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Crystal structures of the co-crystalline adduct 5-(4-bromophenyl)-1,3,4-thiadiazol-2-amine–4-nitrobenzoic acid (1/1) and the salt 2-amino-5-(4-bromophenyl)-1,3,4-thiadiazol-3-ium 2-carboxy-4,6-dinitrophenolate

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Keywords: 5-substituted-2-amino-1,3,4-thiadiazoles; 4-nitrobenzoic acid; 3,5-dinitrosalicylic acid; proton transfer; molecular adducts; co-crystals; hydrogen bonding; π - π interactions; crystal structure

CCDC references: 1025540; 1025541

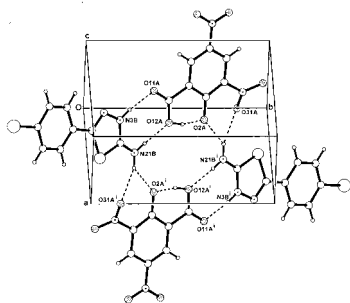
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The structures of the 1:1 co-crystalline adduct $C_8H_6BrN_3S \cdot C_7H_5NO_4$, (I), and the salt $C_8H_7BrN_3S^+ \cdot C_7H_3N_2O_7^-$, (II), obtained from the interaction of 5-(4-bromophenyl)-1,3,4-thiadiazol-2-amine with 4-nitrobenzoic acid and 3,5-dinitrosalicylic acid, respectively, have been determined. The primary inter-species association in both (I) and (II) is through duplex $R_2^2(8)$ ($N-H \cdots O/O-H \cdots O$) or ($N-H \cdots O/N-H \cdots O$) hydrogen bonds, respectively, giving heterodimers. In (II), these are close to planar [the dihedral angles between the thiadiazole ring and the two phenyl rings are 2.1 (3) (intra) and 9.8 (2)° (inter)], while in (I) these angles are 22.11 (15) and 26.08 (18)°, respectively. In the crystal of (I), the heterodimers are extended into a chain along *b* through an amine $N-H \cdots N_{thiadiazole}$ hydrogen bond but in (II), a centrosymmetric cyclic heterotetramer structure is generated through $N-H \cdots O$ hydrogen bonds to phenol and nitro O-atom acceptors and features, together with the primary $R_2^2(8)$ interaction, conjoined $R_6^4(12)$, $R_1^2(6)$ and $S(6)$ ring motifs. Also present in (I) are π - π interactions between thiadiazole rings [minimum ring-centroid separation = 3.4624 (16) Å], as well as short $Br \cdots O_{nitro}$ interactions in both (I) and (II) [3.296 (3) and 3.104 (3) Å, respectively].

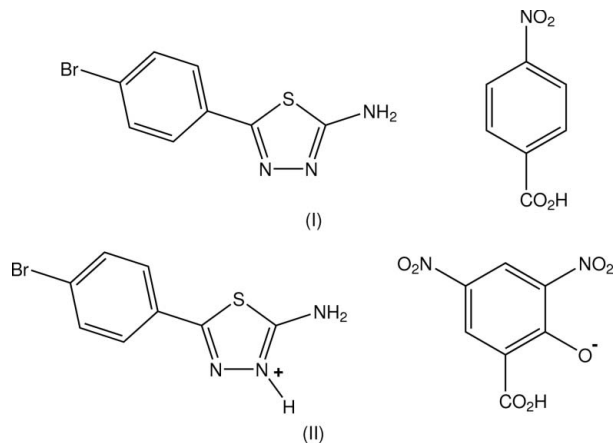
1. Chemical context

1,3,4-Thiadiazole (TZ) and its derivatives, particularly the 2-amino-substituted analogues (ATZ), which are commonly phenyl-substituted at the 5-site of the thiadiazole ring, exhibit a broad range of biological activities (Jain *et al.*, 2013). In the solid state, these 2-amino-1,3,4-thiadiazoles usually interact through duplex $N-H \cdots N$ hydrogen bonds, giving a centrosymmetric cyclic $R_2^2(8)$ hydrogen-bonding homodimer motif, which may be discrete *e.g.* the 5-(3-fluorophenyl)-ATZ derivative (Wang *et al.*, 2009) or more often is extended into a one-dimensional chain structure through the second 2-amino H-atom by an $N-H \cdots N_{4thiadiazole}$ hydrogen bond, *e.g.* in the 5-(4-bromophenyl)-ATZ derivative (Lynch, 2009*a*) and the 5-(4-bromo-2-nitrophenyl)-ATZ derivative (Zhang *et al.*, 2011).

With an interest in the formation of co-crystalline adducts as opposed to proton-transfer salt formation between Lewis bases and aromatic carboxylic acids, we have looked at some of these 5-phenyl-substituted ATZ analogues and have reported examples of both structure types: one-dimensional chain structures in the 1:1 adduct of 5-(4-methoxyphenyl)-2-amino-1,3,4-thiadiazol-2-amine with 4-nitrobenzoic acid (Lynch, 2009*b*) and 5-(4-bromophenyl)-2-amino-1,3,4-thia-



diazol-2-amine (BATZ) with 2-(naphthalen-2-yloxy)acetic acid (Smith & Lynch, 2013), as well as the salt of BATZ with 3,5-dinitrobenzoic acid (Smith & Lynch, 2013). In this salt structure, the carboxylate group gives the previously mentioned primary cyclic $R_2^2(8)$ association through carboxyl $O \cdots H-N$ and amine $N-H \cdots O$ hydrogen bonds but instead of forming the chain structure, a centrosymmetric heterotetramer is formed through a cyclic $R_4^2(8)$ hydrogen-bonding motif.



Herein we report the structures of the 1:1 co-crystalline adduct, $C_8H_6BrN_3S \cdot C_7H_5NO_4$, (I), and the salt $C_8H_7BrN_3S^+ \cdot C_7H_3N_2O_7^-$, (II), obtained from the interaction of BATZ with 4-nitrobenzoic acid (PNBA) and 3,5-dinitrosalicylic acid (DNSA), respectively. The strong acid DNSA ($pK_a = 2.18$) has been employed extensively for the formation of crystalline salts with Lewis bases, forming mainly phenolates (Smith *et al.*, 2007), whereas the weaker acid PNBA ($pK_a = 3.44$) provides examples of both salts (Byriel *et al.*, 1992) and co-crystalline adducts (Aakeröy *et al.*, 2004).

2. Structural commentary

In the structure of the (1:1) PNBA adduct with BATZ, (I), the primary inter-species $R_2^2(8)$ hydrogen-bonded heterodimer is formed (Fig. 1), in which the 4-bromophenyl ring substituent is rotated slightly out of the thiadiazole plane [dihedral angles

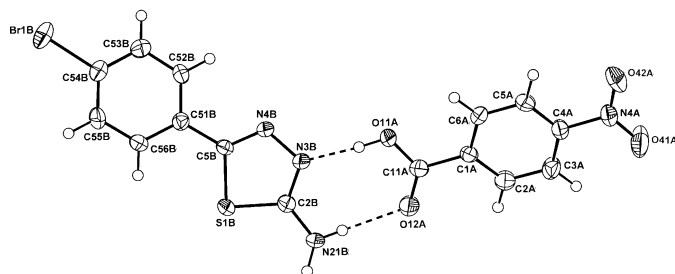


Figure 1
 Molecular conformation and atom-numbering scheme for adduct (I), with inter-species hydrogen bonds shown as dashed lines. Non-H atoms are shown as 50% probability displacement ellipsoids.

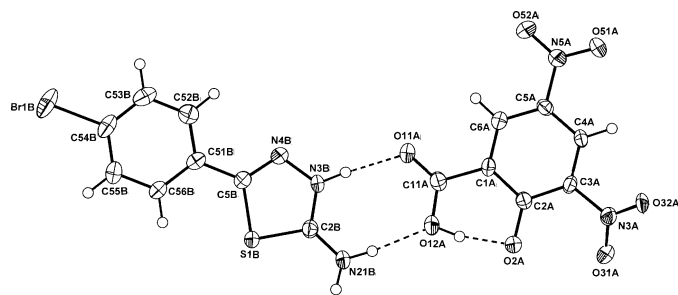


Figure 2
 Molecular conformation and atom-numbering scheme for salt (II), with inter-species hydrogen bonds shown as dashed lines. Non-H atoms are shown as 50% probability displacement ellipsoids.

between the thiadiazole ring and the two benzene rings are 22.11 (15) (intra) and 26.08 (18) ($^\circ$) (inter)]. The carboxylic acid and nitro substituent groups on the PNBA molecule are rotated slightly out of the benzene plane [torsion angles: $C2A-C1A-C11A-O11A = -170.2$ (3) and $C3A-C4A-N4A-O42A = 172.03$ (3) $^\circ$]. This ‘planar’ conformation is found in the parent acid (Bolte, 2009) and in its adducts, *e.g.* with 3-(*N,N*-dimethylamino)benzoic acid (Aakeröy *et al.*, 2004).

In the DNSA salt (II) (Fig. 2), the primary association is also the expected cyclic $R_2^2(8)$ heterodimer, which is essentially planar [comparative dihedral angles 9.8 (2) (intra) and 2.1 (2) $^\circ$ (inter)]. The DNSA anionic moiety is a phenolate with the *anti*-related carboxylic acid H atom forming the common intramolecular $S(6)$ hydrogen bond which is found in *ca.* 70% of DNSA salt structures (Smith *et al.*, 2007). The nitro group at C3A in this anion is rotated significantly out of the benzene plane [torsion angle: $C2A-C3A-N3A-O32A = -147.8$ (4) $^\circ$] whereas the second nitro group and the carboxylate group lie essentially in the plane [torsion angles: $C6A-C5A-N5A-O51A = 179.5$ (4) and $C2A-C1A-C11A-O11A = -178.0$ (4) $^\circ$].

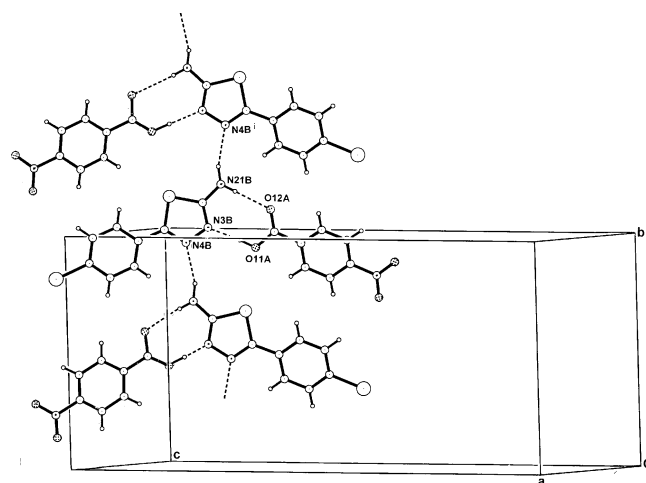


Figure 3
 A perspective view of the one-dimensional hydrogen-bonded extension in the structure of (I). Hydrogen bonds are shown as dashed lines.

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O11 <i>A</i> —H11 <i>A</i> ···N3 <i>B</i>	0.90	1.75	2.648 (3)	175
N21 <i>B</i> —H21 <i>B</i> ···O12 <i>A</i>	0.82	2.04	2.859 (4)	172
N21 <i>B</i> —H22 <i>B</i> ···N4 <i>B</i> ⁱ	0.92	2.16	3.052 (3)	162
C55 <i>B</i> —H55 <i>B</i> ···O41 <i>A</i> ⁱⁱ	0.95	2.47	3.302 (4)	146

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

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O12 <i>A</i> —H12 <i>A</i> ···O2 <i>A</i>	0.87	1.57	2.418 (4)	164
N3 <i>B</i> —H3 <i>B</i> ···O11 <i>A</i>	0.88	1.87	2.744 (4)	172
N21 <i>B</i> —H21 <i>B</i> ···O12 <i>A</i>	0.88	1.89	2.747 (4)	166
N21 <i>B</i> —H22 <i>B</i> ···O2 <i>A</i> ⁱ	0.88	2.22	2.897 (4)	134
N21 <i>B</i> —H22 <i>B</i> ···O31 <i>A</i> ⁱ	0.88	2.19	2.986 (5)	150
C4 <i>A</i> —H4 <i>A</i> ···O32 <i>A</i> ⁱⁱ	0.95	2.44	3.284 (5)	148
C56 <i>B</i> —H56 <i>B</i> ···O51 <i>A</i> ⁱⁱⁱ	0.95	2.44	3.364 (5)	164

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

3. Supramolecular features

In (I), the heterodimers are linked through amine N21*B*—H21*B*···N4*B*ⁱ hydrogen bonds (Table 1) forming chains which extend along *b* (Fig. 3). This is similar to the structure of the BATZ adduct with 2-naphthoxyacetic acid (Smith & Lynch, 2013) and the 5-(4-methoxyphenyl)thiadiazin-2-amine adduct with 4-NBA (Lynch, 2009*b*). A weak aromatic C55*B*—

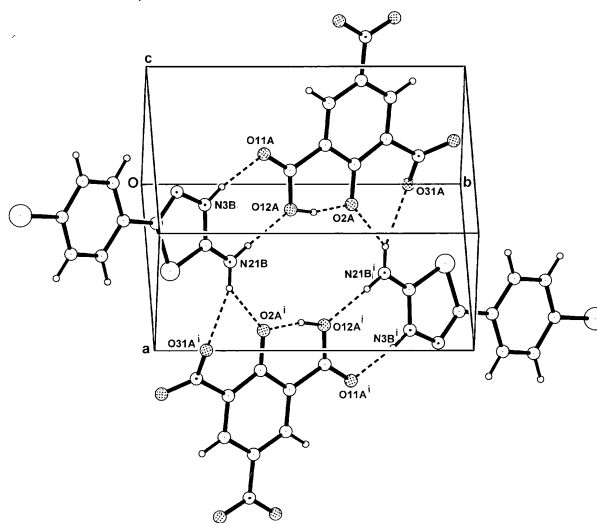


Figure 4
A perspective view of the centrosymmetric hydrogen-bonded heterotetramer units in the unit cell of (II), showing conjoined cyclic $R_6^4(12)$, $R_2^2(8)$, $R_1^1(6)$ and $S(6)$ hydrogen-bonded structural motifs.

H55*B*···O41*A*ⁱⁱ hydrogen-bonding association links the chains across *c* [for symmetry codes, see Table 1] and together with π – π interactions between thiadiazole rings [minimum ring-centroid separation = 3.4624 (16) Å], give a two-dimensional supramolecular structure.

With (II), a secondary symmetric three-centre hydrogen-bonding interaction between the second amine-H atom and

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C ₈ H ₆ BrN ₃ S·C ₇ H ₅ NO ₄	C ₈ H ₇ BrN ₃ S ⁺ ·C ₇ H ₃ N ₂ O ₇ [−]
<i>M_r</i>	423.25	484.25
Crystal system, space group	Monoclinic, <i>C2/c</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	200	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.5205 (6), 12.0394 (7), 31.4321 (18)	5.8017 (3), 10.1903 (5), 15.1592 (9)
α , β , γ (°)	90, 92.982 (6), 90	88.884 (4), 82.438 (5), 85.470 (4)
<i>V</i> (Å ³)	3220.0 (3)	885.62 (8)
<i>Z</i>	8	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ^{−1})	2.71	2.49
Crystal size (mm)	0.30 × 0.10 × 0.05	0.25 × 0.20 × 0.18
Data collection		
Diffractometer	Oxford Diffraction Gemini-S CCD detector	Oxford Diffraction Gemini-S CCD detector
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2013)	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2013)
<i>T_{min}</i> , <i>T_{max}</i>	0.936, 0.980	0.903, 0.980
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	6234, 3164, 2446	5742, 3458, 2479
<i>R_{int}</i>	0.029	0.045
(<i>sin</i> θ / λ) _{max} (Å ^{−1})	0.617	0.617
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.044, 0.093, 1.05	0.058, 0.134, 1.08
No. of reflections	3164	3458
No. of parameters	226	263
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ^{−3})	0.37, −0.30	0.78, −0.82

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SIR92* (Altomare *et al.*, 1993), *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

both the phenolate-O atom (O2B) and the adjacent nitro-O atom (O31A) (Table 2) gives an enlarged centrosymmetric cyclic $R_6^4(12)$ association. This generates a heterotetramer, which comprises a total of seven conjoined cyclic motifs, the central $R_6^4(12)$ plus two each of $R_2^2(8)$, $R_1^2(6)$ and $S(6)$ motifs (Fig. 4). The heterotetramers are weakly linked peripherally through both a centrosymmetric cyclic C—H \cdots O_{nitro} [C4A—H4A \cdots O32Aⁱⁱ] hydrogen-bond pair [graph set $R_2^2(10)$] and a linear C56B—H56B \cdots O51Aⁱⁱⁱ hydrogen bond, giving a two-dimensional supramolecular structure (for symmetry codes, see Table 2). Within the cyclic association there is a short O32A \cdots O32Aⁱⁱ non-bonding contact [2.835 (4) Å]. However, unlike in the structure of (I), no π – π ring interactions are found in (II) [minimum ring-centroid separation = 4.078 (3) Å].

In both (I) and (II), short Br \cdots O_{nitro} contacts are found: for (I) Br1B \cdots O42Aⁱⁱⁱ = 3.314 (4) Å, and for (II), Br1B \cdots O52A^{iv} = 3.104 (3) Å [symmetry codes: (iii) $x + \frac{3}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $-x, -y, -z + 1$].

4. Synthesis and crystallization

The title compounds were prepared by the reaction of 1 mmol (260 mg) of 5-(4-bromophenyl)-1,3,4-thiadiazol-2-amine with 1 mmol of either 4-nitrobenzoic acid (167 mg) [for (I)] or 3,5-dinitrosalicylic acid (228 mg) [for (II)] in 20 mL of 50% ethanol–water, with 10 min refluxing. Partial evaporation of the solvent gave colourless needles of (I) or yellow plates of (II) from which specimens were cleaved for the X-ray analyses.

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms potentially involved in hydrogen-bonding interactions were located by

difference methods but were subsequently included in the refinements with positional parameters fixed and their isotropic displacement parameters riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$. Other H atoms were included at calculated positions [C—H = 0.95 Å] and also treated as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Acknowledgements

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supporting information

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Crystal structures of the co-crystalline adduct 5-(4-bromophenyl)-1,3,4-thiadiazol-2-amine-4-nitrobenzoic acid (1/1) and the salt 2-amino-5-(4-bromophenyl)-1,3,4-thiadiazol-3-ium 2-carboxy-4,6-dinitrophenolate

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Computing details

For both compounds, data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); 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) 5-(4-Bromophenyl)-1,3,4-thiadiazol-2-amine-4-nitrobenzoic acid (1/1)

Crystal data

$C_8H_6BrN_3S \cdot C_7H_5NO_4$

$M_r = 423.25$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 8.5205$ (6) Å

$b = 12.0394$ (7) Å

$c = 31.4321$ (18) Å

$\beta = 92.982$ (6)°

$V = 3220.0$ (3) Å³

$Z = 8$

$F(000) = 1696$

$D_x = 1.754$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1513 reflections

$\theta = 3.2$ – 27.5 °

$\mu = 2.71$ mm⁻¹

$T = 200$ K

Needle, colourless

$0.30 \times 0.10 \times 0.05$ 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, 2013)

$T_{\min} = 0.936$, $T_{\max} = 0.980$

6234 measured reflections

3164 independent reflections

2446 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 3.2$ °

$h = -10 \rightarrow 10$

$k = -14 \rightarrow 13$

$l = -37 \rightarrow 38$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.093$

$S = 1.05$

3164 reflections

226 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 0.5808P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$

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 e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1B	1.32374 (4)	0.82958 (4)	0.95135 (1)	0.0477 (1)
S1B	0.88663 (10)	1.17279 (7)	0.79873 (3)	0.0338 (3)
N3B	0.7467 (3)	1.0355 (2)	0.74804 (8)	0.0298 (8)
N4B	0.8315 (3)	0.9717 (2)	0.77756 (8)	0.0298 (8)
N21B	0.6957 (3)	1.2195 (2)	0.72930 (9)	0.0422 (10)
C2B	0.7637 (4)	1.1422 (3)	0.75456 (10)	0.0306 (10)
C5B	0.9105 (3)	1.0302 (3)	0.80565 (9)	0.0252 (9)
C51B	1.0113 (3)	0.9843 (3)	0.84056 (9)	0.0267 (9)
C52B	1.0714 (4)	0.8778 (3)	0.83755 (10)	0.0333 (11)
C53B	1.1622 (4)	0.8320 (3)	0.87055 (10)	0.0363 (11)
C54B	1.1982 (4)	0.8937 (3)	0.90645 (10)	0.0313 (10)
C55B	1.1420 (4)	1.0005 (3)	0.91008 (10)	0.0398 (11)
C56B	1.0491 (4)	1.0449 (3)	0.87727 (10)	0.0356 (11)
O11A	0.5473 (3)	0.94290 (18)	0.69115 (7)	0.0379 (8)
O12A	0.5398 (3)	1.1075 (2)	0.65888 (8)	0.0526 (10)
O41A	0.0669 (3)	0.8677 (3)	0.49887 (8)	0.0675 (11)
O42A	0.0741 (3)	0.7146 (3)	0.53310 (9)	0.0624 (11)
N4A	0.1096 (3)	0.8111 (3)	0.52893 (9)	0.0347 (10)
C1A	0.3998 (3)	0.9571 (3)	0.62604 (9)	0.0269 (10)
C2A	0.3653 (4)	1.0145 (3)	0.58884 (10)	0.0368 (11)
C3A	0.2695 (4)	0.9678 (3)	0.55671 (10)	0.0393 (11)
C4A	0.2118 (4)	0.8635 (3)	0.56300 (10)	0.0308 (10)
C5A	0.2428 (4)	0.8039 (3)	0.59996 (10)	0.0328 (11)
C6A	0.3384 (3)	0.8522 (3)	0.63168 (10)	0.0307 (10)
C11A	0.5027 (4)	1.0097 (3)	0.66014 (10)	0.0318 (11)
H21B	0.65870	1.18840	0.70780	0.0510*
H22B	0.69870	1.29520	0.73300	0.0510*
H52B	1.04960	0.83580	0.81230	0.0400*
H53B	1.19980	0.75800	0.86850	0.0440*
H55B	1.16720	1.04300	0.93500	0.0480*
H56B	1.01000	1.11840	0.87980	0.0430*
H2A	0.40750	1.08670	0.58520	0.0440*
H3A	0.24450	1.00710	0.53100	0.0470*

H5A	0.19980	0.73190	0.60350	0.0390*
H6A	0.36190	0.81310	0.65750	0.0370*
H11A	0.61080	0.97690	0.71080	0.0570*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1B	0.0445 (2)	0.0621 (3)	0.0354 (2)	0.0020 (2)	-0.0081 (2)	0.0168 (2)
S1B	0.0460 (5)	0.0213 (5)	0.0329 (4)	-0.0032 (4)	-0.0095 (4)	-0.0025 (4)
N3B	0.0351 (14)	0.0206 (15)	0.0326 (14)	-0.0010 (12)	-0.0077 (12)	0.0019 (12)
N4B	0.0358 (14)	0.0205 (15)	0.0321 (14)	0.0016 (12)	-0.0083 (12)	0.0009 (12)
N21B	0.0622 (19)	0.0164 (15)	0.0455 (17)	-0.0013 (14)	-0.0199 (15)	0.0008 (13)
C2B	0.0353 (18)	0.0252 (19)	0.0309 (17)	-0.0036 (15)	-0.0034 (14)	0.0005 (14)
C5B	0.0299 (16)	0.0195 (17)	0.0261 (15)	-0.0016 (14)	0.0006 (13)	-0.0016 (13)
C51B	0.0285 (16)	0.0267 (18)	0.0248 (15)	-0.0020 (14)	0.0004 (12)	0.0021 (13)
C52B	0.0361 (18)	0.032 (2)	0.0309 (17)	0.0019 (16)	-0.0079 (14)	-0.0084 (15)
C53B	0.0367 (18)	0.033 (2)	0.0389 (19)	0.0090 (16)	-0.0015 (15)	-0.0009 (16)
C54B	0.0277 (16)	0.037 (2)	0.0290 (17)	-0.0009 (16)	-0.0006 (13)	0.0064 (15)
C55B	0.056 (2)	0.039 (2)	0.0234 (16)	-0.0020 (19)	-0.0086 (15)	-0.0037 (15)
C56B	0.052 (2)	0.0233 (19)	0.0308 (17)	0.0017 (17)	-0.0039 (15)	-0.0038 (14)
O11A	0.0489 (14)	0.0252 (13)	0.0374 (13)	-0.0043 (11)	-0.0184 (11)	-0.0005 (10)
O12A	0.0744 (18)	0.0289 (16)	0.0515 (16)	-0.0109 (14)	-0.0260 (14)	0.0078 (12)
O41A	0.082 (2)	0.079 (2)	0.0387 (15)	-0.0277 (18)	-0.0246 (15)	0.0108 (15)
O42A	0.078 (2)	0.0484 (19)	0.0578 (18)	-0.0169 (16)	-0.0241 (15)	-0.0068 (15)
N4A	0.0324 (15)	0.040 (2)	0.0311 (15)	-0.0036 (14)	-0.0044 (12)	-0.0060 (14)
C1A	0.0264 (16)	0.0232 (18)	0.0309 (17)	0.0006 (14)	-0.0009 (13)	-0.0030 (14)
C2A	0.0425 (19)	0.030 (2)	0.0376 (18)	-0.0069 (16)	-0.0012 (15)	0.0050 (15)
C3A	0.048 (2)	0.041 (2)	0.0282 (17)	-0.0064 (18)	-0.0053 (15)	0.0089 (16)
C4A	0.0284 (16)	0.035 (2)	0.0286 (16)	-0.0003 (15)	-0.0019 (13)	-0.0056 (14)
C5A	0.0355 (18)	0.024 (2)	0.0386 (19)	-0.0051 (15)	-0.0015 (15)	0.0003 (14)
C6A	0.0336 (17)	0.029 (2)	0.0288 (17)	0.0015 (15)	-0.0058 (14)	0.0037 (14)
C11A	0.0327 (17)	0.026 (2)	0.0363 (18)	0.0011 (15)	-0.0026 (14)	-0.0012 (15)

Geometric parameters (Å, °)

Br1B—C54B	1.891 (3)	C53B—C54B	1.372 (5)
S1B—C2B	1.735 (3)	C54B—C55B	1.379 (5)
S1B—C5B	1.741 (4)	C55B—C56B	1.375 (5)
O11A—C11A	1.305 (4)	C52B—H52B	0.9500
O12A—C11A	1.220 (4)	C53B—H53B	0.9500
O41A—N4A	1.206 (4)	C55B—H55B	0.9500
O42A—N4A	1.209 (5)	C56B—H56B	0.9500
O11A—H11A	0.9000	C1A—C6A	1.382 (5)
N3B—C2B	1.308 (4)	C1A—C11A	1.490 (4)
N3B—N4B	1.380 (4)	C1A—C2A	1.377 (4)
N4B—C5B	1.291 (4)	C2A—C3A	1.384 (5)
N21B—C2B	1.336 (4)	C3A—C4A	1.367 (5)
N21B—H22B	0.9200	C4A—C5A	1.379 (5)

N21B—H21B	0.8200	C5A—C6A	1.383 (5)
N4A—C4A	1.485 (4)	C2A—H2A	0.9500
C5B—C51B	1.466 (4)	C3A—H3A	0.9500
C51B—C56B	1.389 (4)	C5A—H5A	0.9500
C51B—C52B	1.386 (5)	C6A—H6A	0.9500
C52B—C53B	1.377 (5)		
C2B—S1B—C5B	87.27 (15)	C52B—C53B—H53B	120.00
C11A—O11A—H11A	112.00	C54B—C53B—H53B	120.00
N4B—N3B—C2B	113.1 (3)	C54B—C55B—H55B	120.00
N3B—N4B—C5B	113.1 (3)	C56B—C55B—H55B	120.00
H21B—N21B—H22B	124.00	C51B—C56B—H56B	119.00
C2B—N21B—H21B	108.00	C55B—C56B—H56B	119.00
C2B—N21B—H22B	127.00	C2A—C1A—C11A	119.3 (3)
O42A—N4A—C4A	118.1 (3)	C6A—C1A—C11A	120.6 (3)
O41A—N4A—O42A	124.1 (3)	C2A—C1A—C6A	120.1 (3)
O41A—N4A—C4A	117.8 (3)	C1A—C2A—C3A	120.5 (3)
S1B—C2B—N3B	113.0 (2)	C2A—C3A—C4A	118.1 (3)
S1B—C2B—N21B	123.6 (3)	N4A—C4A—C3A	119.2 (3)
N3B—C2B—N21B	123.4 (3)	C3A—C4A—C5A	123.0 (3)
S1B—C5B—N4B	113.5 (2)	N4A—C4A—C5A	117.8 (3)
N4B—C5B—C51B	124.8 (3)	C4A—C5A—C6A	117.9 (3)
S1B—C5B—C51B	121.7 (2)	C1A—C6A—C5A	120.3 (3)
C52B—C51B—C56B	118.2 (3)	O11A—C11A—C1A	114.4 (3)
C5B—C51B—C56B	121.7 (3)	O12A—C11A—C1A	122.0 (3)
C5B—C51B—C52B	120.1 (3)	O11A—C11A—O12A	123.6 (3)
C51B—C52B—C53B	121.0 (3)	C1A—C2A—H2A	120.00
C52B—C53B—C54B	119.7 (3)	C3A—C2A—H2A	120.00
Br1B—C54B—C55B	120.3 (2)	C2A—C3A—H3A	121.00
Br1B—C54B—C53B	119.1 (3)	C4A—C3A—H3A	121.00
C53B—C54B—C55B	120.6 (3)	C4A—C5A—H5A	121.00
C54B—C55B—C56B	119.3 (3)	C6A—C5A—H5A	121.00
C51B—C56B—C55B	121.2 (3)	C1A—C6A—H6A	120.00
C51B—C52B—H52B	119.00	C5A—C6A—H6A	120.00
C53B—C52B—H52B	120.00		
C5B—S1B—C2B—N3B	0.7 (3)	C51B—C52B—C53B—C54B	-2.1 (5)
C5B—S1B—C2B—N21B	-178.1 (3)	C52B—C53B—C54B—Br1B	-179.8 (3)
C2B—S1B—C5B—N4B	-0.7 (2)	C52B—C53B—C54B—C55B	1.1 (5)
C2B—S1B—C5B—C51B	179.5 (2)	C53B—C54B—C55B—C56B	0.0 (5)
C2B—N3B—N4B—C5B	0.0 (4)	Br1B—C54B—C55B—C56B	-179.1 (3)
N4B—N3B—C2B—S1B	-0.5 (3)	C54B—C55B—C56B—C51B	-0.2 (5)
N4B—N3B—C2B—N21B	178.3 (3)	C6A—C1A—C2A—C3A	-0.2 (5)
N3B—N4B—C5B—S1B	0.5 (3)	C11A—C1A—C2A—C3A	-179.7 (3)
N3B—N4B—C5B—C51B	-179.7 (2)	C2A—C1A—C6A—C5A	0.4 (4)
O41A—N4A—C4A—C5A	171.2 (3)	C11A—C1A—C6A—C5A	179.9 (3)
O42A—N4A—C4A—C3A	172.0 (3)	C2A—C1A—C11A—O11A	-170.2 (3)
O42A—N4A—C4A—C5A	-8.6 (4)	C2A—C1A—C11A—O12A	10.5 (5)

O41A—N4A—C4A—C3A	−8.2 (5)	C6A—C1A—C11A—O11A	10.3 (4)
N4B—C5B—C51B—C56B	−157.4 (3)	C6A—C1A—C11A—O12A	−169.0 (3)
S1B—C5B—C51B—C52B	−157.8 (2)	C1A—C2A—C3A—C4A	−0.4 (5)
S1B—C5B—C51B—C56B	22.4 (4)	C2A—C3A—C4A—N4A	−179.6 (3)
N4B—C5B—C51B—C52B	22.5 (4)	C2A—C3A—C4A—C5A	1.0 (5)
C56B—C51B—C52B—C53B	1.9 (5)	N4A—C4A—C5A—C6A	179.7 (3)
C5B—C51B—C56B—C55B	179.1 (3)	C3A—C4A—C5A—C6A	−0.8 (5)
C5B—C51B—C52B—C53B	−178.0 (3)	C4A—C5A—C6A—C1A	0.1 (5)
C52B—C51B—C56B—C55B	−0.8 (5)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O11 <i>A</i> —H11 <i>A</i> ...N3 <i>B</i>	0.90	1.75	2.648 (3)	175
N21 <i>B</i> —H21 <i>B</i> ...O12 <i>A</i>	0.82	2.04	2.859 (4)	172
N21 <i>B</i> —H22 <i>B</i> ...N4 <i>B</i> ⁱ	0.92	2.16	3.052 (3)	162
C55 <i>B</i> —H55 <i>B</i> ...O41 <i>A</i> ⁱⁱ	0.95	2.47	3.302 (4)	146
C56 <i>B</i> —H56 <i>B</i> ...S1 <i>B</i>	0.95	2.78	3.166 (3)	105

Symmetry codes: (i) $-x+3/2, y+1/2, -z+3/2$; (ii) $x+1, -y+2, z+1/2$.**(II) 2-Amino-5-(4-bromophenyl)-1,3,4-thiadiazol-3-ium 2-carboxy-4,6-dinitrophenolate**

Crystal data

 $C_8H_7BrN_3S^+ \cdot C_7H_3N_2O_7^-$ $M_r = 484.25$ Triclinic, $P\bar{1}$ Hall symbol: $-P\ 1$ $a = 5.8017$ (3) Å $b = 10.1903$ (5) Å $c = 15.1592$ (9) Å $\alpha = 88.884$ (4)° $\beta = 82.438$ (5)° $\gamma = 85.470$ (4)° $V = 885.62$ (8) Å³ $Z = 2$ $F(000) = 484$ $D_x = 1.816$ Mg m^{−3}Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1277 reflections

 $\theta = 3.6$ – 24.8° $\mu = 2.49$ mm^{−1} $T = 200$ K

Block, yellow

 $0.25 \times 0.20 \times 0.18$ 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, 2013)

 $T_{\min} = 0.903, T_{\max} = 0.980$

5742 measured reflections

3458 independent reflections

2479 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.045$ $\theta_{\max} = 26.0^\circ, \theta_{\min} = 3.4^\circ$ $h = -7 \rightarrow 7$ $k = -11 \rightarrow 12$ $l = -18 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.058$ $wR(F^2) = 0.134$ $S = 1.08$

3458 reflections

263 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.78 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.82 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97*,

$$FC^* = KFC[1 + 0.001XFC^2\Lambda^3/\text{SIN}(2\Theta)]^{-1/4}$$

Extinction coefficient: 0.042 (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 e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O2A	0.1351 (5)	0.6524 (3)	0.0207 (2)	0.0330 (9)
O11A	-0.0271 (5)	0.3833 (3)	0.2158 (2)	0.0373 (10)
O12A	0.2276 (5)	0.4583 (3)	0.1075 (2)	0.0374 (10)
O31A	-0.0556 (5)	0.8407 (3)	-0.0818 (2)	0.0360 (10)
O32A	-0.2559 (5)	0.9897 (3)	0.0027 (2)	0.0367 (10)
O51A	-0.8459 (5)	0.8277 (3)	0.2177 (2)	0.0434 (11)
O52A	-0.7757 (5)	0.6493 (3)	0.2912 (2)	0.0447 (11)
N3A	-0.1754 (6)	0.8761 (4)	-0.0119 (2)	0.0298 (11)
N5A	-0.7202 (6)	0.7301 (4)	0.2328 (2)	0.0314 (12)
C1A	-0.1349 (7)	0.5803 (4)	0.1393 (3)	0.0245 (12)
C2A	-0.0684 (7)	0.6698 (4)	0.0697 (3)	0.0255 (12)
C3A	-0.2287 (7)	0.7776 (4)	0.0571 (3)	0.0256 (12)
C4A	-0.4397 (7)	0.7983 (4)	0.1105 (3)	0.0248 (12)
C5A	-0.4948 (7)	0.7078 (4)	0.1777 (3)	0.0251 (12)
C6A	-0.3473 (7)	0.5999 (4)	0.1929 (3)	0.0274 (12)
C11A	0.0285 (7)	0.4637 (4)	0.1578 (3)	0.0294 (14)
Br1B	0.60639 (11)	-0.41426 (5)	0.59418 (3)	0.0574 (2)
S1B	0.68942 (18)	0.05777 (11)	0.23777 (7)	0.0314 (3)
N3B	0.2976 (6)	0.1838 (3)	0.2484 (2)	0.0288 (11)
N4B	0.2693 (6)	0.0962 (3)	0.3171 (2)	0.0303 (11)
N21B	0.5551 (6)	0.2544 (3)	0.1290 (2)	0.0346 (11)
C2B	0.5050 (7)	0.1784 (4)	0.1978 (3)	0.0267 (12)
C5B	0.4588 (7)	0.0224 (4)	0.3197 (3)	0.0289 (12)
C51B	0.4894 (7)	-0.0828 (4)	0.3850 (3)	0.0289 (12)
C52B	0.3110 (8)	-0.1094 (5)	0.4517 (3)	0.0383 (17)
C53B	0.3431 (9)	-0.2075 (5)	0.5136 (3)	0.0433 (17)
C54B	0.5553 (9)	-0.2817 (4)	0.5088 (3)	0.0368 (14)
C55B	0.7313 (9)	-0.2594 (5)	0.4423 (3)	0.0420 (17)
C56B	0.6997 (8)	-0.1610 (5)	0.3807 (3)	0.0386 (17)
H4A	-0.54410	0.87240	0.10140	0.0300*

H6A	-0.39030	0.53950	0.23950	0.0330*
H12A	0.22100	0.52990	0.07550	0.0560*
H3B	0.18380	0.24180	0.23770	0.0350*
H21B	0.44930	0.31390	0.11350	0.0410*
H22B	0.69490	0.24630	0.09820	0.0410*
H52B	0.16500	-0.05930	0.45460	0.0460*
H53B	0.22040	-0.22440	0.55940	0.0520*
H55B	0.87510	-0.31180	0.43860	0.0500*
H56B	0.82260	-0.14590	0.33460	0.0460*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2A	0.0266 (15)	0.0346 (17)	0.0350 (17)	0.0035 (14)	0.0012 (13)	0.0106 (13)
O11A	0.0373 (17)	0.0299 (17)	0.0412 (19)	0.0067 (15)	-0.0001 (15)	0.0131 (14)
O12A	0.0308 (17)	0.0316 (17)	0.047 (2)	0.0054 (14)	-0.0018 (15)	0.0162 (14)
O31A	0.0378 (17)	0.0395 (18)	0.0287 (17)	0.0007 (15)	-0.0014 (14)	0.0122 (14)
O32A	0.0308 (16)	0.0224 (16)	0.054 (2)	0.0070 (14)	-0.0025 (15)	0.0143 (14)
O51A	0.0361 (18)	0.0377 (19)	0.050 (2)	0.0159 (16)	0.0058 (15)	0.0097 (16)
O52A	0.0409 (18)	0.043 (2)	0.044 (2)	0.0024 (16)	0.0115 (15)	0.0174 (16)
N3A	0.0237 (19)	0.033 (2)	0.033 (2)	-0.0017 (17)	-0.0063 (17)	0.0097 (17)
N5A	0.030 (2)	0.029 (2)	0.033 (2)	0.0013 (18)	0.0012 (17)	0.0010 (17)
C1A	0.027 (2)	0.019 (2)	0.028 (2)	-0.0007 (18)	-0.0072 (18)	0.0040 (17)
C2A	0.025 (2)	0.025 (2)	0.026 (2)	0.0018 (19)	-0.0040 (18)	0.0008 (18)
C3A	0.027 (2)	0.023 (2)	0.027 (2)	-0.0026 (19)	-0.0055 (18)	0.0093 (17)
C4A	0.024 (2)	0.022 (2)	0.028 (2)	0.0045 (18)	-0.0065 (18)	0.0022 (17)
C5A	0.023 (2)	0.026 (2)	0.025 (2)	0.0037 (18)	-0.0018 (17)	-0.0022 (17)
C6A	0.029 (2)	0.025 (2)	0.028 (2)	-0.0007 (19)	-0.0041 (18)	0.0049 (18)
C11A	0.028 (2)	0.026 (2)	0.034 (3)	0.002 (2)	-0.006 (2)	0.001 (2)
Br1B	0.0977 (5)	0.0413 (3)	0.0352 (3)	-0.0111 (3)	-0.0151 (3)	0.0174 (2)
S1B	0.0254 (6)	0.0321 (6)	0.0341 (6)	0.0043 (5)	0.0000 (5)	0.0122 (5)
N3B	0.0258 (19)	0.0265 (19)	0.032 (2)	0.0067 (16)	-0.0026 (16)	0.0086 (15)
N4B	0.0283 (19)	0.033 (2)	0.028 (2)	0.0002 (17)	0.0002 (16)	0.0068 (16)
N21B	0.0259 (19)	0.034 (2)	0.041 (2)	0.0075 (17)	-0.0015 (17)	0.0154 (17)
C2B	0.026 (2)	0.023 (2)	0.031 (2)	-0.0013 (19)	-0.0047 (19)	0.0041 (18)
C5B	0.031 (2)	0.028 (2)	0.027 (2)	-0.002 (2)	-0.0016 (18)	0.0031 (18)
C51B	0.032 (2)	0.031 (2)	0.024 (2)	-0.007 (2)	-0.0022 (18)	0.0031 (18)
C52B	0.038 (3)	0.039 (3)	0.036 (3)	0.002 (2)	-0.001 (2)	0.000 (2)
C53B	0.048 (3)	0.048 (3)	0.032 (3)	-0.011 (3)	0.005 (2)	0.007 (2)
C54B	0.059 (3)	0.028 (2)	0.025 (2)	-0.009 (2)	-0.009 (2)	0.0066 (19)
C55B	0.047 (3)	0.035 (3)	0.042 (3)	0.006 (2)	-0.006 (2)	0.013 (2)
C56B	0.038 (3)	0.041 (3)	0.033 (3)	0.003 (2)	0.004 (2)	0.015 (2)

Geometric parameters (Å, °)

Br1B—C54B	1.886 (4)	C1A—C6A	1.387 (6)
S1B—C5B	1.756 (4)	C1A—C11A	1.506 (6)
S1B—C2B	1.720 (4)	C1A—C2A	1.416 (6)

O2A—C2A	1.311 (5)	C2A—C3A	1.409 (6)
O11A—C11A	1.220 (5)	C3A—C4A	1.380 (6)
O12A—C11A	1.296 (5)	C4A—C5A	1.384 (6)
O31A—N3A	1.232 (4)	C5A—C6A	1.374 (6)
O32A—N3A	1.227 (5)	C4A—H4A	0.9500
O51A—N5A	1.222 (5)	C6A—H6A	0.9500
O52A—N5A	1.226 (5)	C5B—C51B	1.461 (6)
O12A—H12A	0.8700	C51B—C56B	1.398 (6)
N3A—C3A	1.456 (6)	C51B—C52B	1.388 (6)
N5A—C5A	1.460 (5)	C52B—C53B	1.376 (7)
N3B—C2B	1.337 (5)	C53B—C54B	1.387 (7)
N3B—N4B	1.360 (4)	C54B—C55B	1.367 (7)
N4B—C5B	1.287 (5)	C55B—C56B	1.375 (7)
N21B—C2B	1.302 (5)	C52B—H52B	0.9500
N3B—H3B	0.8800	C53B—H53B	0.9500
N21B—H22B	0.8800	C55B—H55B	0.9500
N21B—H21B	0.8800	C56B—H56B	0.9500
C2B—S1B—C5B	88.1 (2)	O11A—C11A—O12A	124.5 (4)
C11A—O12A—H12A	104.00	O11A—C11A—C1A	121.4 (4)
O32A—N3A—C3A	117.7 (3)	C3A—C4A—H4A	121.00
O31A—N3A—O32A	123.8 (4)	C5A—C4A—H4A	121.00
O31A—N3A—C3A	118.5 (4)	C5A—C6A—H6A	120.00
O51A—N5A—C5A	118.3 (3)	C1A—C6A—H6A	120.00
O51A—N5A—O52A	123.1 (3)	S1B—C2B—N3B	109.7 (3)
O52A—N5A—C5A	118.5 (4)	S1B—C2B—N21B	126.3 (3)
N4B—N3B—C2B	117.4 (3)	N3B—C2B—N21B	124.0 (4)
N3B—N4B—C5B	110.0 (3)	S1B—C5B—N4B	114.8 (3)
C2B—N3B—H3B	121.00	N4B—C5B—C51B	124.5 (4)
N4B—N3B—H3B	121.00	S1B—C5B—C51B	120.7 (3)
C2B—N21B—H21B	120.00	C5B—C51B—C56B	120.4 (4)
H21B—N21B—H22B	120.00	C52B—C51B—C56B	118.2 (4)
C2B—N21B—H22B	120.00	C5B—C51B—C52B	121.3 (4)
C2A—C1A—C11A	120.1 (4)	C51B—C52B—C53B	120.8 (4)
C6A—C1A—C11A	118.9 (4)	C52B—C53B—C54B	119.7 (4)
C2A—C1A—C6A	121.0 (4)	Br1B—C54B—C53B	120.6 (4)
C1A—C2A—C3A	117.0 (4)	C53B—C54B—C55B	120.5 (4)
O2A—C2A—C3A	122.4 (4)	Br1B—C54B—C55B	118.9 (4)
O2A—C2A—C1A	120.6 (4)	C54B—C55B—C56B	119.8 (5)
N3A—C3A—C2A	121.2 (4)	C51B—C56B—C55B	121.0 (4)
N3A—C3A—C4A	116.4 (4)	C51B—C52B—H52B	120.00
C2A—C3A—C4A	122.4 (4)	C53B—C52B—H52B	120.00
C3A—C4A—C5A	118.0 (4)	C52B—C53B—H53B	120.00
N5A—C5A—C4A	117.3 (4)	C54B—C53B—H53B	120.00
N5A—C5A—C6A	120.2 (4)	C54B—C55B—H55B	120.00
C4A—C5A—C6A	122.4 (4)	C56B—C55B—H55B	120.00
C1A—C6A—C5A	119.2 (4)	C51B—C56B—H56B	120.00
O12A—C11A—C1A	114.2 (4)	C55B—C56B—H56B	119.00

C2B—S1B—C5B—C51B	179.2 (4)	C11A—C1A—C6A—C5A	178.5 (4)
C2B—S1B—C5B—N4B	-1.5 (3)	O2A—C2A—C3A—N3A	0.1 (6)
C5B—S1B—C2B—N3B	1.5 (3)	O2A—C2A—C3A—C4A	-177.8 (4)
C5B—S1B—C2B—N21B	-178.6 (4)	C1A—C2A—C3A—C4A	1.3 (6)
O32A—N3A—C3A—C2A	-147.8 (4)	C1A—C2A—C3A—N3A	179.2 (4)
O31A—N3A—C3A—C4A	-148.7 (4)	C2A—C3A—C4A—C5A	-1.1 (6)
O32A—N3A—C3A—C4A	30.3 (5)	N3A—C3A—C4A—C5A	-179.0 (4)
O31A—N3A—C3A—C2A	33.3 (6)	C3A—C4A—C5A—N5A	-179.1 (4)
O51A—N5A—C5A—C4A	-1.1 (6)	C3A—C4A—C5A—C6A	0.3 (6)
O51A—N5A—C5A—C6A	179.5 (4)	C4A—C5A—C6A—C1A	0.1 (7)
O52A—N5A—C5A—C4A	178.0 (4)	N5A—C5A—C6A—C1A	179.5 (4)
O52A—N5A—C5A—C6A	-1.5 (6)	S1B—C5B—C51B—C52B	178.1 (4)
N4B—N3B—C2B—N21B	178.7 (4)	S1B—C5B—C51B—C56B	-3.0 (6)
C2B—N3B—N4B—C5B	0.3 (5)	N4B—C5B—C51B—C52B	-1.1 (7)
N4B—N3B—C2B—S1B	-1.4 (4)	N4B—C5B—C51B—C56B	177.8 (4)
N3B—N4B—C5B—C51B	-179.8 (4)	C5B—C51B—C52B—C53B	-179.1 (4)
N3B—N4B—C5B—S1B	0.9 (4)	C56B—C51B—C52B—C53B	2.0 (7)
C6A—C1A—C2A—C3A	-0.8 (6)	C5B—C51B—C56B—C55B	179.3 (4)
C6A—C1A—C2A—O2A	178.3 (4)	C52B—C51B—C56B—C55B	-1.7 (7)
C2A—C1A—C6A—C5A	0.2 (6)	C51B—C52B—C53B—C54B	-0.7 (7)
C11A—C1A—C2A—O2A	0.0 (6)	C52B—C53B—C54B—Br1B	178.7 (4)
C11A—C1A—C2A—C3A	-179.1 (4)	C52B—C53B—C54B—C55B	-1.0 (7)
C2A—C1A—C11A—O11A	-178.0 (4)	Br1B—C54B—C55B—C56B	-178.4 (4)
C2A—C1A—C11A—O12A	2.2 (6)	C53B—C54B—C55B—C56B	1.3 (7)
C6A—C1A—C11A—O11A	3.7 (6)	C54B—C55B—C56B—C51B	0.1 (7)
C6A—C1A—C11A—O12A	-176.2 (4)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O12 <i>A</i> —H12 <i>A</i> ...O2 <i>A</i>	0.87	1.57	2.418 (4)	164
N3 <i>B</i> —H3 <i>B</i> ...O11 <i>A</i>	0.88	1.87	2.744 (4)	172
N21 <i>B</i> —H21 <i>B</i> ...O12 <i>A</i>	0.88	1.89	2.747 (4)	166
N21 <i>B</i> —H22 <i>B</i> ...O2 <i>A</i> ⁱ	0.88	2.22	2.897 (4)	134
N21 <i>B</i> —H22 <i>B</i> ...O31 <i>A</i> ⁱ	0.88	2.19	2.986 (5)	150
C4 <i>A</i> —H4 <i>A</i> ...O32 <i>A</i> ⁱⁱ	0.95	2.44	3.284 (5)	148
C56 <i>B</i> —H56 <i>B</i> ...O51 <i>A</i> ⁱⁱⁱ	0.95	2.44	3.364 (5)	164
C56 <i>B</i> —H56 <i>B</i> ...S1 <i>B</i>	0.95	2.64	3.081 (5)	109

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