Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Bromoanilinium picrate

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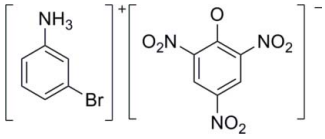
Received 5 November 2009; accepted 14 November 2009

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.047; wR factor = 0.123; data-to-parameter ratio = 10.7.

In the title compound, $C_6H_7BrN^+\cdot C_6H_2N_3O_7^-$, the O atoms of two of the nitro groups are disordered over two sites, the ratios of the refined occupancies being 0.72 (6):0.28 (6) and 0.74 (5):0.26 (5). In the crystal structure, the anions and cations are linked *via* intermolecular N—H···O hydrogen bonds into chains along [100]. Further stabilization is provided by weak intermolecular C—H···O hydrogen bonds.

Related literature

For background information on the crystallization of ammonium salts with picrate derivatives, see: Harrison *et al.* (2007); Pascard *et al.* (1982); Pearson *et al.* (2007); Wang *et al.* (2003).



Experimental

Crystal data

$C_6H_7BrN^+\cdot C_6H_2N_3O_7^-$
M_r = 401.14
Triclinic, $P\overline{1}$
a = 4.3515 (3) Å
b = 12.0757 (8) Å
c = 14.0592 (9) Å
α = 87.783 (1)°
β = 85.945 (1)°
γ = 80.533 (1)°
V = 726.61 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.88 mm^{-1}
T = 298 K
0.16 × 0.12 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.646, T_{max} = 0.762
4689 measured reflections
2818 independent reflections
2225 reflections with $I > 2\sigma(I)$
R_{int} = 0.090

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.123
S = 0.96
2818 reflections
264 parameters
15 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.69 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1C···O7^{i}	0.859 (10)	2.50 (3)	2.966 (12)	115 (3)
N1—H1C···O1^{i}	0.859 (10)	1.934 (14)	2.775 (4)	166 (3)
N1—H1A···O1	0.856 (10)	1.958 (17)	2.766 (4)	157 (3)
N1—H1B···O6^{ii}	0.862 (10)	2.28 (2)	3.047 (12)	148 (3)
C11—H11···O5^{iii}	0.93	2.45	3.296 (4)	152
C4—H4···O3^{iv}	0.93	2.57	3.273 (7)	133

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+2, -y+2, -z$; (iii) $-x+3, -y+1, -z$; (iv) $-x, -y+2, -z+1$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

We thank Wuhan University of Science and Technology for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2949).

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supporting information

Acta Cryst. (2009). E**65**, o3218 [doi:10.1107/S1600536809048405]

3-Bromoanilinium picrate

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S1. Comment

The interaction of picric acid and amines has been widely studied and salt formation takes place readily with very low activation energy. Ammonium salts are easy to crystallize and purify when picrate derivatives are present (Pascard *et al.*,1982;Wang *et al.*,2003; Pearson *et al.*, 2007; Harrison *et al.*, 2007). Herein, we report the crystal structure of the title compound.

In the title compound, the proton has been transferred from the phenolic hydroxylic group to the amine group, resulting in an 1:1 organic salt (Fig.1). In the crystal structure, the molecular components are linked together by intermolecular N—H···O hydrogen bonds forming a one-dimensional chain running parallel to [100]. Adjacent chains are further linked by two weak intermolecular C—H···O hydrogen bonds (see Fig. 2).

S2. Experimental

Picric acid (0.6873 g, 3 mmol) and 3-Bromoaniline (0.5161 g, 3 mmol) were mixed in 10 ml ethanol. The mixture was kept at room temperature for ten days. Yellow block-shaped crystals suitable for the single-crystal X-ray diffraction were collected from the bottom of the vessel.

S3. Refinement

In the picrate anion two of the nitro groups oxygen atoms are disordered over two positions with refined occupancies 0.72 (6):0.28 (6) and 0.74 (5):0.26 (5) for O2/O3:O2′/O3′ and O6/O7:O6′/O7′, respectively.

The carbon-bound hydrogen atoms were placed in ideal positions with C—H=0.93Å and U_{iso}(H) = 1.2U_{eq}(C). H1A, H1B and H1C atoms were located in a difference map and refined with the restraint of N—H = 0.86 (1)Å and U_{iso}(H) = 1.2U_{eq}(N).

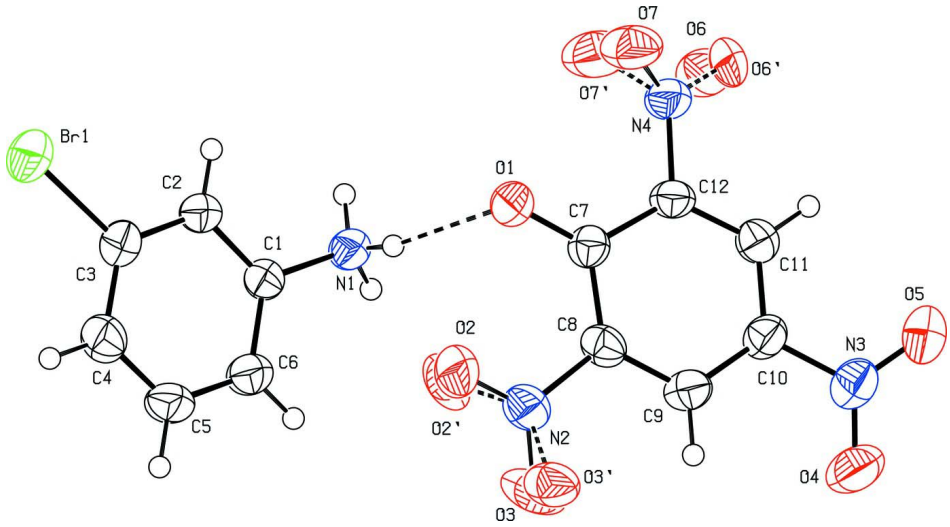

Figure 1

The asymmetric unit with the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. A hydrogen bond is shown by a dashed line. The minor components of disorder are indicated by primed atom labels.

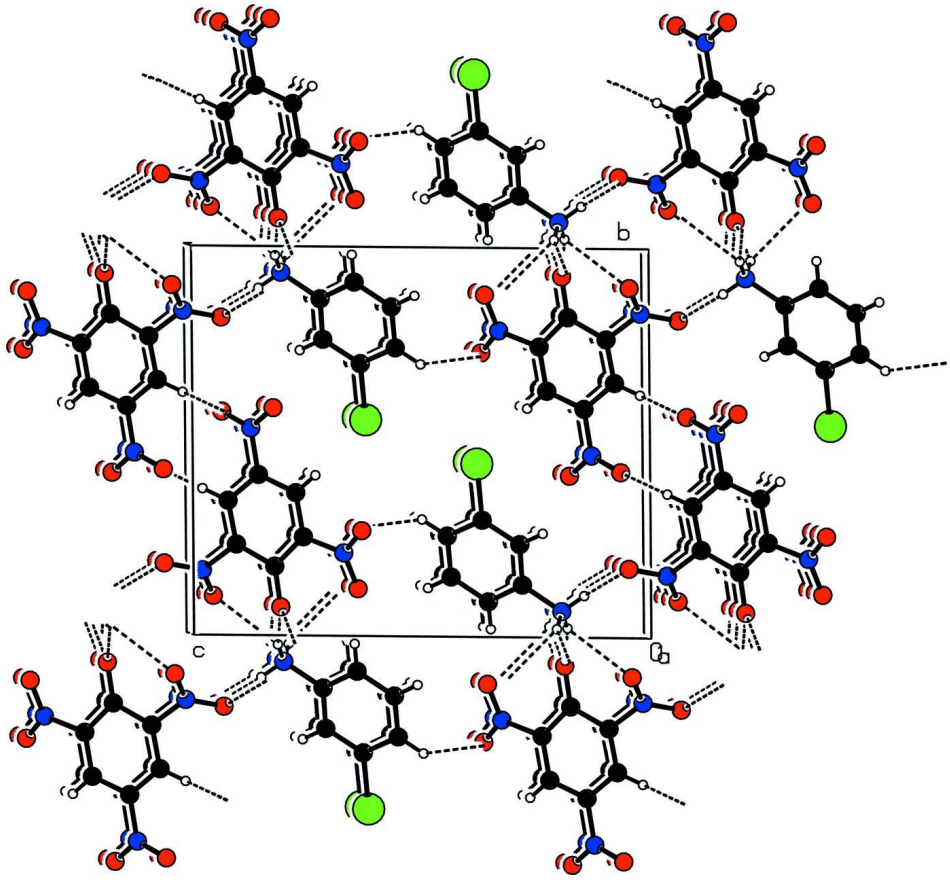

Figure 2

Part of the crystal structure with hydrogen bonds shown as dashed lines.

3-Bromoanilinium picrate

Crystal data

$C_6H_7BrN^+·C_6H_2N_3O_7^-$
M_r = 401.14
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 4.3515 (3) Å
b = 12.0757 (8) Å
c = 14.0592 (9) Å
α = 87.783 (1)°
β = 85.945 (1)°
γ = 80.533 (1)°
V = 726.61 (8) Å^3

Z = 2
F(000) = 400
D_x = 1.833 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2179 reflections
θ = 2.3–27.6°
μ = 2.88 mm^{-1}
T = 298 K
Block, yellow
0.16 × 0.12 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine focus sealed Siemens Mo tube
Graphite monochromator
0.3° wide ω exposures scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.646, T_{max} = 0.762

4689 measured reflections
2818 independent reflections
2225 reflections with $I > 2\sigma(I)$
R_{int} = 0.090
θ_{max} = 26.0°, θ_{min} = 2.2°
h = −5→5
k = −14→12
l = −17→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.123
S = 0.96
2818 reflections
264 parameters
15 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
$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.69 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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}	Occ. (<1)
Br1	0.31978 (9)	1.44651 (3)	0.38403 (3)	0.0620 (2)	
C1	0.2439 (7)	1.1358 (3)	0.2852 (2)	0.0365 (6)	

C2	0.3254 (7)	1.2405 (3)	0.2916 (2)	0.0400 (7)	
H2	0.4488	1.2694	0.2432	0.048*	
C3	0.2197 (7)	1.3015 (3)	0.3716 (2)	0.0418 (7)	
C4	0.0376 (8)	1.2589 (3)	0.4453 (2)	0.0488 (8)	
H4	−0.0312	1.3006	0.4992	0.059*	
C5	−0.0383 (8)	1.1533 (3)	0.4364 (2)	0.0500 (8)	
H5	−0.1593	1.1236	0.4851	0.060*	
C6	0.0623 (8)	1.0912 (3)	0.3568 (2)	0.0451 (7)	
H6	0.0090	1.0204	0.3512	0.054*	
C7	0.9423 (7)	0.8220 (3)	0.1767 (2)	0.0376 (7)	
C8	0.7948 (7)	0.7451 (3)	0.2374 (2)	0.0401 (7)	
C9	0.8229 (8)	0.6320 (3)	0.2218 (2)	0.0432 (7)	
H9	0.7200	0.5862	0.2632	0.052*	
C10	1.0069 (8)	0.5873 (3)	0.1436 (2)	0.0434 (7)	
C11	1.1497 (7)	0.6552 (3)	0.0790 (2)	0.0433 (7)	
H11	1.2660	0.6253	0.0253	0.052*	
C12	1.1162 (7)	0.7672 (3)	0.0960 (2)	0.0398 (7)	
N1	0.3525 (7)	1.0693 (2)	0.20133 (19)	0.0421 (6)	
H1A	0.520 (5)	1.025 (3)	0.215 (2)	0.051*	
H1B	0.400 (8)	1.110 (3)	0.1527 (17)	0.051*	
H1C	0.229 (7)	1.025 (2)	0.187 (2)	0.051*	
N2	0.6000 (7)	0.7845 (3)	0.32217 (19)	0.0484 (7)	
N3	1.0392 (7)	0.4679 (3)	0.1282 (2)	0.0503 (7)	
N4	1.2620 (7)	0.8348 (2)	0.02367 (18)	0.0490 (7)	
O1	0.9193 (5)	0.9265 (2)	0.18883 (16)	0.0489 (6)	
O2	0.623 (5)	0.8764 (8)	0.3531 (10)	0.066 (3)	0.72 (6)
O3	0.419 (6)	0.7259 (14)	0.3589 (15)	0.081 (4)	0.72 (6)
O2′	0.506 (13)	0.8824 (11)	0.334 (2)	0.074 (8)	0.28 (6)
O3′	0.555 (13)	0.7092 (12)	0.3811 (14)	0.058 (8)	0.28 (6)
O4	0.8643 (8)	0.4144 (2)	0.1743 (2)	0.0706 (8)	
O5	1.2388 (7)	0.4267 (2)	0.0683 (2)	0.0661 (7)	
O6	1.223 (5)	0.8179 (12)	−0.0605 (4)	0.068 (3)	0.74 (5)
O7	1.419 (3)	0.9014 (12)	0.0496 (6)	0.064 (3)	0.74 (5)
O6′	1.340 (11)	0.798 (3)	−0.0553 (15)	0.073 (8)	0.26 (5)
O7′	1.27 (2)	0.935 (3)	0.039 (3)	0.099 (14)	0.26 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0788 (3)	0.0419 (2)	0.0677 (3)	−0.01847 (19)	0.0063 (2)	−0.01619 (18)
C1	0.0392 (15)	0.0353 (16)	0.0344 (15)	−0.0054 (13)	0.0003 (12)	−0.0009 (12)
C2	0.0447 (16)	0.0371 (17)	0.0382 (15)	−0.0100 (14)	0.0045 (13)	0.0000 (13)
C3	0.0465 (17)	0.0359 (16)	0.0429 (16)	−0.0051 (14)	−0.0051 (13)	−0.0030 (13)
C4	0.059 (2)	0.050 (2)	0.0356 (16)	−0.0058 (16)	0.0021 (14)	−0.0039 (14)
C5	0.062 (2)	0.050 (2)	0.0379 (17)	−0.0161 (17)	0.0096 (15)	0.0034 (15)
C6	0.0538 (18)	0.0408 (18)	0.0416 (17)	−0.0132 (15)	0.0024 (14)	0.0018 (14)
C7	0.0412 (15)	0.0368 (17)	0.0363 (15)	−0.0098 (13)	−0.0032 (12)	−0.0045 (12)
C8	0.0424 (16)	0.0492 (19)	0.0296 (14)	−0.0107 (14)	0.0006 (12)	−0.0048 (13)

C9	0.0506 (18)	0.0424 (18)	0.0389 (16)	−0.0159 (15)	−0.0021 (13)	0.0025 (14)
C10	0.0568 (19)	0.0354 (17)	0.0389 (16)	−0.0107 (15)	−0.0024 (14)	−0.0016 (13)
C11	0.0495 (18)	0.0429 (18)	0.0375 (16)	−0.0091 (15)	0.0028 (13)	−0.0048 (14)
C12	0.0448 (16)	0.0412 (18)	0.0347 (15)	−0.0139 (14)	0.0033 (12)	0.0007 (13)
N1	0.0517 (16)	0.0350 (15)	0.0405 (14)	−0.0121 (12)	0.0048 (12)	−0.0042 (11)
N2	0.0560 (17)	0.0534 (19)	0.0354 (14)	−0.0103 (15)	0.0051 (12)	−0.0044 (14)
N3	0.0647 (18)	0.0412 (16)	0.0463 (15)	−0.0100 (14)	−0.0090 (14)	−0.0012 (13)
N4	0.0648 (18)	0.0423 (17)	0.0408 (16)	−0.0171 (14)	0.0113 (13)	−0.0026 (12)
O1	0.0499 (13)	0.0405 (13)	0.0580 (14)	−0.0141 (10)	0.0069 (10)	−0.0112 (11)
O2	0.092 (7)	0.048 (4)	0.053 (4)	−0.007 (3)	0.021 (4)	−0.012 (2)
O3	0.078 (8)	0.106 (5)	0.067 (6)	−0.051 (5)	0.035 (6)	−0.029 (4)
O2′	0.079 (18)	0.069 (10)	0.054 (11)	0.028 (8)	0.028 (10)	0.016 (7)
O3′	0.071 (16)	0.066 (8)	0.043 (7)	−0.032 (8)	0.010 (8)	−0.012 (5)
O4	0.099 (2)	0.0506 (16)	0.0676 (17)	−0.0332 (16)	0.0046 (15)	0.0009 (13)
O5	0.0760 (18)	0.0444 (15)	0.0747 (17)	−0.0016 (13)	0.0045 (14)	−0.0115 (13)
O6	0.106 (8)	0.061 (5)	0.040 (3)	−0.029 (5)	0.015 (3)	−0.006 (2)
O7	0.067 (4)	0.071 (5)	0.064 (3)	−0.039 (4)	0.003 (3)	−0.002 (3)
O6′	0.097 (18)	0.044 (9)	0.068 (11)	−0.001 (11)	0.047 (9)	−0.013 (7)
O7′	0.14 (4)	0.084 (13)	0.085 (14)	−0.067 (17)	0.039 (19)	−0.019 (12)

Geometric parameters (Å, º)

Br1—C3	1.890 (3)	C10—C11	1.383 (4)
C1—C2	1.376 (4)	C10—N3	1.449 (4)
C1—C6	1.382 (4)	C11—C12	1.365 (5)
C1—N1	1.459 (4)	C11—H11	0.9300
C2—C3	1.377 (4)	C12—N4	1.455 (4)
C2—H2	0.9300	N1—H1A	0.856 (10)
C3—C4	1.394 (4)	N1—H1B	0.862 (10)
C4—C5	1.382 (5)	N1—H1C	0.859 (10)
C4—H4	0.9300	N2—O2′	1.200 (10)
C5—C6	1.377 (5)	N2—O3	1.218 (5)
C5—H5	0.9300	N2—O2	1.229 (6)
C6—H6	0.9300	N2—O3′	1.237 (9)
C7—O1	1.266 (4)	N3—O4	1.215 (4)
C7—C8	1.435 (4)	N3—O5	1.223 (4)
C7—C12	1.439 (4)	N4—O6′	1.218 (10)
C8—C9	1.375 (5)	N4—O7	1.220 (6)
C8—N2	1.461 (4)	N4—O6	1.236 (6)
C9—C10	1.386 (4)	N4—O7′	1.240 (10)
C9—H9	0.9300		
C2—C1—C6	121.6 (3)	C12—C11—H11	120.7
C2—C1—N1	119.5 (2)	C10—C11—H11	120.7
C6—C1—N1	118.8 (3)	C11—C12—C7	125.2 (3)
C1—C2—C3	118.4 (3)	C11—C12—N4	115.8 (3)
C1—C2—H2	120.8	C7—C12—N4	118.9 (3)
C3—C2—H2	120.8	C1—N1—H1A	108 (3)

C2—C3—C4	121.5 (3)	C1—N1—H1B	112 (2)
C2—C3—Br1	120.4 (2)	H1A—N1—H1B	107 (3)
C4—C3—Br1	118.1 (2)	C1—N1—H1C	114 (2)
C5—C4—C3	118.5 (3)	H1A—N1—H1C	104 (4)
C5—C4—H4	120.8	H1B—N1—H1C	111 (3)
C3—C4—H4	120.8	O2′—N2—O3	111.6 (16)
C6—C5—C4	121.0 (3)	O3—N2—O2	122.5 (6)
C6—C5—H5	119.5	O2′—N2—O3′	123.8 (14)
C4—C5—H5	119.5	O2—N2—O3′	117.4 (10)
C5—C6—C1	119.0 (3)	O2′—N2—C8	121.9 (12)
C5—C6—H6	120.5	O3—N2—C8	119.0 (4)
C1—C6—H6	120.5	O2—N2—C8	118.5 (5)
O1—C7—C8	125.7 (3)	O3′—N2—C8	114.2 (12)
O1—C7—C12	122.5 (3)	O4—N3—O5	123.5 (3)
C8—C7—C12	111.8 (3)	O4—N3—C10	118.4 (3)
C9—C8—C7	124.2 (3)	O5—N3—C10	118.1 (3)
C9—C8—N2	115.3 (3)	O6′—N4—O7	114.7 (18)
C7—C8—N2	120.5 (3)	O7—N4—O6	124.7 (6)
C8—C9—C10	119.1 (3)	O6′—N4—O7′	119.8 (15)
C8—C9—H9	120.5	O6—N4—O7′	113 (2)
C10—C9—H9	120.5	O6′—N4—C12	120.1 (15)
C11—C10—C9	121.1 (3)	O7—N4—C12	118.3 (4)
C11—C10—N3	120.0 (3)	O6—N4—C12	117.0 (6)
C9—C10—N3	118.9 (3)	O7′—N4—C12	119.6 (11)
C12—C11—C10	118.5 (3)	C7—O1—H1A	123.4 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*C*···O7^{i}	0.86 (1)	2.50 (3)	2.966 (12)	115 (3)
N1—H1*C*···O1^{i}	0.86 (1)	1.93 (1)	2.775 (4)	166 (3)
N1—H1*A*···O1	0.86 (1)	1.96 (2)	2.766 (4)	157 (3)
N1—H1*B*···O6^{ii}	0.86 (1)	2.28 (2)	3.047 (12)	148 (3)
C11—H11···O5^{iii}	0.93	2.45	3.296 (4)	152
C4—H4···O3^{iv}	0.93	2.57	3.273 (7)	133

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+2, -y+2, -z$; (iii) $-x+3, -y+1, -z$; (iv) $-x, -y+2, -z+1$.