | 0.0209 (9) | -0.0045 (6) | -0.0004 (7) | 0.0005 (7) |
| C2B   | 0.0225 (9) | 0.0237 (9) | 0.0174 (8) | -0.0015 (7) | -0.0013 (6) | 0.0033 (7) |
| C3B   | 0.0240 (8) | 0.0241 (8) | 0.0179 (8) | -0.0032 (7) | 0.0001 (7) | 0.0010 (7) |
| C4B   | 0.0216 (8) | 0.0195 (9) | 0.0250 (9) | -0.0025 (7) | -0.0011 (7) | -0.0019 (7) |
| C5B   | 0.0322 (9) | 0.0221 (9) | 0.0185 (8) | 0.0004 (8) | -0.0011 (7) | 0.0046 (7) |
| C6B   | 0.0288 (9) | 0.0228 (9) | 0.0166 (8) | -0.0043 (7) | 0.0018 (7) | -0.0017 (7) |
| C11B  | 0.0255 (9) | 0.0221 (9) | 0.0237 (9) | -0.0043 (7) | 0.0028 (7) | 0.0001 (7) |

### Geometric parameters (Å, °)

|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| O11B—C11B | 1.272 (2) | C4A—H41A | 0.9900 |
| O12B—C11B | 1.245 (2) | C5A—H52A | 0.9900 |
| N1A—C11A | 1.471 (2) | C5A—H51A | 0.9900 |
| N1A—C7A | 1.319 (2) | C6A—H61A | 0.9900 |
| N1A—C2A | 1.472 (2) | C6A—H62A | 0.9900 |
| N8A—C7A | 1.317 (2) | C9A—H91A | 0.9900 |
| N8A—C9A | 1.459 (2) | C9A—H92A | 0.9900 |
| Bond                  | Length (Å)     |
|----------------------|----------------|
| N8A—H8A              | 0.892 (18)     |
| N4B—C4B              | 1.363 (2)      |
| N4B—H41B             | 0.892 (18)     |
| N4B—H42B             | 0.916 (17)     |
| C2A—C3A              | 1.513 (3)      |
| C3A—C4A              | 1.526 (3)      |
| C4A—C5A              | 1.520 (3)      |
| C5A—C6A              | 1.533 (2)      |
| C6A—C7A              | 1.499 (2)      |
| C9A—C10A             | 1.509 (2)      |
| C10A—C11A            | 1.513 (2)      |
| C2A—H2H1A            | 0.9900         |
| C2A—H2A2A            | 0.9900         |
| C3A—H31A             | 0.9900         |
| C3A—H32A             | 0.9900         |
| C4A—H42A             | 0.9900         |

| bond                  | angle (°)  |
|-----------------------|------------|
| C2A—N1A—C7A          | 121.49 (15) |
| C2A—N1A—C11A         | 117.17 (14) |
| C7A—N1A—C11A         | 121.26 (15) |
| C7A—N8A—C9A          | 122.97 (15) |
| C7A—N8A—H8A          | 119.3 (11)  |
| C9A—N8A—H8A          | 117.8 (12)  |
| C4B—N4B—H41B         | 120.9 (13)  |
| H41B—N4B—H42B        | 114.5 (17)  |
| C4B—N4B—H42B         | 121.5 (13)  |
| N1A—C2A—C3A          | 113.83 (14) |
| C2A—C3A—C4A          | 114.02 (15) |
| C3A—C4A—C5A          | 114.29 (15) |
| C4A—C5A—C6A          | 114.26 (14) |
| C5A—C6A—C7A          | 111.90 (14) |
| N8A—C7A—C6A          | 117.38 (15) |
| N1A—C7A—N8A          | 122.23 (16) |
| N1A—C7A—C6A          | 120.28 (15) |
| N8A—C9A—C10A         | 108.79 (14) |
| C9A—C10A—C11A        | 109.93 (14) |
| N1A—C11A—C10A        | 109.88 (14) |
| C3A—C2A—H22A         | 109.00       |
| H21A—C2A—H22A        | 108.00       |
| N1A—C2A—H22A         | 109.00       |
| C3A—C2A—H21A         | 109.00       |
| N1A—C2A—H21A         | 109.00       |
| C2A—C3A—H31A         | 109.00       |
| C2A—C3A—H32A         | 109.00       |
| H31A—C3A—H32A        | 108.00       |
| C4A—C3A—H31A         | 109.00       |
| C4A—C3A—H32A         | 109.00       |
| C3A—C4A—H42A         | 109.00       |

Supporting information

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Electronic reprint
H41A—C4A—H42A 108.00  O12B—C11B—C1B 119.74 (17)
C5A—C4A—H41A 109.00  C1B—C2B—H2B 119.00
C5A—C4A—H42A 109.00  C3B—C2B—H2B 119.00
C3A—C4A—H41A 109.00  C2B—C3B—H3B 119.00
C6A—C5A—H52A 108.00  C4B—C3B—H3B 119.00
H51A—C5A—H52A 108.00  C4B—C5B—H5B 120.00
C4A—C5A—H52A 109.00  C6B—C5B—H5B 120.00
C6A—C5A—H51A 109.00  C1B—C6B—H6B 119.00
C4A—C5A—H51A 109.00  C5B—C6B—H6B 119.00
C5A—C6A—H61A 109.00

C7A—N1A—C2A—C3A −74.8 (2)  N8A—C9A—C10A—C11A 52.82 (18)
C11A—N1A—C2A—C3A 108.53 (17)  C9A—C10A—C11A—N1A −52.69 (19)
C2A—N1A—C7A—N8A −173.67 (15)  C6B—C1B—C2B—C3B 1.0 (2)
C2A—N1A—C7A—C6A 10.2 (2)  C11B—C1B—C2B—C3B 178.48 (15)
C11A—N1A—C7A—N8A 2.9 (3)  C2B—C1B—C6B—C5B 0.1 (2)
C11A—N1A—C7A—C6A −173.23 (15)  C11B—C1B—C6B—C5B −177.44 (15)
C2A—N1A—C11A—C10A −157.91 (14)  C2B—C1B—C11B—O11B 179.25 (15)
C7A—N1A—C11A—C10A 25.4 (2)  C2B—C1B—C11B—O12B −1.6 (3)
C9A—N8A—C7A—N1A −2.2 (3)  C6B—C1B—C11B—O11B −3.4 (2)
C9A—N8A—C7A—C6A 174.06 (15)  C6B—C1B—C11B—O12B 175.83 (16)
C7A—N8A—C9A—C10A −26.7 (2)  N4B—C4B—C5B—C6B −177.86 (16)
C5A—C6A—C7A—N8A −115.39 (17)

Hydrogen-bond geometry (Å, °)

| D—H···A      | D—H | H···A | D···A | D—H···A |
|--------------|-----|------|------|--------|
| N8A—H8A···O11B | 0.89 (2) | 1.78 (2) | 2.665 (2) | 170 (2) |
| N4B—H41B···O11B | 0.89 (2) | 2.05 (2) | 2.939 (2) | 176 (2) |
| N4B—H42B···O12B | 0.92 (2) | 1.98 (2) | 2.891 (2) | 176 (2) |

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

(II) Aza-8-azoniabicyclo[5.4.0]undec-7-ene 3,5-dinitrobenzoate

Crystal data

C9H17N2+·C7H3N2O6−  F(000) = 768
Mr = 364.36
Monoclinic, P21/n
Hall symbol: -P 2yn
a = 6.0197 (4) Å
b = 19.6228 (13) Å
c = 14.3866 (8) Å
β = 98.078 (5)°
V = 1682.53 (18) Å³
Z = 4

θ = 4.0–28.0°
μ = 0.11 mm⁻¹
T = 200 K
Needle, colourless
0.30 × 0.13 × 0.08 mm

Cell parameters from 1784 reflections

Supporting information

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### Data collection

Oxford Diffraction Gemini-S CCD-detector
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.077 pixels mm⁻¹
\( \omega \) scans
Absorption correction: multi-scan
\((\text{CrysAlis PRO}; \text{Agilent, 2014})\)

\( T_{\text{min}} = 0.90, \quad T_{\text{max}} = 0.99 \)

| Refinement | Secondary atom site location: difference Fourier map |
|------------|-----------------------------------------------------|
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| \( R[F^2 > 2\sigma(F^2)] = 0.045 \) | H atoms treated by a mixture of independent and constrained refinement |
| \( wR(F^2) = 0.109 \) | \( w = 1/[(\sigma^2(F_o^2) + (0.0435P)^2 + 0.5615P)/3] \) |
| \( S = 1.01 \) | \( \Delta \rho_{\text{max}} = 0.18 \text{ e Å}^{-3} \) |
| 3311 reflections | \( \Delta \rho_{\text{min}} = -0.22 \text{ e Å}^{-3} \) |
| 245 parameters | |
| 3 restraints | |
| Primary atom site location: structure-invariant direct methods | |

### Special details

**Geometry**. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

**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 \( F^2 > 2\sigma(F^2) \) 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           | \( U_{\text{eq}} \) | Occ. (<1) |
|-------------|-------------|-------------|--------------------|-----------|
| O11B        | -0.0061 (2) | 0.68797 (7) | 0.41185 (9)        | 0.0408 (4) |
| O12B        | -0.0380 (2) | 0.64765 (8) | 0.26602 (10)       | 0.0556 (5) |
| O31B        | -0.5921 (3) | 0.46963 (8) | 0.17213 (10)       | 0.0567 (5) |
| O32B        | -0.8865 (3) | 0.46500 (9) | 0.24178 (11)       | 0.0703 (6) |
| O51B        | -0.8471 (2) | 0.55899 (8) | 0.55381 (10)       | 0.0514 (5) |
| O52B        | -0.5787 (3) | 0.62813 (8) | 0.60351 (10)       | 0.0576 (6) |
| N3B         | -0.6966 (3) | 0.48464 (8) | 0.23584 (11)       | 0.0416 (5) |
| N5B         | -0.6770 (3) | 0.59011 (8) | 0.54409 (10)       | 0.0363 (5) |
| C1B         | -0.2967 (3) | 0.60944 (8) | 0.36270 (11)       | 0.0264 (5) |
| C2B         | -0.3972 (3) | 0.56537 (8) | 0.29419 (11)       | 0.0288 (5) |
| C3B         | -0.5892 (3) | 0.53100 (8) | 0.30888 (11)       | 0.0289 (5) |
| C4B         | -0.6880 (3) | 0.53844 (8) | 0.38905 (12)       | 0.0293 (5) |
| C5B         | -0.5807 (3) | 0.58130 (8) | 0.45649 (11)       | 0.0265 (5) |
| C6B         | -0.3873 (3) | 0.61637 (8) | 0.44556 (11)       | 0.0269 (5) |
| C11B        | -0.0952 (3) | 0.65174 (9) | 0.34516 (13)       | 0.0327 (5) |
| N1A         | 0.6514 (2)  | 0.81846 (7) | 0.36517 (9)        | 0.0288 (4) |
|   | U^11  | U^22  | U^33  | U^12  | U^13  | U^23  |
|---|-------|-------|-------|-------|-------|-------|
| O11 | 0.0376 (7) | 0.0403 (8) | 0.0454 (7) | -0.0139 (6) | 0.0099 (6) | -0.0054 (6) |
| O12 | 0.0558 (9) | 0.0740 (11) | 0.0419 (8) | -0.0258 (8) | 0.0238 (7) | -0.0043 (7) |
| O31 | 0.0690 (10) | 0.0566 (10) | 0.0423 (8) | 0.0063 (8) | 0.0003 (7) | -0.0213 (7) |
| O32 | 0.0733 (11) | 0.0811 (12) | 0.0539 (9) | -0.0503 (10) | -0.0006 (8) | -0.0091 (9) |
| O51 | 0.0472 (8) | 0.0586 (9) | 0.0543 (8) | -0.0128 (7) | 0.0276 (7) | 0.0036 (7) |
| O52 | 0.0663 (10) | 0.0729 (11) | 0.0380 (8) | -0.0175 (8) | 0.0228 (7) | -0.0229 (8) |

Atomic displacement parameters (Å²)

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### Geometric parameters (Å, °)

| Bond/Distance | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 |
|---------------|---------|---------|---------|---------|---------|---------|
| O11B—C11B     | 1.253   |         |         |         |         |         |
| O12B—C11B     | 1.238   |         |         |         |         |         |
| O31B—N3B      | 1.218   |         |         |         |         |         |
| O32B—N3B      | 1.221   |         |         |         |         |         |
| O51B—N5B      | 1.217   |         |         |         |         |         |
| O52B—N5B      | 1.223   |         |         |         |         |         |
| N3B—C3B       | 1.469   |         |         |         |         |         |
| N5B—C5B       | 1.470   |         |         |         |         |         |
| N1A—C2A       | 1.469   |         |         |         |         |         |
| N1A—C7A       | 1.315   |         |         |         |         |         |
| N1A—C11A      | 1.469   |         |         |         |         |         |
| N8A—C13A      | 1.497   |         |         |         |         |         |
| N8A—C9A       | 1.468   |         |         |         |         |         |
| N8A—C7A       | 1.308   |         |         |         |         |         |
| N8A—H8A       | 0.895   |         |         |         |         |         |
| C1B—C11B      | 1.520   |         |         |         |         |         |
| C1B—C2B       | 1.385   |         |         |         |         |         |
| C1B—C6B       | 1.386   |         |         |         |         |         |
| C2B—C3B       | 1.380   |         |         |         |         |         |
| C3B—C4B       | 1.378   |         |         |         |         |         |
| C4B—C5B       | 1.375   |         |         |         |         |         |
| C5B—C6B       | 1.380   |         |         |         |         |         |
| C2B—H2B       | 0.950   |         |         |         |         |         |

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sup-8
| Bond / Angle                        | Distance / Angle |
|------------------------------------|------------------|
| C4B—H4B                            | 0.9500           |
| C6B—H6B                            | 0.9500           |
| C2A—C3A                            | 1.515 (3)        |
| C3A—C4A                            | 1.518 (3)        |
| C4A—C5A                            | 1.520 (3)        |
| O31B—N3B—O32B                      | 124.33 (17)      |
| O31B—N3B—C3B                       | 117.77 (17)      |
| O32B—N3B—C3B                       | 117.89 (16)      |
| O51B—N5B—O52B                      | 123.92 (16)      |
| O51B—N5B—C5B                       | 118.63 (15)      |
| O52B—N5B—C5B                       | 117.44 (16)      |
| C2A—N1A—C11A                       | 116.09 (13)      |
| C7A—N1A—C11A                       | 121.95 (14)      |
| C2A—N1A—C7A                        | 121.91 (14)      |
| C7A—N8A—C9A                        | 122.1 (2)        |
| C7A—N8A—C13A                       | 121.6 (4)        |
| C13A—N8A—H8A                       | 118.6 (12)       |
| C9A—N8A—H8A                        | 119.0 (11)       |
| C7A—N8A—H8A                        | 117.9 (11)       |
| C2B—C1B—C6B                        | 119.23 (16)      |
| C2B—C1B—C11B                       | 120.13 (15)      |
| C6B—C1B—C11B                       | 120.60 (15)      |
| C1B—C2B—C3B                        | 119.19 (15)      |
| N3B—C3B—C2B                        | 119.14 (15)      |
| N3B—C3B—C4B                        | 117.78 (16)      |
| C2B—C3B—C4B                        | 123.08 (15)      |
| C3B—C4B—C5B                        | 116.13 (16)      |
| C4B—C5B—C6B                        | 123.01 (16)      |
| N5B—C5B—C4B                        | 118.32 (16)      |
| N5B—C5B—C6B                        | 118.67 (14)      |
| C1B—C6B—C5B                        | 119.30 (15)      |
| O11B—C11B—C1B                      | 116.66 (16)      |
| O11B—C11B—O12B                     | 126.65 (17)      |
| O12B—C11B—C1B                      | 116.68 (16)      |
| C3B—C2B—H2B                        | 120.00           |
| C1B—C2B—H2B                        | 120.00           |
| C3B—C4B—H4B                        | 122.00           |
| C5B—C4B—H4B                        | 122.00           |
| C5B—C6B—H6B                        | 120.00           |
| C1B—C6B—H6B                        | 120.00           |
| N1A—C2A—C3A                        | 113.94 (15)      |
| C2A—C3A—C4A                        | 114.29 (15)      |
| C3A—C4A—C5A                        | 114.95 (15)      |
| C4A—C5A—C6A                        | 114.65 (15)      |
| C5A—C6A—C7A                        | 113.01 (14)      |
| N1A—C7A—N8A                        | 121.94 (15)      |
| N1A—C7A—C6A                        | 120.27 (15)      |
N8A—C7A—C6A 117.79 (16)  
N8A—C9A—C10A 107.5 (2)  
C9A—C10A—C11A 109.8 (2)  
N1A—C11A—C10A 111.27 (16)  
N8A—C13A—C12A 103.6 (7)  
N1A—C2A—H21A 109.00  
N1A—C2A—H22A 109.00  
C3A—C2A—H21A 109.00  

O31B—N3B—C3B—C2B 12.0 (2)  
O31B—N3B—C3B—C4B −168.62 (16)  
O32B—N3B—C3B—C2B −166.31 (17)  
O32B—N3B—C3B—C4B 13.1 (2)  
O51B—N5B—C5B—C4B 0.3 (2)  
O51B—N5B—C5B—C6B −179.75 (16)  
O52B—N5B—C5B—C4B 179.61 (16)  
O52B—N5B—C5B—C6B −0.5 (2)  
C2A—N1A—C11A—C10A −162.56 (17)  
C7A—N1A—C2A—C3A −71.6 (2)  
C11A—N1A—C2A—C3A 110.16 (17)  
C2A—N1A—C7A—N8A −175.79 (16)  
C2A—N1A—C7A—C6A 5.5 (2)  
C11A—N1A—C7A—N8A 2.4 (3)  
C11A—N1A—C7A—C6A −176.35 (15)  
C7A—N1A—C11A—C10A 19.2 (2)  
C9A—N8A—C7A—C6A −173.3 (2)  
C9A—N8A—C7A—N1A 7.9 (3)  
C7A—N8A—C9A—C10A −37.5 (3)  
C6B—C1B—C2B—C3B 2.0 (2)  
C2B—C1B—C11B—O11B −176.60 (16)  
C2B—C1B—C11B—O12B 4.4 (2)  

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|------|---------|
| N8A—H8A···O11B | 0.90 (2) | 1.88 (2) | 2.777 (2) | 177 (2) |
| N8A—H8A···O12B | 0.90 (2) | 2.53 (2) | 3.117 (2) | 124 (1) |
| C10A—H11A···O32B | 0.99 | 2.44 | 3.247 (3) | 138 |
| C11A—H13A···O52B | 0.99 | 2.52 | 3.071 (2) | 115 |
| C2A—H21A···O31B | 0.99 | 2.56 | 3.309 (2) | 133 |
| C6A—H62A···O11B | 0.99 | 2.60 | 3.438 (2) | 143 |
| C9A—H91A···O12B | 0.99 | 2.60 | 3.127 (4) | 114 |

Symmetry codes: (i) −x+1/2, y+1/2, z+1/2; (ii) x+3/2, −y+3/2, z−1/2; (iii) −x+1/2, y+1/2, z+1/2.
(III) 1-Aza-8-azoniabicyclo[5.4.0]undec-7-ene 2-hydroxy-3,5-dinitrobenzoate

Crystal data

C₉H₁₇N₂+·C₇H₃N₂O₇−

Mr = 380.36

Monoclinic, P2₁/n

Hall symbol: -P 2yn

a = 6.1537 (3) Å

b = 19.1541 (14) Å

c = 14.5527 (11) Å

β = 98.343 (6)°

V = 1697.2 (2) Å³

Z = 4

F(000) = 800

Dc = 1.489 Mg m⁻³

Cell parameters from 1891 reflections

θ = 3.5–26.6°

μ = 0.12 mm⁻¹

T = 200 K

Needle, yellow

0.30 × 0.13 × 0.10 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector
diffractometer

Radiation source: Enhance (Mo) X-ray source

Graphite monochromator

Detector resolution: 16.077 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Agilent, 2014)

Tmin = 0.920, Tmax = 0.990

8780 measured reflections

3339 independent reflections

2347 reflections with I > 2σ(I)

Rint = 0.034

θmax = 26.0°, θmin = 3.4°

h = −7→7

k = −23→23

l = −17→17

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.058

wR(F²) = 0.123

S = 1.03

3339 reflections

263 parameters

3 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbour sites

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(Fo)² + (0.0374P)² + 0.7569P]

where P = (F₀² + 2Fc²)/3

(Δ/σ)max < 0.001

Δρmax = 0.29 e Å⁻³

Δρmin = −0.29 e Å⁻³

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F² against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F², conventional R-factors R are based on F, with F set to zero for negative F². The threshold expression of F² > 2σ(F²) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F² 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(eq) | U(eq) | Occ. (<1) |
|----|------|------|------|-------|-------|-----------|
| O2B | 0.8426 (4) | 0.56153 (13) | 0.78929 (15) | 0.0433 (8) | 0.720 |
| O11B | 0.5084 (3) | 0.68879 (9) | 0.59293 (13) | 0.0433 (6) |  
| O12B | 0.5450 (3) | 0.64525 (10) | 0.73596 (13) | 0.0522 (7) |  
| O31B | 1.1116 (4) | 0.45700 (12) | 0.81707 (17) | 0.0819 (10) |  

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### Supporting Information

**O32B**
- 1.4080 (4)
- 0.47261 (13)
- 0.75765 (15)
- 0.0761 (9)

**O51B**
- 1.3286 (3)
- 0.55867 (11)
- 0.44585 (14)
- 0.0594 (7)

**O52B**
- 1.0707 (4)
- 0.63206 (11)
- 0.39870 (14)
- 0.0670 (8)

**N3B**
- 1.2118 (4)
- 0.48306 (12)
- 0.76028 (16)
- 0.0467 (8)

**N5B**
- 1.1654 (3)
- 0.59169 (11)
- 0.45698 (15)
- 0.0407 (7)

**C1B**
- 0.8002 (3)
- 0.60950 (11)
- 0.63899 (16)
- 0.0268 (7)

**C2B**
- 0.9062 (3)
- 0.56600 (12)
- 0.70947 (16)
- 0.0297 (7)

**C3B**
- 1.0956 (4)
- 0.53052 (12)
- 0.69146 (16)
- 0.0310 (7)

**C4B**
- 1.1816 (3)
- 0.53943 (11)
- 0.61041 (16)
- 0.0308 (7)

**C5B**
- 1.0735 (3)
- 0.58226 (11)
- 0.54278 (15)
- 0.0276 (7)

**C6B**
- 0.8810 (3)
- 0.61671 (11)
- 0.55531 (15)
- 0.0263 (7)

**C11B**
- 0.6029 (4)
- 0.65080 (12)
- 0.65595 (19)
- 0.0346 (8)

**O21B**
- 0.7762 (10)
- 0.6571 (3)
- 0.4915 (5)
- 0.052 (3)

**N1A**
- −0.1524 (3)
- 0.82026 (10)
- 0.63820 (13)
- 0.0293 (6)

**N8A**
- 0.1714 (3)
- 0.76040 (11)
- 0.67301 (14)
- 0.0369 (7)

**C2A**
- −0.3262 (3)
- 0.85087 (13)
- 0.56984 (17)
- 0.0357 (8)

**C3A**
- −0.2606 (4)
- 0.91805 (13)
- 0.52684 (18)
- 0.0397 (8)

**C4A**
- −0.1188 (4)
- 0.90797 (14)
- 0.45044 (17)
- 0.0409 (8)

**C5A**
- 0.0934 (4)
- 0.86814 (13)
- 0.48033 (17)
- 0.0393 (9)

**C6A**
- 0.0612 (4)
- 0.79368 (13)
- 0.51409 (16)
- 0.0340 (8)

**C7A**
- 0.0226 (3)
- 0.79083 (11)
- 0.61294 (15)
- 0.0265 (7)

**C9A**
- 0.1399 (9)
- 0.7478 (2)
- 0.7696 (4)
- 0.0366 (18)

**C10A**
- 0.0234 (6)
- 0.8111 (2)
- 0.8005 (3)
- 0.0379 (11)

**C11A**
- −0.1871 (4)
- 0.82349 (13)
- 0.73612 (16)
- 0.0363 (8)

**C13A**
- 0.189 (2)
- 0.7738 (7)
- 0.7752 (11)
- 0.0366 (18)

**C12A**
- −0.0464 (13)
- 0.7704 (5)
- 0.7958 (6)
- 0.0379 (11)

**H4B**
- 1.31350
- 0.51650
- 0.60110
- 0.0370*

**H6B**
- 0.80240
- 0.64380
- 0.50700
- 0.0320* 0.720

**H21B**
- 0.66080
- 0.67200
- 0.50930
- 0.0770* 0.280

**H61B**
- 0.85460
- 0.56120
- 0.76770
- 0.0360* 0.280

**H8A**
- 0.280 (3)
- 0.7394 (11)
- 0.6508 (15)
- 0.0320* 0.686 (4)

**H10A**
- −0.00890
- 0.80380
- 0.86450
- 0.0460* 0.686 (4)

**H21A**
- −0.45670
- 0.85990
- 0.60060
- 0.0430* 0.720

**H22A**
- −0.36910
- 0.81640
- 0.51980
- 0.0430* 0.720

**H31A**
- −0.17940
- 0.94750
- 0.57630
- 0.0480* 0.280

**H32A**
- −0.39530
- 0.94360
- 0.50080
- 0.0480* 0.280

**H41A**
- −0.20570
- 0.88270
- 0.39820
- 0.0490* 0.280

**H42A**
- −0.08210
- 0.95440
- 0.42720
- 0.0490* 0.280

**H51A**
- 0.18300
- 0.89440
- 0.53080
- 0.0470* 0.280

**H52A**
- 0.17720
- 0.86610
- 0.42730
- 0.0470* 0.280

**H61A**
- −0.06570
- 0.77230
- 0.47440
- 0.0410* 0.280

**H62A**
- 0.19310
- 0.76570
- 0.50720
- 0.0410* 0.280

**H91A**
- 0.28350
- 0.74140
- 0.80920
- 0.0440* 0.686 (4)

**H92A**
- 0.05040
- 0.70540
- 0.77390
- 0.0440* 0.686 (4)

**H11A**
- 0.11950
- 0.85260
- 0.80070
- 0.0460* 0.686 (4)

**H12A**
- −0.29640
- 0.78780
- 0.74760
- 0.0440* 0.686 (4)

**H13A**
- −0.24650
- 0.86990
- 0.74910
- 0.0440* 0.686 (4)
H14A −0.10610 0.72290 0.78230 0.0460* 0.314 (4)
H15A −0.04950 0.78040 0.86230 0.0460* 0.314 (4)
H16A 0.25340 0.82040 0.79120 0.0440* 0.314 (4)
H17A 0.28080 0.73790 0.81100 0.0440* 0.314 (4)
H18A −0.34390 0.81460 0.74010 0.0440* 0.314 (4)
H19A −0.15090 0.87100 0.76060 0.0440* 0.314 (4)

Atomic displacement parameters (Å²)

|     | U¹¹  | U¹²  | U¹³  | U²²  | U²³  | U³³  |
|-----|------|------|------|------|------|------|
| O2B | 0.0472 (13) | 0.0563 (16) | 0.0297 (14) | 0.0095 (12) | 0.0168 (11) | 0.0083 (12) |
| O11B| 0.0356 (9) | 0.0369 (10) | 0.0579 (12) | 0.0124 (8) | 0.0087 (8) | 0.0063 (9) |
| O12B| 0.0492 (11) | 0.0640 (13) | 0.0484 (12) | 0.0080 (10) | 0.0245 (9) | −0.0040 (10) |
| O31B| 0.0774 (15) | 0.0847 (18) | 0.0749 (17) | −0.0226 (13) | −0.0181 (12) | 0.0525 (14) |
| O32B| 0.0708 (15) | 0.0894 (18) | 0.0629 (15) | 0.0492 (13) | −0.0082 (11) | 0.0045 (12) |
| O51B| 0.0542 (11) | 0.0636 (13) | 0.0680 (14) | 0.0066 (10) | 0.0346 (10) | −0.0115 (11) |
| O52B| 0.0918 (15) | 0.0703 (15) | 0.0456 (13) | 0.0168 (13) | 0.0323 (11) | 0.0224 (11) |
| N3B | 0.0592 (15) | 0.0338 (13) | 0.0411 (14) | 0.0003 (11) | −0.0127 (12) | 0.0001 (11) |
| N5B | 0.0464 (12) | 0.0388 (13) | 0.0405 (13) | −0.0040 (10) | 0.0189 (10) | −0.0056 (11) |
| C1B | 0.0259 (11) | 0.0216 (12) | 0.0323 (13) | −0.0038 (9) | 0.0021 (9) | −0.0035 (10) |
| C2B | 0.0341 (12) | 0.0270 (13) | 0.0280 (13) | −0.0057 (10) | 0.0044 (10) | −0.0019 (10) |
| C3B | 0.0361 (12) | 0.0241 (12) | 0.0300 (14) | −0.0006 (10) | −0.0049 (10) | 0.0015 (10) |
| C4B | 0.0256 (11) | 0.0245 (12) | 0.0406 (15) | −0.0010 (10) | −0.0006 (10) | −0.0054 (11) |
| C5B | 0.0297 (11) | 0.0257 (12) | 0.0285 (13) | −0.0056 (10) | 0.0077 (10) | −0.0023 (10) |
| C6B | 0.0288 (11) | 0.0214 (12) | 0.0275 (13) | −0.0017 (9) | −0.0001 (9) | 0.0021 (10) |
| C11B| 0.0292 (12) | 0.0284 (13) | 0.0466 (16) | −0.0028 (10) | 0.0068 (11) | −0.0055 (12) |
| O21B| 0.043 (4) | 0.059 (5) | 0.053 (4) | 0.008 (3) | 0.009 (3) | 0.025 (4) |
| N1A | 0.0254 (9) | 0.0319 (11) | 0.0304 (11) | 0.0014 (8) | 0.0038 (8) | −0.0007 (9) |
| N8A | 0.0333 (11) | 0.0476 (13) | 0.0299 (12) | 0.0157 (10) | 0.0051 (9) | 0.0034 (10) |
| C2A | 0.0254 (11) | 0.0378 (14) | 0.0427 (15) | 0.0059 (10) | 0.0006 (10) | −0.0026 (12) |
| C3A | 0.0358 (13) | 0.0339 (14) | 0.0464 (16) | 0.0066 (11) | −0.0044 (11) | 0.0003 (12) |
| C4A | 0.0442 (14) | 0.0384 (15) | 0.0365 (15) | −0.0024 (12) | −0.0061 (11) | 0.0074 (12) |
| C5A | 0.0370 (13) | 0.0508 (17) | 0.0308 (14) | −0.0005 (12) | 0.0075 (10) | 0.0080 (12) |
| C6A | 0.0340 (12) | 0.0413 (15) | 0.0262 (13) | 0.0081 (11) | 0.0029 (10) | −0.0052 (11) |
| C7A | 0.0270 (11) | 0.0226 (12) | 0.0291 (13) | −0.0006 (9) | 0.0014 (9) | −0.0035 (10) |
| C9A | 0.042 (3) | 0.037 (4) | 0.0292 (18) | 0.001 (2) | 0.000 (2) | 0.005 (3) |
| C10A| 0.047 (2) | 0.041 (2) | 0.0263 (17) | −0.0052 (17) | 0.0070 (16) | −0.0033 (19) |
| C11A| 0.0363 (13) | 0.0419 (15) | 0.0335 (14) | −0.0014 (11) | 0.0150 (11) | −0.0058 (12) |
| C13A| 0.042 (3) | 0.037 (4) | 0.0292 (18) | 0.001 (2) | 0.000 (2) | 0.005 (3) |
| C12A| 0.047 (2) | 0.041 (2) | 0.0263 (17) | −0.0052 (17) | 0.0070 (16) | −0.0033 (19) |

Geometric parameters (Å, °)

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| O2B—C2B | 1.281 (3) | C3A—C4A | 1.522 (4) |
| O11B—C11B | 1.247 (3) | C4A—C5A | 1.520 (4) |
| O12B—C11B | 1.271 (3) | C5A—C6A | 1.531 (4) |
| O21B—C6B | 1.305 (7) | C6A—C7A | 1.493 (3) |
| O31B—N3B | 1.208 (3) | C9A—C10A | 1.510 (6) |
| Bond                  | Length (Å) | Angle (°) |
|----------------------|------------|-----------|
| O32B—N3B             | 1.230 (4)  |           |
| O51B—N5B             | 1.217 (3)  |           |
| O52B—N5B             | 1.230 (3)  |           |
| O2B—H2B              | 0.8400     |           |
| O21B—H21B            | 0.8400     |           |
| N3B—C3B              | 1.460 (3)  |           |
| N5B—C5B              | 1.455 (3)  |           |
| N1A—C2A              | 1.473 (3)  |           |
| N1A—C11A             | 1.473 (3)  |           |
| N1A—C7A              | 1.314 (3)  |           |
| N8A—C9A              | 1.467 (6)  |           |
| N8A—C13A             | 1.498 (16) |           |
| N8A—C7A              | 1.308 (3)  |           |
| N8A—H8A              | 0.88 (2)   |           |
| C1B—C11B             | 1.499 (3)  |           |
| C1B—C6B              | 1.387 (3)  |           |
| C1B—C2B              | 1.406 (3)  |           |
| C2B—C3B              | 1.406 (3)  |           |
| C3B—C4B              | 1.372 (3)  |           |
| C4B—C5B              | 1.376 (3)  |           |
| C5B—C6B              | 1.391 (3)  |           |
| C2B—H61B             | 0.9500     |           |
| C4B—H4B              | 0.9500     |           |
| C6B—H6B              | 0.9500     |           |
| C2A—C3A              | 1.511 (3)  |           |
| C2B—O2B—H2B          | 109.00     |           |
| C6B—O21B—H21B        | 110.00     |           |
| O32B—N3B—C3B         | 117.7 (2)  |           |
| O31B—N3B—O32B        | 123.7 (2)  |           |
| O31B—N3B—C3B         | 118.6 (2)  |           |
| O52B—N5B—C5B         | 117.7 (2)  |           |
| O51B—N5B—O52B        | 123.5 (2)  |           |
| C2A—N1A—C11A         | 116.36 (18) |          |
| C7A—N1A—C11A         | 121.90 (19) |          |
| C2A—N1A—C7A          | 121.74 (19) |          |
| C7A—N8A—C13A         | 122.0 (5)  |           |
| C7A—N8A—C9A          | 122.5 (3)  |           |
| C9A—N8A—H8A          | 119.3 (14) |           |
| C13A—N8A—H8A         | 119.6 (15) |           |
| C7A—N8A—H8A          | 117.0 (14) |           |
| C2B—C1B—C6B          | 120.78 (18) |          |
| C2B—C1B—C11B         | 119.6 (2)  |           |
| C6B—C1B—C11B         | 119.6 (2)  |           |
| O2B—C2B—C1B          | 122.0 (2)  |           |
| C1B—C2B—C3B          | 117.4 (2)  |           |
| O2B—C2B—C3B          | 120.5 (2)  |           |
| Bond                        | Angle (deg) | Distances (Å)                  |
|---------------------------|-------------|--------------------------------|
| N3B—C3B—C4B               | 117.1 (2)   | H51A—C5A—H52A 108.00          |
| C2B—C3B—C4B               | 122.3 (2)   | C5A—C6A—H61A 109.00           |
| N3B—C3B—C2B               | 120.6 (2)   | C5A—C6A—H62A 109.00           |
| C3B—C4B—C5B               | 118.84 (19) | C7A—C6A—H62A 109.00           |
| C4B—C5B—C6B               | 121.43 (19) | C7A—C6A—H62A 109.00           |
| N5B—C5B—C4B               | 118.69 (18) | H61A—C6A—H62A 109.00          |
| N5B—C5B—C6B               | 119.88 (19) | N8A—C9A—H91A 110.00           |
| O21B—C6B—C1B              | 118.7 (3)   | N8A—C9A—H92A 110.00           |
| O21B—C6B—C5B              | 122.0 (3)   | C10A—C9A—H91A 110.00          |
| C1B—C6B—C5B               | 119.23 (19) | C10A—C9A—H92A 110.00          |
| O12B—C11B—C1B             | 116.6 (2)   | H91A—C9A—H92A 109.00          |
| O11B—C11B—C1B             | 119.3 (2)   | C9A—C10A—H10A 110.00          |
| O11B—C11B—O12B            | 124.1 (2)   | C9A—C10A—H11A 110.00          |
| C3B—C2B—H61B              | 121.00      | C11A—C10A—H10A 110.00         |
| C1B—C2B—H61B              | 122.00      | C11A—C10A—H11A 110.00         |
| C5B—C4B—H4B               | 121.00      | H10A—C10A—H11A 110.00         |
| C3B—C4B—H4B               | 121.00      | N1A—C11A—H12A 109.00          |
| C1B—C6B—H6B               | 120.00      | N1A—C11A—H13A 109.00          |
| C5B—C6B—H6B               | 121.00      | C10A—C11A—H12A 109.00         |
| N1A—C2A—C3A               | 114.04 (18) | C10A—C11A—H13A 109.00         |
| C2A—C3A—C4A               | 114.2 (2)   | C10A—C11A—H13A 109.00         |
| C3A—C4A—C5A               | 114.5 (2)   | H14A—C12A—H15A 110.00         |
| O31B—N3B—C3B—C2B          | 23.9 (3)    | O2B—C2B—C3B—C4B 5.6 (4)       |
| O31B—N3B—C3B—C4B          | −157.2 (2)  | O2B—C2B—C3B—C4B 5.6 (4)       |
| O32B—N3B—C3B—C2B          | −155.2 (2)  | O2B—C2B—C3B—C4B 5.6 (4)       |
| O32B—N3B—C3B—C4B          | 23.8 (3)    | O2B—C2B—C3B—C4B 5.6 (4)       |
| O51B—N5B—C5B—C4B          | 3.7 (3)     | C1B—C2B—C3B—C4B 2.7 (3)       |
| O51B—N5B—C5B—C6B          | −176.8 (2)  | C1B—C2B—C3B—C4B 2.7 (3)       |
| O52B—N5B—C5B—C4B          | −177.5 (2)  | C1B—C2B—C3B—C4B 2.7 (3)       |
| O52B—N5B—C5B—C6B          | 2.0 (3)     | C1B—C2B—C3B—C4B 2.7 (3)       |
| C2A—N1A—C7A—N8A           | −176.4 (2)  | C1B—C2B—C3B—C4B 2.7 (3)       |
| C2A—N1A—C7A—C6A           | 6.0 (3)     | C2B—C3B—C4B—C5B 178.3 (2)     |
| C11A—N1A—C7A—N8A          | 2.7 (3)     | C2B—C3B—C4B—C5B 178.3 (2)     |
| C11A—N1A—C7A—C6A          | −175.0 (2)  | C2B—C3B—C4B—C5B 178.3 (2)     |
| C2A—N1A—C11A—C10A         | −163.0 (2)  | C3B—C4B—C5B—C6B 0.4 (3)       |
| C7A—N1A—C2A—C3A           | −71.7 (3)   | C3B—C4B—C5B—C6B 0.4 (3)       |
| C11A—N1A—C2A—C3A          | 109.2 (2)   | C3B—C4B—C5B—C6B 0.4 (3)       |
| C7A—N1A—C11A—C10A         | 17.9 (3)    | C3B—C4B—C5B—C6B 0.4 (3)       |
| C7A—N8A—C9A—C10A          | −38.8 (4)   | C3B—C4B—C5B—C6B 0.4 (3)       |
| C9A—N8A—C7A—C6A           | −173.2 (3)  | C3B—C4B—C5B—C6B 0.4 (3)       |
| C9A—N8A—C7A—N1A           | 9.1 (4)     | C3B—C4B—C5B—C6B 0.4 (3)       |
| Bond | Dihedral Angle (°) |
|------|-------------------|
| C6B—C1B—C2B—C3B | 0.0 (3) |
| C11B—C1B—C2B—C3B | -1.6 (3) |
| C11B—C1B—C2B—O2B | -177.5 (2) |
| C2B—C1B—C6B—C5B | -2.3 (3) |
| C6B—C1B—C2B—O2B | 175.9 (2) |
| C5A—C6A—C7A—N1A | 63.3 (3) |
| C5A—C6A—C7A—N8A | -114.5 (2) |
| N8A—C9A—C10A—C11A | 56.2 (4) |
| C9A—C10A—C11A—N1A | -47.7 (4) |

Hydrogen-bond geometry (Å, °)

| D—H···A          | D—H  | H···A  | D···A  | D—H···A |
|------------------|------|--------|--------|---------|
| N8A—H8A···O11B  | 0.88 (2) | 1.99 (2) | 2.871 (3) | 176 (2) |
| O2B—H2B···O12B  | 0.84  | 1.72   | 2.473 (3) | 149     |
| C10A—H11A···O32B^i | 0.99 | 2.45   | 3.251 (5) | 138     |
| C11A—H13A···O52B^ii | 0.99 | 2.59   | 3.093 (3) | 111     |
| C2A—H21A···O31B^iii | 0.99 | 2.48   | 3.281 (3) | 138     |

Symmetry codes: (i) −x+3/2, y+1/2, −z+3/2; (ii) x−3/2, −y+3/2, z+1/2; (iii) −x+1/2, y+1/2, −z+3/2.