

Keywords: benzothiazole; hydrogen bond; molecular salt; crystal structure.

CCDC references: 1886885; 1886884; 1886883; 1886882; 1886881

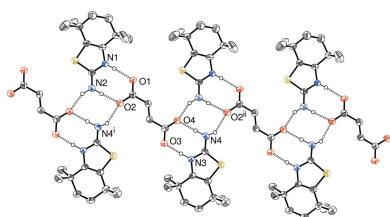
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Hydrogen-bonded molecular salts of reduced benzothiazole derivatives with carboxylates: a robust $R_2^2(8)$ supramolecular motif (even when disordered)

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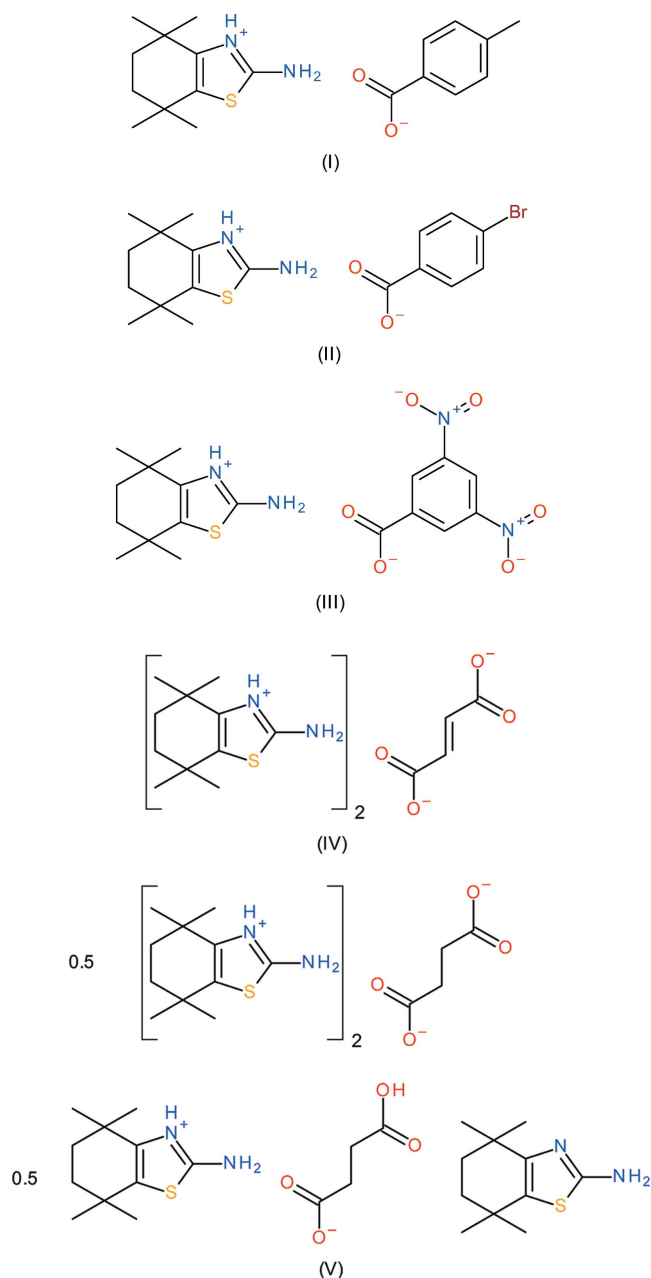
The syntheses and structures of five molecular salts of protonated 4,4,7,7-tetramethyl-3a,5,6,7a-tetrahydrobenzothiazol-2-ylamine ($C_{11}H_{19}N_2S^+$) with different deprotonated carboxylic acids (4-methylbenzoic acid, 4-bromobenzoic acid, 3,5-dinitrobenzoic acid, fumaric acid and succinic acid) are reported, namely 2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium 4-methylbenzoate, $C_{11}H_{19}N_2S^+ \cdot C_8H_7O_2^-$, (I), 2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium 4-bromobenzoate, $C_{11}H_{19}N_2S^+ \cdot C_7H_4BrO_2^-$, (II), 2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium 3,5-dinitrobenzoate, $C_{11}H_{19}N_2S^+ \cdot C_7H_3N_2O_6^-$, (III), bis(2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium) fumarate, $2C_{11}H_{19}N_2S^+ \cdot C_4H_2O_4^{2-}$, (IV), and the 1:1 co-crystal of bis(2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium) succinate and 2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium hydrogen succinate $1.5C_{11}H_{19}N_2S^+ \cdot 0.5C_4H_4O_4^{2-} \cdot 0.5C_4H_5O_4^- \cdot 0.5C_{11}H_{18}N_2S$, (V). In every case, the cation protonation occurs at the N atom of the thiazole ring and the six-membered ring adopts a half-chair conformation (in some cases, the deviating methylene groups are disordered over two sets of sites). The C–N bond lengths of the nominal $-NH^+=C-NH_2$ fragment of the cation are indistinguishable, indicating a significant contribution of the $-NH-C=N^+H_2$ resonance form to the structure. The packing for (I)–(V) features a robust local $R_2^2(8)$ loop motif in which the cation forms two near-linear $N-H \cdots O$ hydrogen bonds from the N^+-H group and *syn* H atom of the amine group to the carboxylate group of an adjacent anion [(V) shows disorder of one of these bonds over $N-H \cdots O$ and $N \cdots H-O$ contributors but the same $R_2^2(8)$ loop results for both disorder components]. The *anti* H atom of the $-NH_2$ group also forms an $N-H \cdots O$ hydrogen bond, which results in [001] chains in (I) and (II), isolated centrosymmetric tetramers in (III) and [100] chains in (IV) and (V). Hirshfeld fingerprint plots and contact percentages for the different types of contacts of the cations are discussed.



1. Chemical context

Some 2-aminobenzothiazole derivatives display important biological properties: riluzole [2-amino-6-(trifluoromethoxy)-benzothiazole] is used in the palliative treatment of amyotrophic lateral sclerosis (Sweeney *et al.*, 2018) and pramipexole dihydrochloride [(*S*)-*N*6-propyl-4,5,6,7-tetrahydrobenzo[*d*]-thiazole-2,6-diamine dihydrochloride] is used to combat Parkinson's disease (Roy *et al.*, 2018). We note that the six-

membered ring in the latter compound is reduced by the addition of four H atoms. In coordination chemistry, 2-aminobenzothiazole has been shown to ligate to various metal ions, for example copper(II) (Kuwar *et al.*, 2018), cadmium(II) (Ma *et al.*, 2012) and palladium(II) (Gao *et al.*, 2011). The utility of 2-aminobenzothiazole in organic synthesis has recently been reviewed (Dadmal *et al.*, 2018).



As part of our ongoing studies in this area (Sagar *et al.*, 2017), we now describe the syntheses and crystal structures of five molecular salts of 4,4,7,7-tetramethyl-3a,4,5,6,7,7a-hydrobenzothiazol-2-ylamine ($C_{11}H_{18}N_2S$) with different carboxylic acids, viz. 2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium 4-methylbenzoate, $C_{11}H_{19}N_2S^+ \cdot C_8H_7O_2^-$, (I); 2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium 4-bromobenzoate,

$C_{11}H_{19}N_2S^+ \cdot C_7H_4BrO_2^-$, (II); 2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium 3,5-dinitrobenzoate, $C_{11}H_{19}N_2S^+ \cdot C_7H_3N_2O_6^-$, (III); bis(2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium) fumarate, $(C_{11}H_{19}N_2S^+)_2 \cdot C_4H_2O_4^{2-}$, (IV); 1:1 co-crystal of bis(2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium) succinate and (2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium) hydrogen succinate

2. Structural commentary

The asymmetric units of (I), (II) and (III) are illustrated in Figs. 1, 2 and 3, respectively. Each one features a 2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium ($C_{11}H_{19}N_2S^+$) cation protonated at the thiazole-ring nitrogen atom N1 accompanied by a substituted benzoate anion. The C7–N1 and C7–N2 bond lengths in the cations in (I) [1.325 (3) and 1.322 (4) Å, respectively], (II) [1.327 (5) and 1.316 (5) Å, respectively] and (III) [1.3267 (19) and 1.322 (2) Å, respectively] are almost identical, presumably indicating a significant contribution of the amidinium cation [$-N1H-C7=N2^+H_2$] resonance form to the overall structure [compare ions *A* and *B* in the chemical scheme of Sagar *et al.* (2017)]. The C1–S1–C7 bond angles [(I) = 90.27 (13); (II) = 90.29 (18); (III) = 90.40 (7)°] are almost identical in the three

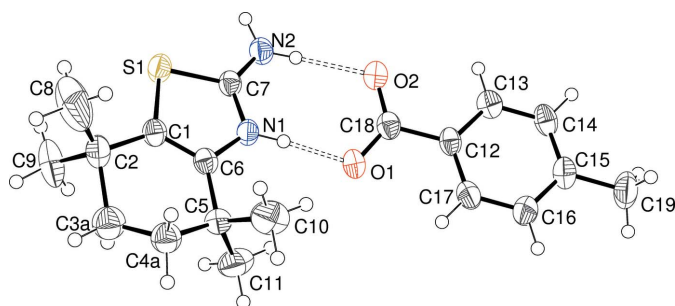


Figure 1
The molecular structure of (I) showing the major disorder component only of the cation (50% displacement ellipsoids) with the hydrogen bonds indicated by double-dashed lines.

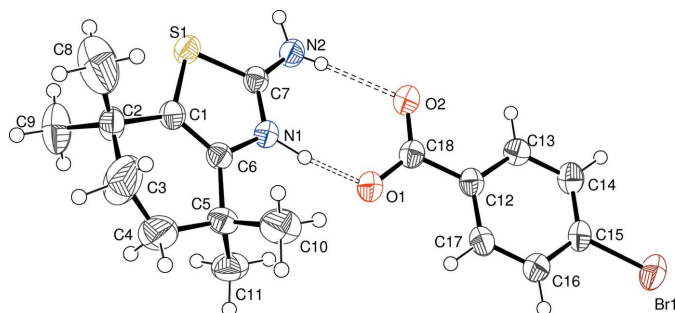


Figure 2
The molecular structure of (II) showing 50% displacement ellipsoids with the hydrogen bonds indicated by double-dashed lines.

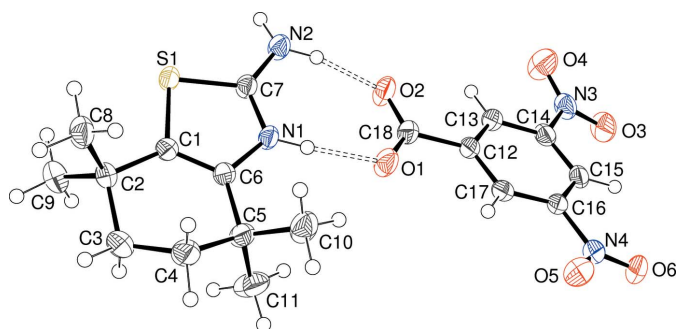


Figure 3
The molecular structure of (III) showing 50% displacement ellipsoids with the hydrogen bonds indicated by double-dashed lines.

salts. The conformation of the reduced (hydrogenated/methylated) six-membered ring of the benzothiazole moiety can be described as a half-chair in each case; in (I), the deviating methylene groups (C3 and C4) are disordered over two sets of sites in a 0.602 (10):0.398 (10) ratio. For (II), atoms C3 and C4 deviate from the plane defined by C1/C2/C5/C6 by -0.388 (13) and 0.130 (11) Å, respectively; comparable data for (III) are -0.276 (3) and 0.432 (3) Å, respectively. The dihedral angles between the C1/C2/C5/C6 moiety and the C1/C6/C7/N1/S1 thiazole ring for (I) [1.3 (2)°], (II) [1.2 (3)°] and (III) [2.84 (13)°] indicate a slight, but statistically significant, puckering in each case.

In the substituted benzoate anion in (I), the C18—O1 [1.252 (3) Å] and C18—O2 [1.267 (3) Å] distances indicate substantial electronic delocalization within the carboxylate group; the dihedral angle between the C12—C17 benzene ring and C18/O1/O2 is 7.0 (6)°. The equivalent data for (II) are C18—O1 = 1.260 (5), C18—O2 = 1.263 (5) Å and C12—C17 + C18/O1/O2 dihedral angle = 6.2 (8)°. The data for (III) are C18—O1 = 1.2475 (19), C18—O2 = 1.2506 (19) Å and dihedral angle = 4.9 (4)°. Additionally, the dihedral angles between the benzene ring and the N3 and N4 nitro groups in (III) are 16.0 (3) and 11.9 (3)°, respectively.

The asymmetric unit of (IV) (Fig. 4) features two $C_{11}H_{19}N_2S^+$ cations and one dianion, which of course ensures charge balance. The structural features of the cations in (IV) are very similar to those of the equivalent species in (I)–(III): the C7—N1 and C7—N2 bond lengths of the S1 cation are 1.325 (6) and 1.318 (6) Å, respectively and the C18—N3 and C18—N4 bond lengths of the S2 cation are 1.320 (6) and 1.319 (7) Å, respectively and the same conclusion regarding delocalization of the $[-N^+H=C7-N_2H_2]$ moiety as was noted for (I)–(III) can be drawn. The conformations of the six-membered rings are half-chairs in each case; in the N1 cation, the deviating methylene groups (C3 and C4) are disordered over two sets of sites in a 0.78 (2):0.22 (2) ratio but these species are ordered in the N3 cation [deviations of C14 and C15 from the C12/C13/C16/C17 plane = 0.408 (11) and -0.309 (11) Å, respectively]. The fused rings are slightly puckered [dihedral angles (as defined above) = 0.7 (5) and 6.0 (3)° for the N1 and N3 cations, respectively]. In the fumarate anion in (IV), the carboxylate bond lengths are

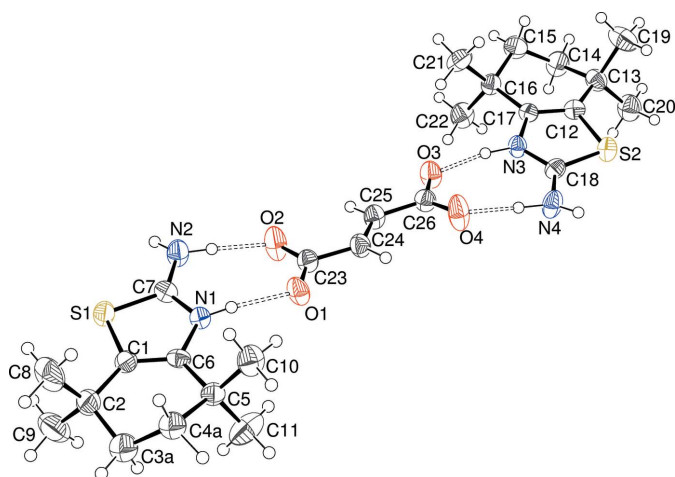


Figure 4
The molecular structure of (IV) showing the major disorder component only (50% displacement ellipsoids) with the hydrogen bonds indicated by double-dashed lines.

C23—O1 = 1.251 (6), C23—O2 = 1.258 (6), C26—O3 = 1.267 (6) and C26—O4 = 1.232 (6) Å.

The asymmetric unit of (V) (Fig. 5) is more complex due to disorder of one of the transferable protons and can be envisaged as a 1:1 co-crystal of $(C_{11}H_{19}N_2S^+)_2 \cdot (C_4H_4O_4^{2-})$ (*i.e.* proton transfer from both carboxylate groups of the anion) and $(C_{11}H_{19}N_2S^+) \cdot (C_4H_5O_4^-) (C_{11}H_{18}N_2S)$ (*i.e.*: proton transfer from one of carboxylate groups of the anion). This is further discussed below under supramolecular features. Despite this disorder, the situation for the N1 and N3 cations in (V) is very similar to that in (IV): C7—N1 = 1.325 (3); C7—N2 = 1.317 (4); C18—N3 = 1.322 (3); C18—N4 = 1.336 (4) Å. The C1—C6 ring is disordered over two half-chair conformations in a 0.596 (11):0.404 (11) ratio but the C12—C17 ring is ordered with C14 and C15 deviating from the other atoms by

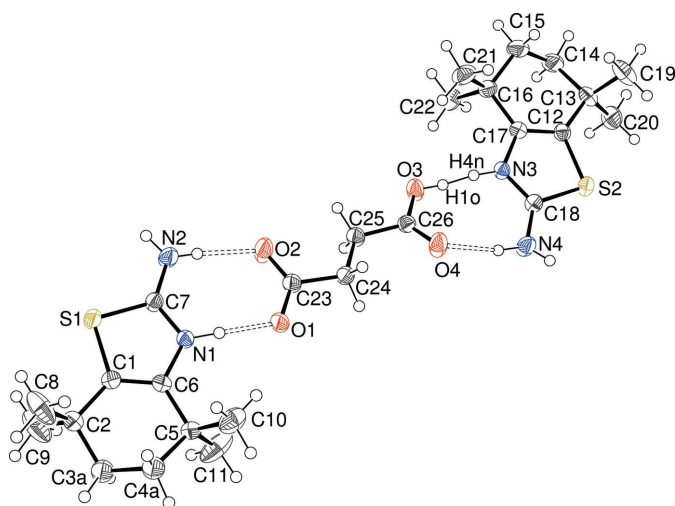


Figure 5
The molecular structure of (V) showing the major disorder component of the methylene groups only (50% displacement ellipsoids) and both disorder components for the N3—H...O3 and N3...H—O3 hydrogen bonds; the hydrogen bonds are indicated by double-dashed lines.

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>
N1—H1N...O1	0.88 (3)	1.76 (3)	2.632 (3)	175 (3)
N2—H2N...O2	0.83 (3)	1.98 (4)	2.801 (3)	170 (3)
N2—H3N...O2 ⁱ	0.89 (3)	1.93 (3)	2.805 (3)	164 (3)

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

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>
N1—H1N...O1	1.01 (5)	1.62 (5)	2.626 (4)	172 (4)
N2—H2N...O2	0.72 (5)	2.12 (5)	2.816 (5)	162 (6)
N2—H3N...O2 ⁱ	0.88 (5)	1.94 (5)	2.808 (5)	170 (4)

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

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

<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>
N1—H1N...O1	0.885 (19)	1.838 (19)	2.7187 (17)	173.4 (17)
N2—H3N...O2 ⁱ	0.90 (2)	2.01 (2)	2.8509 (19)	156.3 (17)
N2—H2N...O2	0.91 (2)	1.86 (2)	2.7551 (18)	168.3 (18)
C8—H8A...O6 ⁱⁱ	0.98	2.43	3.397 (2)	170

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

Table 4
Hydrogen-bond geometry (Å, °) for (IV).

<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>
N1—H1N...O1	0.85 (5)	1.84 (5)	2.670 (5)	167 (5)
N2—H2N...O2	0.94 (6)	1.77 (6)	2.704 (6)	177 (5)
N2—H3N...O4 ⁱ	0.91 (6)	1.90 (6)	2.746 (6)	153 (5)
N3—H4N...O3	0.96 (5)	1.67 (5)	2.617 (5)	169 (5)
N4—H5N...O4	1.00 (6)	1.75 (6)	2.754 (7)	178 (5)
N4—H6N...O2 ⁱⁱ	0.81 (6)	2.09 (6)	2.763 (6)	141 (6)

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

Table 5
Hydrogen-bond geometry (Å, °) for (V).

<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>
N1—H1N...O1	0.93 (3)	1.70 (3)	2.632 (3)	175 (3)
N2—H2N...O4 ⁱ	0.89 (4)	1.98 (4)	2.779 (3)	149 (3)
N2—H3N...O2	0.82 (4)	1.89 (4)	2.716 (4)	176 (4)
N3—H4N...O3	0.87 (8)	1.73 (8)	2.594 (3)	166 (6)
N4—H5N...O2 ⁱⁱ	0.82 (4)	2.07 (4)	2.804 (4)	148 (4)
N4—H6N...O4	0.92 (4)	1.93 (4)	2.842 (4)	169 (3)
O3—H1O...N3	0.82 (10)	1.78 (10)	2.594 (3)	174 (8)

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

0.424 (6) and -0.313 (6) Å, respectively. The inter-ring dihedral angles are 0.6 (3) (N1 cation) and 1.3 (3)° (N3 cation). Key bond-length data for the succinate anion in (V) are C23—O1 = 1.254 (4), C23—O2 = 1.249 (4), C26—O3 = 1.284 (4) and C26—O4 = 1.229 (4) Å. These data indicate that the C—O single and double bonds within the C26/O3/O4 moiety are more localized than in the other structures reported here, which correlates with the proton disorder model associated with O3.

The ‘anomalous’ situation of incomplete proton transfer for (V) might be correlated with pK_a values for the acids involved: 4-methylbenzoic acid ($pK_a = 4.25$), 4-bromobenzoic acid (3.99), 3,5-dinitrobenzoic acid (2.77), fumaric acid ($pK_{a1} = 3.03$, $pK_{a2} = 4.54$) and succinic acid (4.21, 5.64). These data apply to the acids dissolved in water (Jover *et al.*, 2008), but we might guess that a similar trend applies in the crystals and the pK_{a2} value for succinic acid is clearly larger than the others. Incomplete (or partial) proton transfer processes have been observed in other crystals (*e.g.* Biliškov *et al.*, 2011) and can lead to interesting physical properties (*e.g.* Noohinejad *et al.*, 2015).

3. Supramolecular features

The most notable supramolecular feature (which occur within the asymmetric units as defined here) of (I)–(V) is an $R_2^2(8)$ loop in which the protonated N1⁺—H1 moiety of the thiazole ring and the *syn* H atom of the —N2H₂ amine group both form near-linear N—H...O hydrogen bonds to the O atoms of the carboxylate group of an adjacent anion [Tables 1–5 for compounds (I)–(V), respectively]. In (V), the proton disorder associated with N3 and O3 leads to the same motif for both disorder components (two N—H...O bonds or one N—H...O and one N...H—O bond). Despite the presumed electronic delocalization of the cation noted above, it may be seen that for (I)–(III), the H...O distance for the charge-assisted hydrogen bond arising from N1 is notably shorter than the bond arising from N2. The situation for (IV) and (V) is less clear-cut: the H...O separations for the N1 and N2 (and equivalent N3 and N4) hydrogen bonds tend to be closer in magnitude and indeed the N2 bond in (IV) is marginally shorter than the N1 bond. The intermolecular dihedral angles between the thiazole and benzoate rings are 17.13 (14), 16.42 (19) and 20.15 (8)° for (I), (II) and (III), respectively, suggesting that the pairwise hydrogen bonds tend to align the aromatic rings of the cation and the anion in roughly the same plane.

In every case, the amine N2—H3N group *anti* to the N⁺H group of the thiazole ring also forms an N—H...O hydrogen bond, but the different anions lead to different overall structures. Salts (I) and (II) are isostructural (*i.e.* the same space

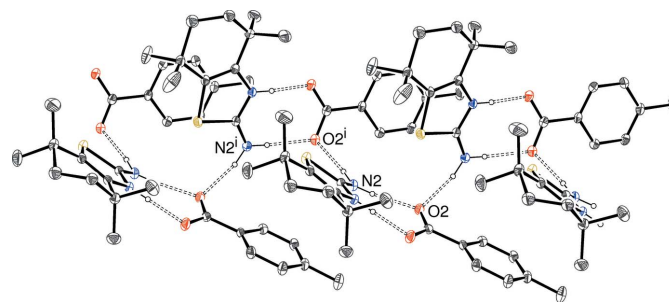


Figure 6
Fragment of an [001] hydrogen-bonded chain in the crystal of (I); the chain in (II) is almost identical to this. C-bound H atoms omitted for clarity. Symmetry code: (i) $x, 1 - y, \frac{1}{2} + z$.

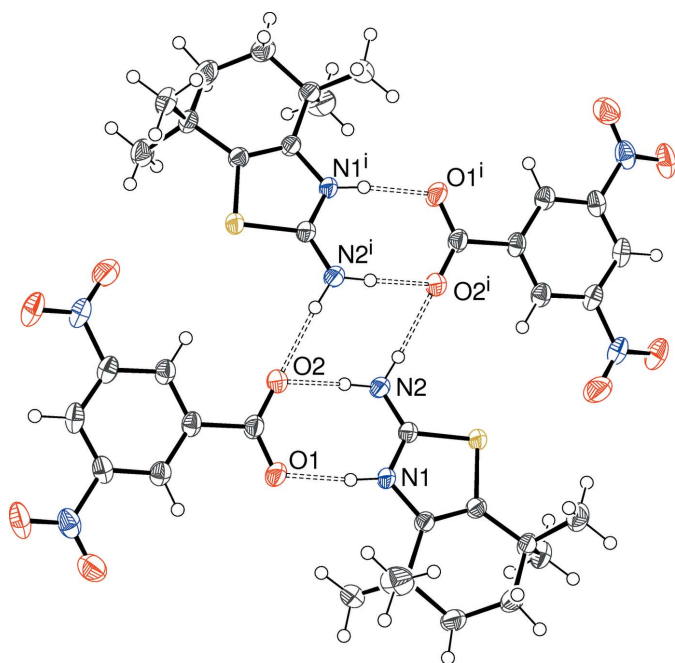


Figure 7
A centrosymmetric hydrogen-bonded tetramer in (III). Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

group and packing with slight differences in the unit-cell parameters to accommodate the different para-substituents of the benzoate anion), with the N2–H3N group linking the ion pairs into [001] chains (Fig. 6), with adjacent molecules related by *c*-glide symmetry. It may be noted that O2 accepts both hydrogen bonds from the amide H atoms and O1 accepts the charge-assisted bond from the thiazole ring.

The situation for (III) is quite different, with isolated centrosymmetric tetramers (two cations and two anions) arising (Fig. 7) in which pairs of $R_4^2(8)$ loops linking one cation to two anions are apparent as well as the cation-to-anion $R_2^2(8)$ loops already mentioned. A weak C–H···O interaction (Table 3) arising from a methyl group occurs between tetramers.

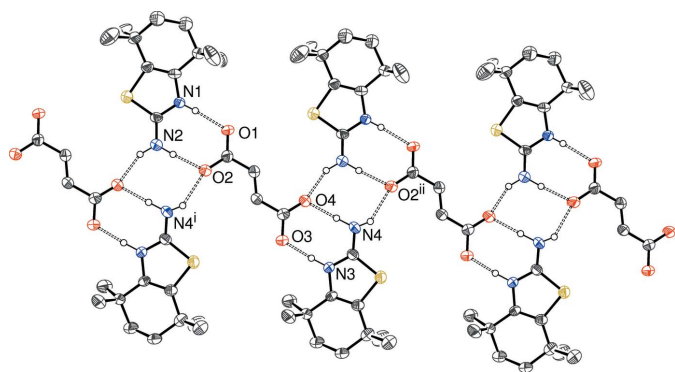


Figure 8
Fragment of a [100] hydrogen-bonded chain in the crystal of (IV); the chain in (V) is almost identical to this. C-bound H atoms omitted for clarity. Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$.

Crystals (IV) and (V) are isostructural and feature [100] chains in each case (Fig. 8). It may be seen that locally the cation has the same hydrogen-bonding pattern to the anion as in (I) and (II) but because the dianions accept hydrogen bonds at ‘both ends’, a different overall structure arises, which features the same $R_4^2(8)$ loop seen in (III), but is not generated by a crystallographic centre of symmetry.

4. Hirshfeld surface analyses

The Hirshfeld surfaces of the $C_{11}H_{19}N_2S^+$ cations in (I)–(V) were calculated using *CrystalExplorer* (Turner *et al.*, 2017) and fingerprint plots (McKinnon *et al.*, 2007) were also generated. An example fingerprint plot for (I) is shown in Fig. 9; plots for (II)–(V) are available in the supporting information. The prominent ‘spike’ feature terminating at ($d_i, d_e = \sim 0.62, 0.98$) corresponds to the N–H···O hydrogen bonds. Less prominent spikes at (1.30, 2.05) and (2.05, 1.30) correspond to H···S and S···H contacts, respectively: if these are indicative of attractive directional interactions, they must be very weak at best, as the shortest H···S/S···H contact is 3.31 Å, compared to the van der Waals separation of 3.0 Å for these atoms.

The percentage surface contact data (Table 6) for the $C_{11}H_{19}N_2S^+$ species in the five structures reveal a number of similarities but also some differences: H···H contacts dominate the packing in each case, although the percentage for (III) is significantly less than for the others. The H···O contacts associated with the hydrogen bonds are very consistent for (I), (II), (IV) and (V), but those for (II) are much higher and presumably reflect the presence of the ‘extra’ O atoms of the nitro substituents of the anion, although no significant directional interactions could be identified for these

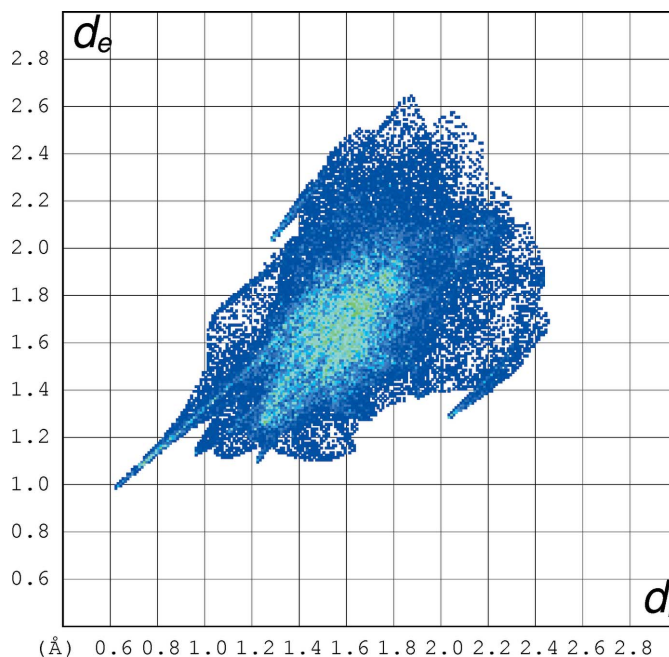


Figure 9
Hirshfeld fingerprint plot for (I).

Table 6
Hirshfeld contact interactions arising from the $C_{11}H_{19}N_2S^+$ cation (%) in (I)–(V).

Contact type	(I)	(II)	(III)	(IV) <i>a</i>	(IV) <i>b</i>	(V) <i>a</i>	(V) <i>b</i>
H···H	68.7	60.9	47.6	62.2	63.3	65.2	65.4
H···Br	–	6.2	–	–	–	–	–
H···O	10.9	12.0	29.1	13.5	13.0	13.4	12.0
H···C	5.9	6.7	6.6	6.0	5.5	3.7	4.2
H···S	2.1	1.8	1.6	3.5	3.0	3.3	2.6
C···all	2.8	2.9	2.9	3.1	3.1	3.1	3.0
N···all	2.7	2.7	2.7	3.0	2.9	2.8	3.2
S···all	6.5	6.3	6.4	6.2	6.4	6.2	6.5

a refers to the S1-containing cation and *b* to the S2-cation.

O atoms apart from one weak C–H···O bond. The C···all, N···all and S···all contact percentages are almost identical for the five structures.

5. Database survey

So far as we are aware, the only reported crystal structures to contain the 4,4,7,7-tetramethyl-3a,4,5,6,7,7a-hexahydrobenzothiazol-2-ylamine cation are those described recently by Sagar *et al.* (2017) (refcodes NEFTIE and NEFTOK), where it was crystallized with benzoate and picrate anions, respectively. The benzoate structure contains essentially the same hydrogen-bonded chains of cations and anions generated by *c*-glide symmetry as in (I) and (II) although it is not isostructural (space group *Cc* rather than *Pc*). The centrosymmetric, hydrogen-bonded tetramers in the picrate structure bear a resemblance to those in (III) but in the picrate anion, the acceptor oxygen atoms are the deprotonated phenol –OH group and adjacent nitro-group O atoms rather than carboxylate O atoms.

A search of the Cambridge Structural Database (Groom *et al.*, 2016, updated to August 2018) for 2-aminobenzothiazole with any substituents (including protonation) revealed 189 matches, but this number dropped to just five for a hydrogenated/methylated six-membered ring, viz. (–)-2,6-diamino-4,5,6,7-tetrahydrobenzothiazole (L)-(+)-tartrate trihydrate (refcode FECZES; Schneider & Mierau, 1987); *rac*-4,5,5a,6,7,8-hexahydro-6-*n*-propylthiazolo(4,5-*f*)quinolin-2-amine methanol solvate (SONZIE; Caprathe *et al.*, 1991); 2-amino-5,6-dihydro-1,3-benzothiazol-7(4*H*)-one (TESGUV; Zhu *et al.*, 2012), as well as NEFTIE and NEFTOK referred to in the previous paragraph.

6. Synthesis and crystallization

4,4,7,7-Tetramethyl-3a,4,5,6,7,7a-tetrahydrobenzothiazol-2-ylamine (200 mg, 0.94 mmol) and the equivalent amount of the respective acids, *i.e.* 4-methylbenzoic acid (135 mg, 0.94 mmol) for (I), 4-bromobenzoic acid (200 mg, 0.94 mmol) for (II), 3,5-dinitrobenzoic acid (208 mg, 0.94 mmol) for (III), fumaric acid (112 mg, 0.94 mmol) for (IV) and succinic acid (115 mg, 0.94 mmol) for (V), were dissolved in hot methanol and stirred over a heating magnetic stirrer for few minutes. The solution

was allowed to cool slowly at room temperature and the resulting solids were recovered by filtration and drying in air. These were recrystallized at room temperature using a 1:1 solvent mixture of DMF and DMSO: crystals of (I) (m.p. 441–443 K), (II) (m.p. 473 K), (III) (m.p. 453–456 K), (IV) (m.p. 446–450 K) and (V) (m.p. 393–396 K) appeared after a week.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 7. The methylene groups in (I), (IV) and (V) were modelled as being disordered over two sets of sites and the C atoms were refined with isotropic displacement parameters. The N-bound H atoms were located in difference-Fourier maps and their positions were freely refined without difficulty in every case except for the proton associated with atoms N3 and O3 in compound (V). Careful scrutiny of difference maps indicated two electron density maxima in the vicinity of these two atoms, one in a reasonable location for an N3–H···O3 hydrogen bond (*i.e.* proton transferred) and the other corresponding to an N3···H–O3 hydrogen bond (*i.e.* proton not transferred): for a detailed discussion of proton location in potentially disordered hydrogen bonds, see Fábry (2018). Despite their feeble scattering power, when included in the atomic model these refined well as disordered H atoms: their occupancy sum was constrained to unity and revealed equal occupancies [0.50 (5):0.50 (5)] for the two sites. H atoms for all structures were placed geometrically (C–H = 0.95–0.99 Å) and refined as riding atoms. The methyl groups were allowed to rotate, but not to tip, to best fit the electron density. In every case, the constraint $U_{iso}(H) = 1.2U_{eq}(\text{carrier})$ or $1.5U_{eq}(\text{methyl carrier})$ was applied. The absolute structures of (I), (II), (IV) and (V) were established by refinement of the Flack absolute structure parameter (Parsons *et al.*, 2013). It may be noted that despite being isostructural, the crystal of (IV) chosen for data collection was found to be an inversion twin, whereas the chosen crystal of (V) has a well-defined absolute structure (despite disorder).

Acknowledgements

MAES thanks the University of Mysore for provision of research facilities.

Funding information

HSY thanks UGC for the award of a UGC–BSR Faculty Fellowship for three years. BKS thanks the UGC for the award of a Rajeev Gandhi fellowship.

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Table 7
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_{11}H_{19}N_2S^+ \cdot C_8H_7O_2^-$	$C_{11}H_{19}N_2S^+ \cdot C_7H_4BrO_2^-$	$C_{11}H_{19}N_2S^+ \cdot C_7H_3N_2O_6^-$
M_r	346.48	411.35	422.45
Crystal system, space group	Monoclinic, Pc	Monoclinic, Pc	Monoclinic, $P2_1/n$
Temperature (K)	173	173	173
a, b, c (Å)	10.1879 (5), 11.6149 (5), 8.7790 (4)	10.2506 (5), 11.5855 (4), 8.8269 (4)	17.3232 (6), 5.84087 (17), 21.0876 (8)
β (°)	113.480 (6)	113.807 (6)	109.875 (4)
V (Å ³)	952.82 (9)	959.07 (8)	2006.60 (12)
Z	2	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.18	2.26	0.21
Crystal size (mm)	0.24 × 0.11 × 0.02	0.12 × 0.08 × 0.02	0.27 × 0.10 × 0.03
Data collection			
Diffractometer	Rigaku XtaLAB P200 HPC	Rigaku XtaLAB P200 HPC	Rigaku XtaLAB P200 HPC
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku, 2017)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku, 2017)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku, 2017)
T_{min} , T_{max}	0.793, 1.000	0.761, 1.000	0.566, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12189, 4056, 3440	12220, 3993, 3311	25034, 4698, 3712
R_{int}	0.029	0.026	0.056
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.683	0.683	0.686
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.089, 1.03	0.032, 0.083, 1.06	0.042, 0.116, 1.05
No. of reflections	4056	3993	4698
No. of parameters	230	230	275
No. of restraints	2	2	0
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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.20, -0.17	0.62, -0.38	0.49, -0.25
Absolute structure	Flack x determined using 1371 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013).	Flack x determined using 1344 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013).	-
Absolute structure parameter	0.03 (3)	0.005 (4)	-
	(IV)	(V)	
Crystal data			
Chemical formula	$2C_{11}H_{19}N_2S^+ \cdot C_4H_2O_4^{2-}$	$1.5C_{11}H_{19}N_2S^+ \cdot 0.5C_4H_4O_4^{2-} \cdot 0.5C_4H_5O_4^- \cdot 0.5C_{11}H_{18}N_2S$	
M_r	536.74	538.75	
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1$	
Temperature (K)	173	173	
a, b, c (Å)	9.0259 (6), 14.7314 (11), 11.1993 (8)	8.9437 (3), 14.7253 (4), 11.2676 (4)	
β (°)	101.943 (6)	100.493 (3)	
V (Å ³)	1456.87 (18)	1459.11 (8)	
Z	2	2	
Radiation type	Mo $K\alpha$	Mo $K\alpha$	
μ (mm ⁻¹)	0.22	0.22	
Crystal size (mm)	0.15 × 0.08 × 0.02	0.32 × 0.15 × 0.02	
Data collection			
Diffractometer	Rigaku XtaLAB P200 HPC	Rigaku XtaLAB P200 HPC	
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku, 2017)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku, 2017)	
T_{min} , T_{max}	0.333, 1.000	0.779, 1.000	
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19263, 6424, 3792	19079, 6272, 5511	
R_{int}	0.080	0.034	
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.684	0.685	
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.062, 0.128, 1.00	0.039, 0.094, 1.04	
No. of reflections	6424	6272	
No. of parameters	350	354	
No. of restraints	1	1	
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	

Table 7 (continued)

	(IV)	(V)
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ ($\text{e } \text{\AA}^{-3}$)	0.27, -0.26	0.26, -0.25
Absolute structure	Flack x determined using 1279 quotients [[I^+]-(I^-)]/[I^+]+(I^-)] (Parsons <i>et al.</i> , 2013).	Flack x determined using 2211 quotients [[I^+]-(I^-)]/[I^+]+(I^-)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.46 (7)	0.00 (3)

Computer programs: *CrystalClear-SM* (Rigaku, 2017), *CrysAlis PRO* (Rigaku, 2017), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

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supporting information

Acta Cryst. (2019). E75, 167-174 [https://doi.org/10.1107/S2056989018018224]

Hydrogen-bonded molecular salts of reduced benzothiazole derivatives with carboxylates: a robust $[R_2^2](8)$ supramolecular motif (even when disordered)

Mohammed A. E. Shaibah, Belakavadi K. Sagar, Hemmige S. Yathirajan, David B. Cordes, Alexandra M. Z. Slawin and William T. A. Harrison

Computing details

For all structures, data collection: *CrystalClear-SM* (Rigaku, 2017); cell refinement: *CrysAlis PRO* (Rigaku, 2017); data reduction: *CrysAlis PRO* (Rigaku, 2017); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

2-Amino-4,4,7,7-tetramethyl-3a,5,6,7a-tetrahydrobenzothiazol-3-ium 4-methylbenzoate (I)

Crystal data

$C_{11}H_{19}N_2S^+ \cdot C_8H_7O_2^-$
 $M_r = 346.48$
 Monoclinic, *Pc*
 $a = 10.1879$ (5) Å
 $b = 11.6149$ (5) Å
 $c = 8.7790$ (4) Å
 $\beta = 113.480$ (6)°
 $V = 952.82$ (9) Å³
 $Z = 2$

$F(000) = 372$
 $D_x = 1.208$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 5914 reflections
 $\theta = 2.2$ – 28.1 °
 $\mu = 0.18$ mm⁻¹
 $T = 173$ K
 Plate, colourless
 $0.24 \times 0.11 \times 0.02$ mm

Data collection

Rigaku XtaLAB P200 HPC
 diffractometer
 Radiation source: rotating anode, Rigaku FR-X
 Rigaku Osmic Confocal Optical System
 monochromator
 ω scans
 Absorption correction: multi-scan
 (CrysAlis PRO; Rigaku, 2017)
 $T_{\min} = 0.793$, $T_{\max} = 1.000$

12189 measured reflections
 4056 independent reflections
 3440 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 29.0$ °, $\theta_{\min} = 1.8$ °
 $h = -13 \rightarrow 12$
 $k = -15 \rightarrow 15$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.089$
 $S = 1.03$

4056 reflections
 230 parameters
 2 restraints
 Primary atom site location: structure-invariant
 direct methods

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.0807P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack x determined using
 1371 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013).
 Absolute structure parameter: 0.03 (3)

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.3617 (3)	0.6584 (2)	0.8458 (3)	0.0363 (6)	
C2	0.2322 (3)	0.6675 (3)	0.8865 (4)	0.0466 (7)	
C3A	0.1685 (10)	0.7939 (8)	0.8152 (12)	0.058 (3)*	0.398 (10)
H3A1	0.0740	0.8028	0.8210	0.069*	0.398 (10)
H3A2	0.2329	0.8534	0.8878	0.069*	0.398 (10)
C4A	0.1525 (10)	0.8143 (9)	0.6457 (13)	0.048 (2)*	0.398 (10)
H4A1	0.1003	0.8874	0.6050	0.058*	0.398 (10)
H4A2	0.0957	0.7512	0.5735	0.058*	0.398 (10)
C3B	0.1217 (6)	0.7333 (5)	0.7440 (7)	0.0467 (18)*	0.602 (10)
H3B1	0.0401	0.7535	0.7730	0.056*	0.602 (10)
H3B2	0.0852	0.6836	0.6441	0.056*	0.602 (10)
C4B	0.1860 (7)	0.8447 (6)	0.7047 (9)	0.0468 (15)*	0.602 (10)
H4B1	0.1081	0.8907	0.6225	0.056*	0.602 (10)
H4B2	0.2291	0.8911	0.8074	0.056*	0.602 (10)
C5	0.3013 (3)	0.8207 (2)	0.6356 (4)	0.0412 (7)	
C6	0.3917 (3)	0.7225 (2)	0.7371 (3)	0.0342 (6)	
C7	0.5894 (3)	0.6071 (2)	0.8256 (3)	0.0341 (6)	
C8	0.1541 (6)	0.5542 (4)	0.8622 (7)	0.111 (2)	
H8A	0.0673	0.5643	0.8833	0.167*	
H8B	0.2164	0.4971	0.9397	0.167*	
H8C	0.1280	0.5275	0.7480	0.167*	
C9	0.2747 (4)	0.7056 (4)	1.0652 (5)	0.0783 (12)	
H9A	0.1884	0.7226	1.0847	0.117*	
H9B	0.3342	0.7749	1.0862	0.117*	
H9C	0.3288	0.6440	1.1401	0.117*	
C10	0.2527 (4)	0.7945 (3)	0.4504 (4)	0.0648 (10)	
H10A	0.1905	0.8566	0.3853	0.097*	
H10B	0.2000	0.7216	0.4246	0.097*	
H10C	0.3366	0.7886	0.4227	0.097*	
C11	0.3888 (4)	0.9315 (3)	0.6748 (5)	0.0622 (9)	
H11A	0.4216	0.9487	0.7935	0.093*	
H11B	0.3293	0.9950	0.6100	0.093*	
H11C	0.4718	0.9220	0.6461	0.093*	

N1	0.5199 (2)	0.69242 (19)	0.7257 (3)	0.0352 (5)
H1N	0.559 (3)	0.719 (3)	0.660 (4)	0.042*
N2	0.7129 (3)	0.5644 (2)	0.8356 (3)	0.0406 (6)
H2N	0.738 (3)	0.583 (3)	0.759 (4)	0.049*
H3N	0.742 (3)	0.502 (3)	0.900 (4)	0.049*
S1	0.49793 (8)	0.55753 (6)	0.94144 (8)	0.04197 (19)
C12	0.7414 (3)	0.7561 (2)	0.3383 (3)	0.0353 (6)
C13	0.8440 (3)	0.6995 (3)	0.2992 (3)	0.0393 (6)
H13	0.8915	0.6339	0.3613	0.047*
C14	0.8774 (3)	0.7387 (3)	0.1694 (3)	0.0428 (7)
H14	0.9470	0.6986	0.1432	0.051*
C15	0.8121 (3)	0.8343 (3)	0.0779 (4)	0.0457 (7)
C16	0.7089 (4)	0.8898 (3)	0.1168 (4)	0.0533 (8)
H16	0.6618	0.9556	0.0547	0.064*
C17	0.6734 (3)	0.8509 (3)	0.2443 (4)	0.0474 (8)
H17	0.6015	0.8898	0.2678	0.057*
C18	0.7053 (3)	0.7165 (2)	0.4803 (3)	0.0382 (6)
C19	0.8510 (4)	0.8777 (4)	-0.0609 (4)	0.0688 (10)
H19A	0.8263	0.9595	-0.0806	0.103*
H19B	0.7981	0.8339	-0.1624	0.103*
H19C	0.9541	0.8680	-0.0298	0.103*
O1	0.6233 (2)	0.77900 (19)	0.5192 (3)	0.0518 (5)
O2	0.7604 (2)	0.62322 (16)	0.5523 (2)	0.0428 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0372 (15)	0.0423 (14)	0.0285 (13)	-0.0010 (12)	0.0124 (11)	-0.0022 (11)
C2	0.0447 (17)	0.0600 (18)	0.0416 (16)	0.0010 (14)	0.0240 (14)	0.0026 (13)
C5	0.0452 (17)	0.0385 (14)	0.0416 (15)	0.0057 (13)	0.0193 (13)	0.0040 (12)
C6	0.0349 (14)	0.0371 (14)	0.0302 (13)	-0.0036 (11)	0.0125 (11)	-0.0062 (11)
C7	0.0367 (15)	0.0371 (14)	0.0297 (12)	-0.0024 (12)	0.0145 (11)	-0.0032 (11)
C8	0.093 (3)	0.120 (4)	0.166 (5)	-0.062 (3)	0.099 (4)	-0.071 (4)
C9	0.071 (3)	0.121 (3)	0.061 (2)	-0.016 (2)	0.046 (2)	-0.024 (2)
C10	0.067 (2)	0.070 (2)	0.0382 (17)	0.0162 (19)	-0.0001 (16)	0.0003 (15)
C11	0.078 (3)	0.0420 (18)	0.060 (2)	-0.0011 (17)	0.0206 (19)	0.0045 (16)
N1	0.0393 (13)	0.0379 (12)	0.0330 (11)	-0.0016 (10)	0.0193 (10)	0.0002 (9)
N2	0.0422 (15)	0.0462 (14)	0.0355 (13)	0.0056 (12)	0.0176 (11)	0.0022 (11)
S1	0.0427 (4)	0.0504 (4)	0.0366 (3)	0.0040 (4)	0.0197 (3)	0.0082 (3)
C12	0.0346 (14)	0.0440 (15)	0.0286 (12)	-0.0072 (12)	0.0138 (11)	-0.0075 (11)
C13	0.0291 (14)	0.0486 (16)	0.0385 (15)	-0.0007 (12)	0.0116 (12)	-0.0027 (12)
C14	0.0293 (15)	0.0632 (19)	0.0391 (15)	-0.0007 (14)	0.0171 (13)	-0.0070 (14)
C15	0.0437 (17)	0.0619 (19)	0.0347 (14)	-0.0018 (15)	0.0190 (13)	-0.0020 (14)
C16	0.065 (2)	0.0589 (19)	0.0413 (17)	0.0144 (17)	0.0273 (16)	0.0111 (14)
C17	0.0539 (19)	0.0529 (18)	0.0432 (17)	0.0113 (15)	0.0276 (15)	0.0007 (14)
C18	0.0381 (15)	0.0422 (15)	0.0364 (14)	-0.0066 (13)	0.0173 (12)	-0.0057 (12)
C19	0.075 (2)	0.095 (3)	0.0514 (19)	0.017 (2)	0.0410 (18)	0.0169 (18)
O1	0.0653 (14)	0.0525 (12)	0.0554 (13)	0.0081 (10)	0.0429 (11)	0.0050 (10)

O2	0.0452 (11)	0.0479 (11)	0.0386 (10)	-0.0012 (9)	0.0203 (9)	0.0012 (9)
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Geometric parameters (Å, °)

C1—C6	1.338 (4)	C9—H9A	0.9800
C1—C2	1.502 (4)	C9—H9B	0.9800
C1—S1	1.753 (3)	C9—H9C	0.9800
C2—C8	1.509 (5)	C10—H10A	0.9800
C2—C3B	1.514 (6)	C10—H10B	0.9800
C2—C9	1.518 (5)	C10—H10C	0.9800
C2—C3A	1.626 (9)	C11—H11A	0.9800
C3A—C4A	1.451 (14)	C11—H11B	0.9800
C3A—H3A1	0.9900	C11—H11C	0.9800
C3A—H3A2	0.9900	N1—H1N	0.88 (3)
C4A—C5	1.555 (9)	N2—H2N	0.83 (3)
C4A—H4A1	0.9900	N2—H3N	0.89 (3)
C4A—H4A2	0.9900	C12—C17	1.385 (4)
C3B—C4B	1.551 (9)	C12—C13	1.389 (4)
C3B—H3B1	0.9900	C12—C18	1.506 (4)
C3B—H3B2	0.9900	C13—C14	1.389 (4)
C4B—C5	1.547 (6)	C13—H13	0.9500
C4B—H4B1	0.9900	C14—C15	1.377 (4)
C4B—H4B2	0.9900	C14—H14	0.9500
C5—C6	1.514 (4)	C15—C16	1.386 (4)
C5—C11	1.524 (4)	C15—C19	1.510 (4)
C5—C10	1.529 (4)	C16—C17	1.383 (4)
C6—N1	1.394 (4)	C16—H16	0.9500
C7—N2	1.322 (4)	C17—H17	0.9500
C7—N1	1.325 (3)	C18—O1	1.252 (3)
C7—S1	1.729 (3)	C18—O2	1.267 (3)
C8—H8A	0.9800	C19—H19A	0.9800
C8—H8B	0.9800	C19—H19B	0.9800
C8—H8C	0.9800	C19—H19C	0.9800
C6—C1—C2	127.0 (3)	H8A—C8—H8C	109.5
C6—C1—S1	110.6 (2)	H8B—C8—H8C	109.5
C2—C1—S1	122.4 (2)	C2—C9—H9A	109.5
C1—C2—C8	111.6 (3)	C2—C9—H9B	109.5
C1—C2—C3B	105.9 (3)	H9A—C9—H9B	109.5
C8—C2—C3B	98.4 (4)	C2—C9—H9C	109.5
C1—C2—C9	110.6 (3)	H9A—C9—H9C	109.5
C8—C2—C9	108.5 (3)	H9B—C9—H9C	109.5
C3B—C2—C9	121.2 (4)	C5—C10—H10A	109.5
C1—C2—C3A	103.1 (4)	C5—C10—H10B	109.5
C8—C2—C3A	128.8 (5)	H10A—C10—H10B	109.5
C9—C2—C3A	92.3 (4)	C5—C10—H10C	109.5
C4A—C3A—C2	114.0 (8)	H10A—C10—H10C	109.5
C4A—C3A—H3A1	108.8	H10B—C10—H10C	109.5

C2—C3A—H3A1	108.8	C5—C11—H11A	109.5
C4A—C3A—H3A2	108.8	C5—C11—H11B	109.5
C2—C3A—H3A2	108.8	H11A—C11—H11B	109.5
H3A1—C3A—H3A2	107.7	C5—C11—H11C	109.5
C3A—C4A—C5	110.6 (8)	H11A—C11—H11C	109.5
C3A—C4A—H4A1	109.5	H11B—C11—H11C	109.5
C5—C4A—H4A1	109.5	C7—N1—C6	114.1 (2)
C3A—C4A—H4A2	109.5	C7—N1—H1N	116 (2)
C5—C4A—H4A2	109.5	C6—N1—H1N	130.1 (19)
H4A1—C4A—H4A2	108.1	C7—N2—H2N	116 (2)
C2—C3B—C4B	111.3 (5)	C7—N2—H3N	115 (2)
C2—C3B—H3B1	109.4	H2N—N2—H3N	126 (3)
C4B—C3B—H3B1	109.4	C7—S1—C1	90.27 (13)
C2—C3B—H3B2	109.4	C17—C12—C13	118.4 (3)
C4B—C3B—H3B2	109.4	C17—C12—C18	120.5 (3)
H3B1—C3B—H3B2	108.0	C13—C12—C18	121.1 (3)
C5—C4B—C3B	113.0 (5)	C14—C13—C12	120.2 (3)
C5—C4B—H4B1	109.0	C14—C13—H13	119.9
C3B—C4B—H4B1	109.0	C12—C13—H13	119.9
C5—C4B—H4B2	109.0	C15—C14—C13	121.6 (3)
C3B—C4B—H4B2	109.0	C15—C14—H14	119.2
H4B1—C4B—H4B2	107.8	C13—C14—H14	119.2
C6—C5—C11	109.8 (2)	C14—C15—C16	117.9 (3)
C6—C5—C10	109.8 (2)	C14—C15—C19	121.2 (3)
C11—C5—C10	108.7 (3)	C16—C15—C19	120.8 (3)
C6—C5—C4B	106.5 (3)	C17—C16—C15	121.1 (3)
C11—C5—C4B	103.1 (4)	C17—C16—H16	119.4
C10—C5—C4B	118.6 (4)	C15—C16—H16	119.4
C6—C5—C4A	107.9 (4)	C16—C17—C12	120.8 (3)
C11—C5—C4A	121.6 (5)	C16—C17—H17	119.6
C10—C5—C4A	98.1 (5)	C12—C17—H17	119.6
C1—C6—N1	113.5 (2)	O1—C18—O2	124.9 (2)
C1—C6—C5	125.6 (3)	O1—C18—C12	117.2 (3)
N1—C6—C5	121.0 (2)	O2—C18—C12	117.9 (2)
N2—C7—N1	124.6 (2)	C15—C19—H19A	109.5
N2—C7—S1	123.9 (2)	C15—C19—H19B	109.5
N1—C7—S1	111.6 (2)	H19A—C19—H19B	109.5
C2—C8—H8A	109.5	C15—C19—H19C	109.5
C2—C8—H8B	109.5	H19A—C19—H19C	109.5
H8A—C8—H8B	109.5	H19B—C19—H19C	109.5
C2—C8—H8C	109.5		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N \cdots O1	0.88 (3)	1.76 (3)	2.632 (3)	175 (3)

N2—H2N···O2	0.83 (3)	1.98 (4)	2.801 (3)	170 (3)
N2—H3N···O2 ⁱ	0.89 (3)	1.93 (3)	2.805 (3)	164 (3)

Symmetry code: (i) $x, -y+1, z+1/2$.

2-Amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium 4-bromobenzoate (II)

Crystal data

$C_{11}H_{19}N_2S^+ \cdot C_7H_4BrO_2^-$

$M_r = 411.35$

Monoclinic, Pc

$a = 10.2506$ (5) Å

$b = 11.5855$ (4) Å

$c = 8.8269$ (4) Å

$\beta = 113.807$ (6)°

$V = 959.07$ (8) Å³

$Z = 2$

$F(000) = 424$

$D_x = 1.424$ Mg m⁻³

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

Cell parameters from 6835 reflections

$\theta = 2.2$ – 28.2 °

$\mu = 2.26$ mm⁻¹

$T = 173$ K

Plate, colourless

$0.12 \times 0.08 \times 0.02$ mm

Data collection

Rigaku XtaLAB P200 HPC

diffractometer

Radiation source: rotating anode, Rigaku FR-X

Rigaku Osmic Confocal Optical System

monochromator

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku, 2017)

$T_{\min} = 0.761$, $T_{\max} = 1.000$

12220 measured reflections

3993 independent reflections

3311 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 29.1$ °, $\theta_{\min} = 2.2$ °

$h = -13 \rightarrow 13$

$k = -15 \rightarrow 15$

$l = -10 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.083$

$S = 1.06$

3993 reflections

230 parameters

2 restraints

Primary atom site location: structure-invariant

direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.0111P]$

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

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

$\Delta\rho_{\max} = 0.62$ e Å⁻³

$\Delta\rho_{\min} = -0.38$ e Å⁻³

Absolute structure: Flack x determined using

1344 quotients $[(F^+)-(F^-)]/[(F^+)+(F^-)]$ (Parsons *et al.*, 2013).

Absolute structure parameter: 0.005 (4)

Special details

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

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6357 (4)	0.6587 (3)	0.1418 (5)	0.0359 (8)
C2	0.7655 (5)	0.6679 (4)	0.1027 (5)	0.0446 (9)
C3	0.8711 (8)	0.7399 (8)	0.2385 (10)	0.113 (3)

H3A	0.9213	0.6883	0.3338	0.136*
H3B	0.9431	0.7681	0.1991	0.136*
C4	0.8218 (6)	0.8359 (5)	0.2982 (9)	0.0780 (17)
H4A	0.7931	0.8956	0.2105	0.094*
H4B	0.9040	0.8673	0.3937	0.094*
C5	0.6976 (4)	0.8213 (3)	0.3532 (5)	0.0403 (9)
C6	0.6067 (4)	0.7238 (3)	0.2502 (5)	0.0339 (8)
C7	0.4084 (4)	0.6086 (3)	0.1598 (5)	0.0345 (8)
C8	0.8389 (8)	0.5492 (7)	0.1190 (12)	0.110 (3)
H8A	0.9299	0.5590	0.1087	0.164*
H8B	0.7771	0.4976	0.0314	0.164*
H8C	0.8561	0.5156	0.2274	0.164*
C9	0.7278 (7)	0.7092 (6)	-0.0719 (7)	0.0772 (17)
H9A	0.8147	0.7152	-0.0923	0.116*
H9B	0.6820	0.7850	-0.0868	0.116*
H9C	0.6622	0.6541	-0.1501	0.116*
C10	0.7484 (6)	0.7930 (5)	0.5371 (6)	0.0664 (14)
H10A	0.8122	0.8542	0.6028	0.100*
H10B	0.7995	0.7193	0.5604	0.100*
H10C	0.6659	0.7875	0.5663	0.100*
C11	0.6095 (6)	0.9320 (4)	0.3150 (6)	0.0578 (12)
H11A	0.5714	0.9473	0.1957	0.087*
H11B	0.6699	0.9966	0.3751	0.087*
H11C	0.5304	0.9231	0.3496	0.087*
N1	0.4781 (3)	0.6939 (3)	0.2604 (4)	0.0348 (7)
H1N	0.441 (5)	0.732 (4)	0.339 (5)	0.042*
N2	0.2855 (4)	0.5667 (3)	0.1482 (5)	0.0408 (8)
H2N	0.257 (6)	0.582 (4)	0.208 (6)	0.049*
H3N	0.264 (5)	0.505 (4)	0.086 (6)	0.049*
S1	0.49893 (11)	0.55873 (9)	0.04481 (11)	0.0398 (2)
C12	0.2601 (4)	0.7536 (3)	0.6483 (4)	0.0352 (8)
C13	0.1566 (4)	0.6980 (3)	0.6846 (5)	0.0369 (8)
H13	0.1094	0.6326	0.6213	0.044*
C14	0.1208 (4)	0.7360 (4)	0.8116 (5)	0.0422 (9)
H14	0.0501	0.6970	0.8361	0.051*
C15	0.1893 (4)	0.8310 (4)	0.9017 (5)	0.0402 (9)
C16	0.2946 (5)	0.8860 (3)	0.8709 (6)	0.0490 (11)
H16	0.3434	0.9499	0.9369	0.059*
C17	0.3291 (5)	0.8481 (4)	0.7443 (5)	0.0466 (10)
H17	0.4009	0.8871	0.7220	0.056*
C18	0.2979 (4)	0.7141 (3)	0.5095 (5)	0.0370 (8)
O1	0.3836 (4)	0.7755 (3)	0.4748 (4)	0.0505 (7)
O2	0.2410 (3)	0.6225 (2)	0.4343 (4)	0.0419 (6)
Br1	0.13945 (5)	0.88476 (4)	1.07398 (5)	0.0676 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.037 (2)	0.0392 (18)	0.0320 (18)	0.0012 (17)	0.0138 (17)	0.0030 (16)
C2	0.043 (2)	0.057 (2)	0.040 (2)	−0.004 (2)	0.0238 (19)	−0.0023 (19)
C3	0.087 (5)	0.160 (7)	0.120 (6)	−0.057 (5)	0.071 (5)	−0.073 (6)
C4	0.061 (3)	0.080 (3)	0.109 (5)	−0.032 (3)	0.050 (3)	−0.039 (3)
C5	0.037 (2)	0.0370 (19)	0.043 (2)	−0.0060 (17)	0.0129 (17)	−0.0009 (17)
C6	0.036 (2)	0.0329 (18)	0.0323 (18)	0.0019 (16)	0.0131 (16)	0.0038 (15)
C7	0.037 (2)	0.0365 (19)	0.0293 (18)	0.0022 (17)	0.0123 (16)	0.0043 (16)
C8	0.091 (5)	0.109 (5)	0.167 (8)	0.055 (5)	0.092 (6)	0.064 (5)
C9	0.074 (4)	0.113 (4)	0.058 (3)	0.020 (3)	0.040 (3)	0.028 (3)
C10	0.071 (3)	0.066 (3)	0.039 (2)	−0.016 (3)	−0.002 (2)	−0.001 (2)
C11	0.072 (3)	0.037 (2)	0.059 (3)	0.003 (2)	0.022 (3)	−0.001 (2)
N1	0.0359 (18)	0.0375 (16)	0.0333 (17)	0.0013 (14)	0.0163 (14)	−0.0001 (14)
N2	0.042 (2)	0.0461 (19)	0.037 (2)	−0.0047 (17)	0.0190 (16)	−0.0057 (16)
S1	0.0407 (5)	0.0451 (5)	0.0352 (5)	−0.0029 (5)	0.0168 (4)	−0.0061 (4)
C12	0.034 (2)	0.0390 (19)	0.0305 (19)	0.0064 (16)	0.0109 (16)	0.0081 (16)
C13	0.030 (2)	0.0416 (19)	0.036 (2)	−0.0015 (16)	0.0102 (16)	−0.0011 (16)
C14	0.030 (2)	0.056 (2)	0.041 (2)	0.0004 (19)	0.0153 (18)	0.0030 (19)
C15	0.042 (2)	0.050 (2)	0.0308 (19)	0.0041 (19)	0.0170 (18)	0.0051 (18)
C16	0.060 (3)	0.050 (2)	0.039 (2)	−0.012 (2)	0.023 (2)	−0.0053 (19)
C17	0.055 (3)	0.049 (2)	0.042 (2)	−0.010 (2)	0.026 (2)	0.0014 (19)
C18	0.036 (2)	0.040 (2)	0.035 (2)	0.0061 (18)	0.0153 (17)	0.0025 (18)
O1	0.060 (2)	0.0519 (16)	0.0526 (18)	−0.0091 (15)	0.0365 (16)	−0.0072 (14)
O2	0.0422 (16)	0.0477 (16)	0.0367 (15)	0.0025 (13)	0.0168 (12)	−0.0012 (12)
Br1	0.0863 (4)	0.0796 (3)	0.0542 (3)	−0.0123 (3)	0.0462 (3)	−0.0134 (3)

Geometric parameters (Å, °)

C1—C6	1.342 (5)	C9—H9C	0.9800
C1—C2	1.508 (6)	C10—H10A	0.9800
C1—S1	1.752 (4)	C10—H10B	0.9800
C2—C3	1.503 (8)	C10—H10C	0.9800
C2—C9	1.507 (7)	C11—H11A	0.9800
C2—C8	1.546 (8)	C11—H11B	0.9800
C3—C4	1.408 (10)	C11—H11C	0.9800
C3—H3A	0.9900	N1—H1N	1.01 (5)
C3—H3B	0.9900	N2—H2N	0.72 (5)
C4—C5	1.544 (7)	N2—H3N	0.88 (5)
C4—H4A	0.9900	C12—C13	1.385 (5)
C4—H4B	0.9900	C12—C17	1.391 (6)
C5—C6	1.513 (6)	C12—C18	1.498 (5)
C5—C11	1.526 (6)	C13—C14	1.385 (5)
C5—C10	1.528 (6)	C13—H13	0.9500
C6—N1	1.400 (5)	C14—C15	1.374 (6)
C7—N2	1.316 (5)	C14—H14	0.9500
C7—N1	1.327 (5)	C15—C16	1.371 (6)

C7—S1	1.728 (4)	C15—Br1	1.895 (4)
C8—H8A	0.9800	C16—C17	1.373 (7)
C8—H8B	0.9800	C16—H16	0.9500
C8—H8C	0.9800	C17—H17	0.9500
C9—H9A	0.9800	C18—O1	1.260 (5)
C9—H9B	0.9800	C18—O2	1.263 (5)
C6—C1—C2	126.4 (4)	H9A—C9—H9C	109.5
C6—C1—S1	110.8 (3)	H9B—C9—H9C	109.5
C2—C1—S1	122.7 (3)	C5—C10—H10A	109.5
C3—C2—C9	116.4 (5)	C5—C10—H10B	109.5
C3—C2—C1	105.9 (4)	H10A—C10—H10B	109.5
C9—C2—C1	111.8 (4)	C5—C10—H10C	109.5
C3—C2—C8	104.7 (6)	H10A—C10—H10C	109.5
C9—C2—C8	107.0 (5)	H10B—C10—H10C	109.5
C1—C2—C8	110.9 (4)	C5—C11—H11A	109.5
C4—C3—C2	119.0 (6)	C5—C11—H11B	109.5
C4—C3—H3A	107.6	H11A—C11—H11B	109.5
C2—C3—H3A	107.6	C5—C11—H11C	109.5
C4—C3—H3B	107.6	H11A—C11—H11C	109.5
C2—C3—H3B	107.6	H11B—C11—H11C	109.5
H3A—C3—H3B	107.0	C7—N1—C6	114.0 (3)
C3—C4—C5	119.8 (5)	C7—N1—H1N	122 (2)
C3—C4—H4A	107.4	C6—N1—H1N	124 (2)
C5—C4—H4A	107.4	C7—N2—H2N	121 (4)
C3—C4—H4B	107.4	C7—N2—H3N	110 (3)
C5—C4—H4B	107.4	H2N—N2—H3N	126 (5)
H4A—C4—H4B	106.9	C7—S1—C1	90.29 (18)
C6—C5—C11	109.2 (3)	C13—C12—C17	118.3 (4)
C6—C5—C10	110.0 (3)	C13—C12—C18	121.5 (3)
C11—C5—C10	109.4 (4)	C17—C12—C18	120.2 (4)
C6—C5—C4	106.2 (4)	C14—C13—C12	121.2 (4)
C11—C5—C4	109.2 (4)	C14—C13—H13	119.4
C10—C5—C4	112.8 (5)	C12—C13—H13	119.4
C1—C6—N1	113.1 (3)	C15—C14—C13	118.9 (4)
C1—C6—C5	126.0 (3)	C15—C14—H14	120.6
N1—C6—C5	120.9 (3)	C13—C14—H14	120.6
N2—C7—N1	124.5 (4)	C16—C15—C14	121.2 (4)
N2—C7—S1	123.7 (3)	C16—C15—Br1	119.7 (3)
N1—C7—S1	111.7 (3)	C14—C15—Br1	119.2 (3)
C2—C8—H8A	109.5	C15—C16—C17	119.6 (4)
C2—C8—H8B	109.5	C15—C16—H16	120.2
H8A—C8—H8B	109.5	C17—C16—H16	120.2
C2—C8—H8C	109.5	C16—C17—C12	120.9 (4)
H8A—C8—H8C	109.5	C16—C17—H17	119.5
H8B—C8—H8C	109.5	C12—C17—H17	119.5
C2—C9—H9A	109.5	O1—C18—O2	124.5 (4)
C2—C9—H9B	109.5	O1—C18—C12	117.5 (4)

H9A—C9—H9B	109.5	O2—C18—C12	118.0 (3)
C2—C9—H9C	109.5		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1N \cdots O1	1.01 (5)	1.62 (5)	2.626 (4)	172 (4)
N2—H2N \cdots O2	0.72 (5)	2.12 (5)	2.816 (5)	162 (6)
N2—H3N \cdots O2 ⁱ	0.88 (5)	1.94 (5)	2.808 (5)	170 (4)

Symmetry code: (i) *x*, $-y+1$, $z-1/2$.**2-Amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium 3,5-dinitrobenzoate (III)***Crystal data*C₁₁H₁₉N₂S⁺·C₇H₃N₂O₆⁻*M_r* = 422.45Monoclinic, *P*2₁/*n**a* = 17.3232 (6) Å*b* = 5.84087 (17) Å*c* = 21.0876 (8) Å β = 109.875 (4)°*V* = 2006.60 (12) Å³*Z* = 4*F*(000) = 888*D_x* = 1.398 Mg m⁻³Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 10667 reflections

 θ = 2.0–27.8° μ = 0.21 mm⁻¹*T* = 173 K

Plate, colourless

0.27 × 0.10 × 0.03 mm

*Data collection*Rigaku XtaLAB P200 HPC
diffractometer

Radiation source: rotating anode, Rigaku FR-X

Rigaku Osmic Confocal Optical System
monochromator ω scansAbsorption correction: multi-scan
(CrysAlis PRO; Rigaku, 2017)*T_{min}* = 0.566, *T_{max}* = 1.000

25034 measured reflections

4698 independent reflections

3712 reflections with *I* > 2 σ (*I*)*R_{int}* = 0.056 θ_{\max} = 29.2°, θ_{\min} = 1.9°*h* = $-21 \rightarrow 23$ *k* = $-7 \rightarrow 7$ *l* = $-26 \rightarrow 26$ *Refinement*Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.042*wR*(*F*²) = 0.116*S* = 1.05

4698 reflections

275 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.5151P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.49 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.25 \text{ e } \text{Å}^{-3}$ *Special details*

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.26545 (9)	0.4584 (3)	0.49126 (7)	0.0264 (3)
C2	0.19150 (9)	0.3629 (3)	0.50428 (8)	0.0298 (3)
C3	0.13800 (10)	0.2456 (3)	0.43879 (9)	0.0419 (4)
H3A	0.0996	0.1392	0.4494	0.050*
H3B	0.1048	0.3636	0.4077	0.050*
C4	0.18675 (11)	0.1131 (3)	0.40303 (9)	0.0397 (4)
H4A	0.1479	0.0344	0.3634	0.048*
H4B	0.2196	-0.0059	0.4340	0.048*
C5	0.24503 (10)	0.2636 (3)	0.37920 (8)	0.0319 (4)
C6	0.28907 (9)	0.4173 (3)	0.43809 (7)	0.0260 (3)
C7	0.39559 (9)	0.6469 (3)	0.49858 (7)	0.0266 (3)
C8	0.21999 (11)	0.1932 (3)	0.56307 (9)	0.0388 (4)
H8A	0.1720	0.1286	0.5713	0.058*
H8B	0.2547	0.2727	0.6037	0.058*
H8C	0.2514	0.0697	0.5518	0.058*
C9	0.14165 (11)	0.5539 (3)	0.52232 (10)	0.0427 (4)
H9A	0.0925	0.4881	0.5283	0.064*
H9B	0.1253	0.6672	0.4859	0.064*
H9C	0.1753	0.6282	0.5643	0.064*
C10	0.30657 (12)	0.1076 (3)	0.36271 (10)	0.0442 (4)
H10A	0.2769	-0.0070	0.3294	0.066*
H10B	0.3410	0.0304	0.4039	0.066*
H10C	0.3413	0.1996	0.3443	0.066*
C11	0.19849 (13)	0.4072 (4)	0.31745 (9)	0.0516 (5)
H11A	0.1707	0.3058	0.2795	0.077*
H11B	0.2372	0.5057	0.3054	0.077*
H11C	0.1577	0.5024	0.3278	0.077*
N1	0.36224 (8)	0.5279 (2)	0.44229 (6)	0.0271 (3)
H1N	0.3856 (11)	0.524 (3)	0.4110 (9)	0.033*
N2	0.46553 (9)	0.7605 (3)	0.51363 (7)	0.0337 (3)
H2N	0.4887 (12)	0.780 (3)	0.4812 (10)	0.040*
H3N	0.4791 (12)	0.857 (3)	0.5486 (10)	0.040*
S1	0.33701 (2)	0.63371 (7)	0.55004 (2)	0.02882 (12)
C12	0.53091 (9)	0.7205 (3)	0.30278 (7)	0.0283 (3)
C13	0.58549 (9)	0.8968 (3)	0.30559 (8)	0.0304 (3)
H13	0.5992	1.0042	0.3416	0.037*
C14	0.61975 (9)	0.9144 (3)	0.25552 (8)	0.0313 (4)
C15	0.60233 (9)	0.7633 (3)	0.20218 (8)	0.0327 (4)
H15	0.6256	0.7796	0.1676	0.039*
C16	0.54918 (9)	0.5872 (3)	0.20198 (8)	0.0306 (3)
C17	0.51322 (9)	0.5616 (3)	0.25084 (7)	0.0294 (3)
H17	0.4770	0.4375	0.2489	0.035*
C18	0.49110 (10)	0.7013 (3)	0.35667 (8)	0.0312 (3)
N3	0.67709 (8)	1.1050 (3)	0.25924 (7)	0.0380 (3)
N4	0.52907 (8)	0.4200 (3)	0.14618 (7)	0.0386 (4)

O1	0.43858 (8)	0.5479 (2)	0.34910 (6)	0.0427 (3)
O2	0.51480 (8)	0.8407 (2)	0.40440 (6)	0.0410 (3)
O3	0.69300 (8)	1.1515 (2)	0.20855 (7)	0.0500 (4)
O4	0.70535 (9)	1.2066 (3)	0.31259 (7)	0.0596 (4)
O5	0.49224 (9)	0.2464 (3)	0.15173 (7)	0.0508 (3)
O6	0.54967 (8)	0.4645 (3)	0.09754 (6)	0.0522 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0251 (7)	0.0287 (8)	0.0255 (8)	-0.0025 (6)	0.0086 (6)	-0.0005 (6)
C2	0.0252 (8)	0.0364 (8)	0.0307 (8)	-0.0032 (6)	0.0130 (6)	0.0006 (7)
C3	0.0301 (9)	0.0543 (11)	0.0417 (10)	-0.0134 (8)	0.0129 (7)	-0.0047 (9)
C4	0.0385 (10)	0.0457 (10)	0.0350 (9)	-0.0158 (8)	0.0126 (7)	-0.0077 (8)
C5	0.0335 (8)	0.0374 (9)	0.0250 (8)	-0.0096 (7)	0.0103 (6)	-0.0039 (7)
C6	0.0252 (7)	0.0286 (8)	0.0248 (7)	-0.0034 (6)	0.0094 (6)	0.0005 (6)
C7	0.0290 (8)	0.0282 (8)	0.0250 (8)	-0.0031 (6)	0.0123 (6)	-0.0006 (6)
C8	0.0378 (9)	0.0441 (10)	0.0412 (10)	-0.0014 (8)	0.0222 (8)	0.0061 (8)
C9	0.0329 (9)	0.0470 (10)	0.0535 (11)	0.0034 (8)	0.0215 (8)	0.0005 (9)
C10	0.0509 (11)	0.0441 (10)	0.0437 (10)	-0.0122 (8)	0.0239 (9)	-0.0160 (8)
C11	0.0576 (12)	0.0607 (13)	0.0276 (9)	-0.0091 (10)	0.0029 (8)	0.0015 (9)
N1	0.0296 (7)	0.0320 (7)	0.0236 (6)	-0.0064 (5)	0.0140 (5)	-0.0029 (5)
N2	0.0352 (8)	0.0398 (8)	0.0304 (7)	-0.0140 (6)	0.0168 (6)	-0.0085 (6)
S1	0.0292 (2)	0.0350 (2)	0.0259 (2)	-0.00573 (16)	0.01407 (16)	-0.00554 (15)
C12	0.0239 (7)	0.0392 (9)	0.0224 (7)	0.0017 (6)	0.0088 (6)	0.0036 (6)
C13	0.0273 (8)	0.0396 (9)	0.0254 (8)	-0.0003 (7)	0.0103 (6)	0.0020 (7)
C14	0.0230 (8)	0.0425 (9)	0.0291 (8)	0.0021 (7)	0.0099 (6)	0.0083 (7)
C15	0.0236 (8)	0.0520 (10)	0.0243 (8)	0.0090 (7)	0.0106 (6)	0.0086 (7)
C16	0.0230 (7)	0.0451 (9)	0.0220 (7)	0.0085 (7)	0.0056 (6)	0.0002 (7)
C17	0.0221 (7)	0.0390 (8)	0.0257 (8)	0.0006 (6)	0.0063 (6)	0.0015 (7)
C18	0.0300 (8)	0.0392 (9)	0.0271 (8)	-0.0042 (7)	0.0133 (6)	-0.0005 (7)
N3	0.0305 (7)	0.0491 (9)	0.0396 (8)	-0.0014 (6)	0.0184 (6)	0.0090 (7)
N4	0.0273 (7)	0.0557 (10)	0.0313 (8)	0.0099 (7)	0.0081 (6)	-0.0056 (7)
O1	0.0462 (7)	0.0556 (8)	0.0347 (7)	-0.0218 (6)	0.0244 (6)	-0.0106 (6)
O2	0.0512 (8)	0.0453 (7)	0.0363 (7)	-0.0158 (6)	0.0275 (6)	-0.0114 (5)
O3	0.0466 (8)	0.0666 (9)	0.0461 (8)	-0.0058 (6)	0.0280 (6)	0.0147 (6)
O4	0.0662 (10)	0.0704 (10)	0.0507 (9)	-0.0328 (8)	0.0311 (7)	-0.0119 (7)
O5	0.0504 (8)	0.0563 (9)	0.0448 (8)	-0.0036 (7)	0.0149 (6)	-0.0156 (6)
O6	0.0452 (8)	0.0852 (10)	0.0316 (7)	0.0108 (7)	0.0199 (6)	-0.0082 (7)

Geometric parameters (Å, °)

C1—C6	1.340 (2)	C10—H10B	0.9800
C1—C2	1.506 (2)	C10—H10C	0.9800
C1—S1	1.7540 (15)	C11—H11A	0.9800
C2—C8	1.532 (2)	C11—H11B	0.9800
C2—C9	1.535 (2)	C11—H11C	0.9800
C2—C3	1.538 (2)	N1—H1N	0.885 (19)

C3—C4	1.521 (3)	N2—H2N	0.91 (2)
C3—H3A	0.9900	N2—H3N	0.90 (2)
C3—H3B	0.9900	C12—C13	1.385 (2)
C4—C5	1.546 (2)	C12—C17	1.388 (2)
C4—H4A	0.9900	C12—C18	1.521 (2)
C4—H4B	0.9900	C13—C14	1.380 (2)
C5—C6	1.512 (2)	C13—H13	0.9500
C5—C11	1.528 (2)	C14—C15	1.380 (2)
C5—C10	1.529 (2)	C14—N3	1.476 (2)
C6—N1	1.3981 (19)	C15—C16	1.380 (2)
C7—N2	1.322 (2)	C15—H15	0.9500
C7—N1	1.3267 (19)	C16—C17	1.381 (2)
C7—S1	1.7211 (15)	C16—N4	1.477 (2)
C8—H8A	0.9800	C17—H17	0.9500
C8—H8B	0.9800	C18—O1	1.2475 (19)
C8—H8C	0.9800	C18—O2	1.2506 (19)
C9—H9A	0.9800	N3—O4	1.2178 (19)
C9—H9B	0.9800	N3—O3	1.2218 (18)
C9—H9C	0.9800	N4—O6	1.2231 (19)
C10—H10A	0.9800	N4—O5	1.224 (2)
C6—C1—C2	127.39 (14)	C5—C10—H10B	109.5
C6—C1—S1	110.64 (11)	H10A—C10—H10B	109.5
C2—C1—S1	121.88 (11)	C5—C10—H10C	109.5
C1—C2—C8	109.11 (13)	H10A—C10—H10C	109.5
C1—C2—C9	111.17 (13)	H10B—C10—H10C	109.5
C8—C2—C9	108.85 (13)	C5—C11—H11A	109.5
C1—C2—C3	106.95 (12)	C5—C11—H11B	109.5
C8—C2—C3	111.61 (14)	H11A—C11—H11B	109.5
C9—C2—C3	109.15 (14)	C5—C11—H11C	109.5
C4—C3—C2	113.90 (14)	H11A—C11—H11C	109.5
C4—C3—H3A	108.8	H11B—C11—H11C	109.5
C2—C3—H3A	108.8	C7—N1—C6	114.09 (12)
C4—C3—H3B	108.8	C7—N1—H1N	120.8 (12)
C2—C3—H3B	108.8	C6—N1—H1N	125.1 (12)
H3A—C3—H3B	107.7	C7—N2—H2N	119.0 (12)
C3—C4—C5	113.96 (15)	C7—N2—H3N	118.5 (12)
C3—C4—H4A	108.8	H2N—N2—H3N	118.8 (17)
C5—C4—H4A	108.8	C7—S1—C1	90.40 (7)
C3—C4—H4B	108.8	C13—C12—C17	119.67 (14)
C5—C4—H4B	108.8	C13—C12—C18	119.95 (14)
H4A—C4—H4B	107.7	C17—C12—C18	120.38 (14)
C6—C5—C11	110.26 (14)	C14—C13—C12	119.18 (15)
C6—C5—C10	110.14 (13)	C14—C13—H13	120.4
C11—C5—C10	109.86 (15)	C12—C13—H13	120.4
C6—C5—C4	105.88 (12)	C13—C14—C15	122.97 (15)
C11—C5—C4	112.06 (15)	C13—C14—N3	118.18 (15)
C10—C5—C4	108.56 (14)	C15—C14—N3	118.85 (14)

C1—C6—N1	113.12 (13)	C16—C15—C14	116.12 (14)
C1—C6—C5	125.55 (13)	C16—C15—H15	121.9
N1—C6—C5	121.31 (12)	C14—C15—H15	121.9
N2—C7—N1	124.23 (14)	C15—C16—C17	123.23 (15)
N2—C7—S1	124.04 (12)	C15—C16—N4	118.16 (14)
N1—C7—S1	111.72 (11)	C17—C16—N4	118.60 (15)
C2—C8—H8A	109.5	C16—C17—C12	118.79 (15)
C2—C8—H8B	109.5	C16—C17—H17	120.6
H8A—C8—H8B	109.5	C12—C17—H17	120.6
C2—C8—H8C	109.5	O1—C18—O2	126.60 (14)
H8A—C8—H8C	109.5	O1—C18—C12	116.98 (14)
H8B—C8—H8C	109.5	O2—C18—C12	116.42 (13)
C2—C9—H9A	109.5	O4—N3—O3	124.09 (15)
C2—C9—H9B	109.5	O4—N3—C14	117.95 (13)
H9A—C9—H9B	109.5	O3—N3—C14	117.96 (15)
C2—C9—H9C	109.5	O6—N4—O5	124.50 (15)
H9A—C9—H9C	109.5	O6—N4—C16	118.07 (16)
H9B—C9—H9C	109.5	O5—N4—C16	117.43 (14)
C5—C10—H10A	109.5		
C6—C1—C2—C8	109.98 (18)	N1—C7—S1—C1	0.11 (12)
S1—C1—C2—C8	-66.27 (17)	C6—C1—S1—C7	0.86 (12)
C6—C1—C2—C9	-129.96 (17)	C2—C1—S1—C7	177.68 (13)
S1—C1—C2—C9	53.79 (18)	C17—C12—C13—C14	1.7 (2)
C6—C1—C2—C3	-10.9 (2)	C18—C12—C13—C14	-178.67 (14)
S1—C1—C2—C3	172.86 (12)	C12—C13—C14—C15	-0.1 (2)
C1—C2—C3—C4	40.0 (2)	C12—C13—C14—N3	179.39 (13)
C8—C2—C3—C4	-79.31 (18)	C13—C14—C15—C16	-1.3 (2)
C9—C2—C3—C4	160.33 (15)	N3—C14—C15—C16	179.18 (13)
C2—C3—C4—C5	-62.4 (2)	C14—C15—C16—C17	1.3 (2)
C3—C4—C5—C6	46.04 (19)	C14—C15—C16—N4	-179.58 (13)
C3—C4—C5—C11	-74.21 (19)	C15—C16—C17—C12	0.2 (2)
C3—C4—C5—C10	164.27 (15)	N4—C16—C17—C12	-178.97 (14)
C2—C1—C6—N1	-178.20 (14)	C13—C12—C17—C16	-1.7 (2)
S1—C1—C6—N1	-1.60 (17)	C18—C12—C17—C16	178.65 (14)
C2—C1—C6—C5	0.1 (3)	C13—C12—C18—O1	175.54 (15)
S1—C1—C6—C5	176.71 (13)	C17—C12—C18—O1	-4.8 (2)
C11—C5—C6—C1	104.46 (19)	C13—C12—C18—O2	-4.8 (2)
C10—C5—C6—C1	-134.13 (17)	C17—C12—C18—O2	174.86 (15)
C4—C5—C6—C1	-16.9 (2)	C13—C14—N3—O4	15.8 (2)
C11—C5—C6—N1	-77.36 (19)	C15—C14—N3—O4	-164.70 (16)
C10—C5—C6—N1	44.0 (2)	C13—C14—N3—O3	-164.01 (15)
C4—C5—C6—N1	161.23 (14)	C15—C14—N3—O3	15.5 (2)
N2—C7—N1—C6	178.54 (15)	C15—C16—N4—O6	-11.4 (2)
S1—C7—N1—C6	-1.05 (17)	C17—C16—N4—O6	167.84 (14)
C1—C6—N1—C7	1.76 (19)	C15—C16—N4—O5	169.17 (14)
C5—C6—N1—C7	-176.63 (14)	C17—C16—N4—O5	-11.6 (2)
N2—C7—S1—C1	-179.48 (15)		

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>
N1—H1N···O1	0.885 (19)	1.838 (19)	2.7187 (17)	173.4 (17)
N2—H3N···O2 ⁱ	0.90 (2)	2.01 (2)	2.8509 (19)	156.3 (17)
N2—H2N···O2	0.91 (2)	1.86 (2)	2.7551 (18)	168.3 (18)
C8—H8A···O6 ⁱⁱ	0.98	2.43	3.397 (2)	170

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

Bis(2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium) fumarate (IV)

Crystal data

$2C_{11}H_{19}N_2S^+ \cdot C_4H_2O_4^{2-}$

$M_r = 536.74$

Monoclinic, $P2_1$

$a = 9.0259$ (6) Å

$b = 14.7314$ (11) Å

$c = 11.1993$ (8) Å

$\beta = 101.943$ (6)°

$V = 1456.87$ (18) Å³

$Z = 2$

$F(000) = 576$

$D_x = 1.224$ Mg m⁻³

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

Cell parameters from 4569 reflections

$\theta = 2.3$ – 23.7 °

$\mu = 0.22$ mm⁻¹

$T = 173$ K

Prism, orange

$0.15 \times 0.08 \times 0.02$ mm

Data collection

Rigaku XtaLAB P200 HPC

diffractometer

Radiation source: rotating anode, Rigaku FR-X

Rigaku Osmic Confocal Optical System

monochromator

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku, 2017)

$T_{\min} = 0.333$, $T_{\max} = 1.000$

19263 measured reflections

6424 independent reflections

3792 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.080$

$\theta_{\max} = 29.1$ °, $\theta_{\min} = 1.9$ °

$h = -12 \rightarrow 11$

$k = -18 \rightarrow 20$

$l = -14 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.062$

$wR(F^2) = 0.128$

$S = 1.00$

6424 reflections

350 parameters

1 restraint

Primary atom site location: structure-invariant

direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2]$

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

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

$\Delta\rho_{\max} = 0.27$ e Å⁻³

$\Delta\rho_{\min} = -0.26$ e Å⁻³

Absolute structure: Flack x determined using

1279 quotients $[(I^-)-(I^+)]/[(I^-)+(I^+)]$ (Parsons *et*

al., 2013).

Absolute structure parameter: 0.46 (7)

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	1.2869 (6)	0.3952 (4)	0.6937 (4)	0.0339 (13)	
C2	1.3939 (6)	0.4406 (4)	0.7989 (5)	0.0467 (15)	
C3A	1.2984 (8)	0.5068 (7)	0.8546 (8)	0.052 (3)*	0.78 (2)
H3A1	1.2720	0.5596	0.7996	0.062*	0.78 (2)
H3A2	1.3578	0.5293	0.9334	0.062*	0.78 (2)
C4A	1.1520 (10)	0.4615 (8)	0.8755 (8)	0.047 (2)*	0.78 (2)
H4A1	1.1017	0.5022	0.9252	0.056*	0.78 (2)
H4A2	1.1780	0.4044	0.9216	0.056*	0.78 (2)
C3B	1.284 (3)	0.456 (3)	0.899 (3)	0.063 (12)*	0.22 (2)
H3B1	1.2677	0.3968	0.9362	0.075*	0.22 (2)
H3B2	1.3377	0.4959	0.9657	0.075*	0.22 (2)
C4B	1.130 (3)	0.498 (2)	0.846 (3)	0.033 (8)*	0.22 (2)
H4B1	1.0735	0.5078	0.9121	0.039*	0.22 (2)
H4B2	1.1445	0.5582	0.8102	0.039*	0.22 (2)
C5	1.0394 (6)	0.4401 (4)	0.7513 (4)	0.0372 (13)	
C6	1.1349 (6)	0.3955 (3)	0.6728 (4)	0.0312 (13)	
C7	1.1687 (6)	0.3114 (3)	0.5087 (4)	0.0320 (13)	
C8	1.4824 (7)	0.3683 (4)	0.8815 (6)	0.067 (2)	
H8A	1.5474	0.3975	0.9519	0.101*	
H8B	1.5451	0.3337	0.8359	0.101*	
H8C	1.4115	0.3272	0.9098	0.101*	
C9	1.5096 (8)	0.4998 (5)	0.7490 (6)	0.076 (2)	
H9A	1.5751	0.5316	0.8168	0.114*	
H9B	1.4553	0.5443	0.6909	0.114*	
H9C	1.5715	0.4610	0.7077	0.114*	
C10	0.9232 (6)	0.3732 (4)	0.7813 (5)	0.0506 (16)	
H10A	0.8700	0.4009	0.8400	0.076*	
H10B	0.9750	0.3180	0.8167	0.076*	
H10C	0.8501	0.3578	0.7065	0.076*	
C11	0.9553 (8)	0.5223 (5)	0.6843 (6)	0.070 (2)	
H11A	0.8941	0.5512	0.7364	0.105*	
H11B	0.8892	0.5020	0.6083	0.105*	
H11C	1.0291	0.5661	0.6656	0.105*	
N1	1.0694 (5)	0.3476 (3)	0.5669 (4)	0.0298 (11)	
H1N	0.976 (6)	0.334 (4)	0.544 (4)	0.036*	
N2	1.1307 (6)	0.2614 (4)	0.4096 (4)	0.0452 (13)	
H2N	1.029 (7)	0.263 (4)	0.369 (5)	0.054*	
H3N	1.202 (6)	0.248 (4)	0.365 (5)	0.054*	
S1	1.35226 (14)	0.33370 (9)	0.58194 (12)	0.0396 (4)	
C12	-0.1633 (6)	0.1107 (4)	-0.1894 (4)	0.0340 (13)	
C13	-0.2578 (6)	0.0698 (4)	-0.3022 (5)	0.0408 (14)	
C14	-0.1503 (6)	0.0460 (4)	-0.3869 (5)	0.0501 (16)	
H14A	-0.2031	0.0048	-0.4519	0.060*	
H14B	-0.1244	0.1022	-0.4265	0.060*	
C15	-0.0046 (6)	0.0005 (4)	-0.3204 (5)	0.0493 (15)	

H15A	0.0557	-0.0170	-0.3813	0.059*
H15B	-0.0312	-0.0558	-0.2816	0.059*
C16	0.0948 (6)	0.0599 (4)	-0.2219 (4)	0.0353 (13)
C17	-0.0114 (5)	0.1088 (3)	-0.1552 (4)	0.0286 (12)
C18	-0.0619 (6)	0.1945 (4)	0.0014 (5)	0.0338 (13)
C19	-0.3410 (7)	-0.0144 (4)	-0.2709 (6)	0.0662 (19)
H19A	-0.4097	-0.0366	-0.3446	0.099*
H19B	-0.3995	0.0012	-0.2092	0.099*
H19C	-0.2672	-0.0618	-0.2389	0.099*
C20	-0.3760 (6)	0.1378 (4)	-0.3673 (6)	0.0556 (17)
H20A	-0.4356	0.1098	-0.4412	0.083*
H20B	-0.3246	0.1919	-0.3896	0.083*
H20C	-0.4432	0.1552	-0.3127	0.083*
C21	0.2029 (6)	-0.0017 (4)	-0.1334 (5)	0.0498 (15)
H21A	0.2615	-0.0391	-0.1793	0.075*
H21B	0.1441	-0.0412	-0.0901	0.075*
H21C	0.2720	0.0357	-0.0743	0.075*
C22	0.1855 (7)	0.1290 (4)	-0.2784 (5)	0.0520 (17)
H22A	0.2544	0.0971	-0.3212	0.078*
H22B	0.2443	0.1671	-0.2140	0.078*
H22C	0.1162	0.1671	-0.3364	0.078*
N3	0.0446 (5)	0.1575 (3)	-0.0477 (4)	0.0329 (11)
H4N	0.151 (6)	0.163 (4)	-0.013 (4)	0.040*
N4	-0.0317 (6)	0.2444 (4)	0.1013 (4)	0.0457 (13)
H5N	0.078 (7)	0.242 (4)	0.141 (5)	0.055*
H6N	-0.104 (7)	0.256 (4)	0.130 (5)	0.055*
S2	-0.24072 (14)	0.17401 (9)	-0.08375 (12)	0.0386 (4)
C23	0.7409 (6)	0.2901 (4)	0.3641 (5)	0.0358 (13)
C24	0.5781 (6)	0.2738 (4)	0.3122 (5)	0.0392 (14)
H24	0.5076	0.2871	0.3621	0.047*
C25	0.5242 (6)	0.2420 (4)	0.2013 (5)	0.0380 (13)
H25	0.5942	0.2310	0.1502	0.046*
C26	0.3622 (6)	0.2223 (4)	0.1512 (5)	0.0371 (14)
O1	0.7763 (4)	0.3234 (3)	0.4689 (3)	0.0469 (10)
O2	0.8346 (4)	0.2695 (3)	0.2995 (3)	0.0591 (12)
O3	0.3301 (4)	0.1922 (3)	0.0429 (3)	0.0473 (11)
O4	0.2689 (4)	0.2349 (4)	0.2157 (3)	0.0642 (14)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.035 (3)	0.035 (3)	0.031 (3)	0.003 (2)	0.003 (2)	-0.002 (2)
C2	0.040 (3)	0.053 (4)	0.042 (3)	0.004 (3)	-0.001 (3)	-0.011 (3)
C5	0.039 (3)	0.040 (3)	0.033 (3)	0.001 (3)	0.008 (3)	-0.007 (3)
C6	0.041 (3)	0.026 (3)	0.025 (3)	-0.002 (3)	0.003 (2)	-0.003 (2)
C7	0.039 (3)	0.035 (3)	0.022 (3)	-0.004 (2)	0.007 (2)	0.000 (2)
C8	0.064 (4)	0.073 (5)	0.048 (4)	-0.007 (3)	-0.028 (3)	0.007 (3)
C9	0.070 (5)	0.058 (5)	0.090 (5)	-0.021 (4)	-0.006 (4)	-0.004 (4)

C10	0.047 (4)	0.064 (4)	0.047 (4)	-0.003 (3)	0.022 (3)	0.002 (3)
C11	0.085 (5)	0.060 (5)	0.077 (5)	0.025 (4)	0.044 (4)	0.015 (4)
N1	0.030 (2)	0.035 (3)	0.024 (2)	-0.001 (2)	0.006 (2)	0.000 (2)
N2	0.035 (3)	0.064 (4)	0.037 (3)	0.003 (3)	0.007 (2)	-0.013 (3)
S1	0.0327 (7)	0.0473 (9)	0.0377 (8)	0.0049 (7)	0.0045 (6)	-0.0037 (7)
C12	0.039 (3)	0.033 (3)	0.029 (3)	0.001 (3)	0.005 (2)	0.002 (2)
C13	0.038 (3)	0.043 (4)	0.039 (3)	-0.005 (3)	0.001 (3)	0.002 (3)
C14	0.046 (3)	0.066 (4)	0.035 (3)	0.003 (3)	0.000 (3)	-0.018 (3)
C15	0.049 (4)	0.053 (4)	0.043 (3)	-0.002 (3)	0.004 (3)	-0.017 (3)
C16	0.035 (3)	0.041 (3)	0.031 (3)	0.002 (3)	0.007 (2)	-0.005 (3)
C17	0.031 (3)	0.029 (3)	0.024 (3)	0.000 (2)	0.000 (2)	0.003 (2)
C18	0.036 (3)	0.035 (4)	0.030 (3)	0.005 (2)	0.008 (3)	-0.001 (2)
C19	0.068 (4)	0.055 (4)	0.070 (4)	-0.023 (4)	0.001 (4)	-0.004 (3)
C20	0.047 (4)	0.068 (5)	0.048 (4)	0.000 (3)	0.000 (3)	-0.003 (3)
C21	0.054 (4)	0.044 (4)	0.046 (3)	0.016 (3)	0.000 (3)	-0.007 (3)
C22	0.053 (4)	0.064 (5)	0.044 (4)	-0.002 (3)	0.021 (3)	-0.006 (3)
N3	0.027 (2)	0.043 (3)	0.028 (2)	0.000 (2)	0.0033 (19)	-0.003 (2)
N4	0.035 (3)	0.071 (4)	0.033 (3)	0.009 (3)	0.011 (2)	-0.012 (3)
S2	0.0323 (7)	0.0488 (10)	0.0352 (8)	0.0019 (7)	0.0081 (6)	0.0029 (7)
C23	0.033 (3)	0.040 (4)	0.035 (3)	-0.002 (3)	0.008 (3)	0.000 (3)
C24	0.032 (3)	0.047 (4)	0.040 (4)	-0.004 (3)	0.011 (3)	-0.008 (3)
C25	0.035 (3)	0.050 (4)	0.031 (3)	-0.002 (3)	0.011 (3)	-0.003 (3)
C26	0.036 (3)	0.042 (4)	0.032 (3)	0.000 (3)	0.004 (3)	-0.002 (3)
O1	0.036 (2)	0.072 (3)	0.031 (2)	-0.010 (2)	0.0048 (17)	-0.019 (2)
O2	0.037 (2)	0.108 (4)	0.033 (2)	-0.007 (2)	0.0091 (19)	-0.020 (2)
O3	0.037 (2)	0.071 (3)	0.033 (2)	-0.0045 (19)	0.0055 (17)	-0.017 (2)
O4	0.035 (2)	0.121 (4)	0.039 (2)	-0.010 (2)	0.013 (2)	-0.028 (2)

Geometric parameters (Å, °)

C1—C6	1.344 (7)	C12—C13	1.496 (7)
C1—C2	1.514 (7)	C12—S2	1.761 (5)
C1—S1	1.744 (5)	C13—C19	1.527 (8)
C2—C3A	1.520 (9)	C13—C14	1.532 (7)
C2—C8	1.524 (8)	C13—C20	1.533 (8)
C2—C9	1.551 (9)	C14—C15	1.526 (8)
C2—C3B	1.66 (3)	C14—H14A	0.9900
C3A—C4A	1.541 (14)	C14—H14B	0.9900
C3A—H3A1	0.9900	C15—C16	1.542 (7)
C3A—H3A2	0.9900	C15—H15A	0.9900
C4A—C5	1.575 (10)	C15—H15B	0.9900
C4A—H4A1	0.9900	C16—C17	1.513 (7)
C4A—H4A2	0.9900	C16—C22	1.523 (7)
C3B—C4B	1.53 (5)	C16—C21	1.536 (7)
C3B—H3B1	0.9900	C17—N3	1.404 (6)
C3B—H3B2	0.9900	C18—N4	1.319 (7)
C4B—C5	1.47 (2)	C18—N3	1.320 (6)
C4B—H4B1	0.9900	C18—S2	1.723 (5)

C4B—H4B2	0.9900	C19—H19A	0.9800
C5—C6	1.504 (7)	C19—H19B	0.9800
C5—C10	1.526 (8)	C19—H19C	0.9800
C5—C11	1.540 (8)	C20—H20A	0.9800
C6—N1	1.401 (6)	C20—H20B	0.9800
C7—N2	1.318 (6)	C20—H20C	0.9800
C7—N1	1.325 (6)	C21—H21A	0.9800
C7—S1	1.721 (5)	C21—H21B	0.9800
C8—H8A	0.9800	C21—H21C	0.9800
C8—H8B	0.9800	C22—H22A	0.9800
C8—H8C	0.9800	C22—H22B	0.9800
C9—H9A	0.9800	C22—H22C	0.9800
C9—H9B	0.9800	N3—H4N	0.96 (5)
C9—H9C	0.9800	N4—H5N	1.00 (6)
C10—H10A	0.9800	N4—H6N	0.81 (6)
C10—H10B	0.9800	C23—O1	1.251 (6)
C10—H10C	0.9800	C23—O2	1.258 (6)
C11—H11A	0.9800	C23—C24	1.484 (7)
C11—H11B	0.9800	C24—C25	1.321 (6)
C11—H11C	0.9800	C24—H24	0.9500
N1—H1N	0.85 (5)	C25—C26	1.483 (7)
N2—H2N	0.94 (6)	C25—H25	0.9500
N2—H3N	0.91 (6)	C26—O4	1.232 (6)
C12—C17	1.345 (7)	C26—O3	1.267 (6)
C6—C1—C2	126.7 (5)	C7—N2—H3N	119 (4)
C6—C1—S1	111.2 (4)	H2N—N2—H3N	118 (5)
C2—C1—S1	122.1 (4)	C7—S1—C1	90.3 (2)
C1—C2—C3A	106.1 (5)	C17—C12—C13	127.0 (5)
C1—C2—C8	109.5 (5)	C17—C12—S2	110.0 (4)
C3A—C2—C8	118.0 (6)	C13—C12—S2	122.9 (4)
C1—C2—C9	109.7 (5)	C12—C13—C19	110.8 (5)
C3A—C2—C9	105.5 (6)	C12—C13—C14	106.9 (4)
C8—C2—C9	107.7 (5)	C19—C13—C14	111.1 (5)
C1—C2—C3B	102.3 (11)	C12—C13—C20	110.9 (5)
C8—C2—C3B	89.8 (15)	C19—C13—C20	108.2 (5)
C9—C2—C3B	134.9 (15)	C14—C13—C20	108.8 (5)
C2—C3A—C4A	111.1 (9)	C15—C14—C13	113.0 (5)
C2—C3A—H3A1	109.4	C15—C14—H14A	109.0
C4A—C3A—H3A1	109.4	C13—C14—H14A	109.0
C2—C3A—H3A2	109.4	C15—C14—H14B	109.0
C4A—C3A—H3A2	109.4	C13—C14—H14B	109.0
H3A1—C3A—H3A2	108.0	H14A—C14—H14B	107.8
C3A—C4A—C5	111.7 (8)	C14—C15—C16	114.5 (5)
C3A—C4A—H4A1	109.3	C14—C15—H15A	108.6
C5—C4A—H4A1	109.3	C16—C15—H15A	108.6
C3A—C4A—H4A2	109.3	C14—C15—H15B	108.6
C5—C4A—H4A2	109.3	C16—C15—H15B	108.6

H4A1—C4A—H4A2	107.9	H15A—C15—H15B	107.6
C4B—C3B—C2	114 (3)	C17—C16—C22	109.7 (4)
C4B—C3B—H3B1	108.7	C17—C16—C21	110.2 (4)
C2—C3B—H3B1	108.7	C22—C16—C21	109.8 (5)
C4B—C3B—H3B2	108.7	C17—C16—C15	106.8 (4)
C2—C3B—H3B2	108.7	C22—C16—C15	111.4 (4)
H3B1—C3B—H3B2	107.6	C21—C16—C15	108.9 (5)
C5—C4B—C3B	112 (3)	C12—C17—N3	113.5 (4)
C5—C4B—H4B1	109.3	C12—C17—C16	125.6 (4)
C3B—C4B—H4B1	109.3	N3—C17—C16	120.9 (4)
C5—C4B—H4B2	109.3	N4—C18—N3	122.9 (5)
C3B—C4B—H4B2	109.3	N4—C18—S2	124.9 (4)
H4B1—C4B—H4B2	107.9	N3—C18—S2	112.1 (4)
C4B—C5—C6	112.1 (10)	C13—C19—H19A	109.5
C4B—C5—C10	121.4 (12)	C13—C19—H19B	109.5
C6—C5—C10	110.5 (5)	H19A—C19—H19B	109.5
C4B—C5—C11	92.1 (15)	C13—C19—H19C	109.5
C6—C5—C11	110.1 (4)	H19A—C19—H19C	109.5
C10—C5—C11	108.9 (5)	H19B—C19—H19C	109.5
C6—C5—C4A	105.1 (5)	C13—C20—H20A	109.5
C10—C5—C4A	106.4 (5)	C13—C20—H20B	109.5
C11—C5—C4A	115.8 (6)	H20A—C20—H20B	109.5
C1—C6—N1	112.5 (4)	C13—C20—H20C	109.5
C1—C6—C5	126.0 (4)	H20A—C20—H20C	109.5
N1—C6—C5	121.5 (4)	H20B—C20—H20C	109.5
N2—C7—N1	123.7 (5)	C16—C21—H21A	109.5
N2—C7—S1	124.4 (4)	C16—C21—H21B	109.5
N1—C7—S1	111.8 (4)	H21A—C21—H21B	109.5
C2—C8—H8A	109.5	C16—C21—H21C	109.5
C2—C8—H8B	109.5	H21A—C21—H21C	109.5
H8A—C8—H8B	109.5	H21B—C21—H21C	109.5
C2—C8—H8C	109.5	C16—C22—H22A	109.5
H8A—C8—H8C	109.5	C16—C22—H22B	109.5
H8B—C8—H8C	109.5	H22A—C22—H22B	109.5
C2—C9—H9A	109.5	C16—C22—H22C	109.5
C2—C9—H9B	109.5	H22A—C22—H22C	109.5
H9A—C9—H9B	109.5	H22B—C22—H22C	109.5
C2—C9—H9C	109.5	C18—N3—C17	113.9 (4)
H9A—C9—H9C	109.5	C18—N3—H4N	123 (3)
H9B—C9—H9C	109.5	C17—N3—H4N	123 (3)
C5—C10—H10A	109.5	C18—N4—H5N	112 (3)
C5—C10—H10B	109.5	C18—N4—H6N	115 (4)
H10A—C10—H10B	109.5	H5N—N4—H6N	130 (5)
C5—C10—H10C	109.5	C18—S2—C12	90.5 (2)
H10A—C10—H10C	109.5	O1—C23—O2	124.2 (5)
H10B—C10—H10C	109.5	O1—C23—C24	118.1 (5)
C5—C11—H11A	109.5	O2—C23—C24	117.7 (5)
C5—C11—H11B	109.5	C25—C24—C23	124.6 (5)

H11A—C11—H11B	109.5	C25—C24—H24	117.7
C5—C11—H11C	109.5	C23—C24—H24	117.7
H11A—C11—H11C	109.5	C24—C25—C26	124.6 (5)
H11B—C11—H11C	109.5	C24—C25—H25	117.7
C7—N1—C6	114.1 (4)	C26—C25—H25	117.7
C7—N1—H1N	119 (3)	O4—C26—O3	124.4 (5)
C6—N1—H1N	126 (3)	O4—C26—C25	119.2 (5)
C7—N2—H2N	117 (4)	O3—C26—C25	116.3 (5)
C6—C1—C2—C3A	-15.4 (9)	N1—C7—S1—C1	-0.6 (4)
S1—C1—C2—C3A	165.0 (6)	C6—C1—S1—C7	0.8 (4)
C6—C1—C2—C8	113.1 (6)	C2—C1—S1—C7	-179.5 (5)
S1—C1—C2—C8	-66.6 (6)	C17—C12—C13—C19	107.5 (6)
C6—C1—C2—C9	-128.9 (6)	S2—C12—C13—C19	-75.3 (6)
S1—C1—C2—C9	51.4 (6)	C17—C12—C13—C14	-13.7 (7)
C6—C1—C2—C3B	18.8 (17)	S2—C12—C13—C14	163.5 (4)
S1—C1—C2—C3B	-160.8 (16)	C17—C12—C13—C20	-132.2 (6)
C1—C2—C3A—C4A	47.8 (10)	S2—C12—C13—C20	45.0 (6)
C8—C2—C3A—C4A	-75.5 (9)	C12—C13—C14—C15	44.1 (6)
C9—C2—C3A—C4A	164.1 (8)	C19—C13—C14—C15	-77.0 (6)
C2—C3A—C4A—C5	-69.2 (12)	C20—C13—C14—C15	163.9 (5)
C1—C2—C3B—C4B	-48 (3)	C13—C14—C15—C16	-62.5 (7)
C8—C2—C3B—C4B	-158 (3)	C14—C15—C16—C17	40.9 (6)
C9—C2—C3B—C4B	87 (3)	C14—C15—C16—C22	-78.9 (6)
C2—C3B—C4B—C5	62 (4)	C14—C15—C16—C21	159.9 (5)
C3B—C4B—C5—C6	-38 (3)	C13—C12—C17—N3	176.7 (5)
C3B—C4B—C5—C10	95 (3)	S2—C12—C17—N3	-0.8 (6)
C3B—C4B—C5—C11	-151 (3)	C13—C12—C17—C16	-3.4 (8)
C3A—C4A—C5—C6	47.3 (10)	S2—C12—C17—C16	179.1 (4)
C3A—C4A—C5—C10	164.5 (8)	C22—C16—C17—C12	111.1 (6)
C3A—C4A—C5—C11	-74.4 (10)	C21—C16—C17—C12	-127.9 (5)
C2—C1—C6—N1	179.6 (5)	C15—C16—C17—C12	-9.8 (7)
S1—C1—C6—N1	-0.7 (5)	C22—C16—C17—N3	-69.1 (6)
C2—C1—C6—C5	-0.9 (9)	C21—C16—C17—N3	51.9 (6)
S1—C1—C6—C5	178.8 (4)	C15—C16—C17—N3	170.1 (5)
C4B—C5—C6—C1	9.7 (17)	N4—C18—N3—C17	-178.6 (5)
C10—C5—C6—C1	-129.1 (5)	S2—C18—N3—C17	-1.4 (6)
C11—C5—C6—C1	110.6 (6)	C12—C17—N3—C18	1.5 (6)
C4A—C5—C6—C1	-14.7 (8)	C16—C17—N3—C18	-178.4 (4)
C4B—C5—C6—N1	-170.9 (16)	N4—C18—S2—C12	177.9 (5)
C10—C5—C6—N1	50.4 (6)	N3—C18—S2—C12	0.8 (4)
C11—C5—C6—N1	-69.9 (6)	C17—C12—S2—C18	0.0 (4)
C4A—C5—C6—N1	164.7 (6)	C13—C12—S2—C18	-177.6 (4)
N2—C7—N1—C6	177.7 (5)	O1—C23—C24—C25	177.5 (5)
S1—C7—N1—C6	0.3 (6)	O2—C23—C24—C25	-2.4 (8)
C1—C6—N1—C7	0.3 (6)	C23—C24—C25—C26	177.5 (5)
C5—C6—N1—C7	-179.2 (5)	C24—C25—C26—O4	-0.8 (8)
N2—C7—S1—C1	-177.9 (5)	C24—C25—C26—O3	179.9 (5)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1N \cdots O1	0.85 (5)	1.84 (5)	2.670 (5)	167 (5)
N2—H2N \cdots O2	0.94 (6)	1.77 (6)	2.704 (6)	177 (5)
N2—H3N \cdots O4 ⁱ	0.91 (6)	1.90 (6)	2.746 (6)	153 (5)
N3—H4N \cdots O3	0.96 (5)	1.67 (5)	2.617 (5)	169 (5)
N4—H5N \cdots O4	1.00 (6)	1.75 (6)	2.754 (7)	178 (5)
N4—H6N \cdots O2 ⁱⁱ	0.81 (6)	2.09 (6)	2.763 (6)	141 (6)

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

Bis(2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium) succinate–2-amino-4,4,7,7-tetramethyl-4,5,6,7-tetrahydro-1,3-benzothiazol-3-ium hydrogen succinate 4,4,7,7-tetramethyl-3a,5,6,7a-tetrahydrobenzothiazol-2-ylamine (1/1) (V)

Crystal data

1.5C₁₁H₁₉N₂S⁺·0.5C₄H₄O₄²⁻·0.5C₄H₅O₄⁻·0.5C₁₁H₁₈N₂S
M_r = 538.75
 Monoclinic, *P*2₁
a = 8.9437 (3) Å
b = 14.7253 (4) Å
c = 11.2676 (4) Å
 β = 100.493 (3)°
V = 1459.11 (8) Å³
Z = 2

F(000) = 580
D_x = 1.226 Mg m⁻³
 Mo *K* α radiation, λ = 0.71073 Å
 Cell parameters from 9613 reflections
 θ = 2.3–28.0°
 μ = 0.22 mm⁻¹
T = 173 K
 Plate, colourless
 0.32 × 0.15 × 0.02 mm

Data collection

Rigaku XtaLAB P200 HPC
 diffractometer
 Radiation source: rotating anode, Rigaku FR-X
 Rigaku Osmic Confocal Optical System
 monochromator
 ω scans
 Absorption correction: multi-scan
 (CrysAlis PRO; Rigaku, 2017)
T_{min} = 0.779, *T_{max}* = 1.000

19079 measured reflections
 6272 independent reflections
 5511 reflections with *I* > 2 σ (*I*)
R_{int} = 0.034
 θ_{\max} = 29.1°, θ_{\min} = 2.3°
h = -10→12
k = -19→19
l = -14→14

Refinement

Refinement on *F*²
 Least-squares matrix: full
R [*F*² > 2 σ (*F*²)] = 0.039
wR(*F*²) = 0.094
S = 1.04
 6272 reflections
 354 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods
 Hydrogen site location: mixed

H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.1056P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.26$ e Å⁻³
 $\Delta\rho_{\min} = -0.25$ e Å⁻³
 Absolute structure: Flack *x* determined using
 2211 quotients [(*I*⁺)-(*I*)]/[(*I*⁺)+(*I*)] (Parsons *et al.*, 2013)
 Absolute structure parameter: 0.00 (3)

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	1.2888 (3)	0.39542 (19)	0.6860 (2)	0.0263 (6)	
C2	1.3946 (3)	0.4407 (2)	0.7881 (3)	0.0357 (7)	
C3A	1.2962 (6)	0.5069 (4)	0.8461 (5)	0.0365 (17)*	0.593 (11)
H3A1	1.2689	0.5598	0.7923	0.044*	0.593 (11)
H3A2	1.3548	0.5293	0.9237	0.044*	0.593 (11)
C4A	1.1500 (6)	0.4594 (5)	0.8685 (6)	0.0366 (16)*	0.593 (11)
H4A1	1.0979	0.4985	0.9198	0.044*	0.593 (11)
H4A2	1.1768	0.4015	0.9118	0.044*	0.593 (11)
C3B	1.2917 (10)	0.4598 (8)	0.8865 (9)	0.049 (3)*	0.407 (11)
H3B1	1.2754	0.4020	0.9271	0.059*	0.407 (11)
H3B2	1.3468	0.5015	0.9483	0.059*	0.407 (11)
C4B	1.1399 (9)	0.5005 (7)	0.8353 (8)	0.038 (2)*	0.407 (11)
H4B1	1.1564	0.5586	0.7954	0.046*	0.407 (11)
H4B2	1.0860	0.5143	0.9025	0.046*	0.407 (11)
C5	1.0393 (3)	0.4400 (2)	0.7449 (3)	0.0308 (6)	
C6	1.1354 (3)	0.39467 (18)	0.6659 (2)	0.0236 (6)	
C7	1.1723 (3)	0.30960 (19)	0.5050 (2)	0.0265 (6)	
C8	1.4933 (5)	0.3708 (3)	0.8639 (4)	0.0612 (11)	
H8A	1.5574	0.4010	0.9324	0.092*	
H8B	1.5579	0.3404	0.8146	0.092*	
H8C	1.4285	0.3258	0.8939	0.092*	
C9	1.5000 (5)	0.5061 (3)	0.7370 (4)	0.0690 (12)	
H9A	1.5592	0.5414	0.8030	0.103*	
H9B	1.4390	0.5474	0.6793	0.103*	
H9C	1.5691	0.4714	0.6961	0.103*	
C10	0.9296 (4)	0.3719 (2)	0.7834 (3)	0.0480 (9)	
H10A	0.8715	0.4014	0.8385	0.072*	
H10B	0.9869	0.3207	0.8245	0.072*	
H10C	0.8596	0.3499	0.7121	0.072*	
C11	0.9468 (5)	0.5170 (3)	0.6769 (4)	0.0669 (13)	
H11A	0.8820	0.5444	0.7285	0.100*	
H11B	0.8830	0.4928	0.6036	0.100*	
H11C	1.0158	0.5631	0.6547	0.100*	
N1	1.0710 (3)	0.34631 (16)	0.5629 (2)	0.0246 (5)	
H1N	0.968 (4)	0.335 (2)	0.534 (3)	0.030*	
N2	1.1368 (3)	0.2592 (2)	0.4072 (2)	0.0397 (7)	
H2N	1.209 (4)	0.241 (3)	0.369 (3)	0.048*	
H3N	1.047 (4)	0.257 (3)	0.374 (3)	0.048*	
S1	1.35670 (7)	0.33342 (5)	0.57387 (6)	0.03090 (18)	

C12	-0.1518 (3)	0.11232 (19)	-0.1824 (3)	0.0261 (6)	
C13	-0.2459 (4)	0.0700 (2)	-0.2927 (3)	0.0345 (7)	
C14	-0.1355 (4)	0.0472 (2)	-0.3784 (3)	0.0405 (8)	
H14A	-0.1871	0.0066	-0.4431	0.049*	
H14B	-0.1081	0.1038	-0.4167	0.049*	
C15	0.0097 (4)	0.0011 (2)	-0.3133 (3)	0.0426 (8)	
H15A	0.0715	-0.0172	-0.3738	0.051*	
H15B	-0.0183	-0.0547	-0.2736	0.051*	
C16	0.1071 (3)	0.06150 (19)	-0.2180 (3)	0.0295 (6)	
C17	0.0007 (3)	0.11035 (18)	-0.1495 (2)	0.0245 (6)	
C18	-0.0513 (3)	0.19535 (18)	0.0048 (2)	0.0263 (6)	
C19	-0.3270 (5)	-0.0149 (3)	-0.2585 (4)	0.0581 (10)	
H19A	-0.3866	-0.0421	-0.3315	0.087*	
H19B	-0.3950	0.0018	-0.2030	0.087*	
H19C	-0.2516	-0.0588	-0.2193	0.087*	
C20	-0.3652 (4)	0.1381 (2)	-0.3552 (3)	0.0459 (8)	
H20A	-0.4216	0.1112	-0.4295	0.069*	
H20B	-0.3141	0.1936	-0.3748	0.069*	
H20C	-0.4358	0.1530	-0.3010	0.069*	
C21	0.2173 (4)	0.0007 (2)	-0.1322 (3)	0.0446 (8)	
H21A	0.2785	-0.0351	-0.1789	0.067*	
H21B	0.1593	-0.0401	-0.0890	0.067*	
H21C	0.2844	0.0388	-0.0739	0.067*	
C22	0.1982 (4)	0.1307 (2)	-0.2773 (3)	0.0426 (8)	
H22A	0.2681	0.0986	-0.3203	0.064*	
H22B	0.2564	0.1697	-0.2150	0.064*	
H22C	0.1283	0.1680	-0.3344	0.064*	
N3	0.0575 (3)	0.15834 (16)	-0.0442 (2)	0.0248 (5)	
H4N	0.153 (9)	0.165 (5)	-0.011 (6)	0.030*	0.50 (5)
N4	-0.0255 (3)	0.2469 (2)	0.1041 (2)	0.0387 (7)	
H5N	-0.096 (4)	0.249 (3)	0.142 (3)	0.046*	
H6N	0.073 (4)	0.245 (2)	0.147 (3)	0.046*	
S2	-0.23122 (8)	0.17442 (5)	-0.07649 (6)	0.02918 (18)	
C26	0.3743 (3)	0.22426 (19)	0.1462 (3)	0.0271 (6)	
C25	0.5352 (3)	0.2536 (2)	0.1889 (3)	0.0298 (6)	
H25A	0.5538	0.3096	0.1451	0.036*	
H25B	0.6039	0.2060	0.1676	0.036*	
C24	0.5760 (3)	0.2717 (2)	0.3238 (3)	0.0300 (7)	
H24A	0.5202	0.3264	0.3427	0.036*	
H24B	0.5406	0.2199	0.3672	0.036*	
C23	0.7441 (3)	0.2859 (2)	0.3709 (3)	0.0284 (6)	
O1	0.7810 (2)	0.32184 (16)	0.47272 (18)	0.0379 (5)	
O2	0.8363 (2)	0.2585 (2)	0.3079 (2)	0.0575 (7)	
O3	0.3395 (3)	0.20074 (16)	0.03486 (19)	0.0388 (6)	
H1O	0.249 (11)	0.191 (5)	0.008 (7)	0.047*	0.50 (5)
O4	0.2832 (2)	0.2213 (2)	0.21545 (19)	0.0500 (7)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0280 (14)	0.0258 (13)	0.0253 (14)	0.0017 (11)	0.0051 (11)	-0.0003 (12)
C2	0.0308 (15)	0.0380 (16)	0.0364 (17)	0.0002 (13)	0.0009 (13)	-0.0095 (15)
C5	0.0322 (15)	0.0316 (15)	0.0295 (15)	-0.0011 (13)	0.0082 (13)	-0.0073 (13)
C6	0.0287 (14)	0.0218 (12)	0.0207 (13)	-0.0020 (11)	0.0050 (11)	0.0005 (11)
C7	0.0236 (14)	0.0331 (15)	0.0223 (14)	0.0018 (11)	0.0032 (11)	0.0001 (12)
C8	0.063 (2)	0.059 (2)	0.048 (2)	-0.019 (2)	-0.0263 (19)	0.0101 (19)
C9	0.069 (3)	0.047 (2)	0.079 (3)	-0.026 (2)	-0.018 (2)	0.003 (2)
C10	0.054 (2)	0.0462 (19)	0.053 (2)	0.0011 (17)	0.0319 (18)	0.0051 (17)
C11	0.079 (3)	0.048 (2)	0.088 (3)	0.031 (2)	0.052 (3)	0.023 (2)
N1	0.0226 (12)	0.0286 (12)	0.0226 (12)	-0.0009 (10)	0.0037 (9)	-0.0015 (10)
N2	0.0287 (14)	0.0613 (19)	0.0288 (15)	0.0056 (13)	0.0044 (12)	-0.0156 (14)
S1	0.0231 (3)	0.0400 (4)	0.0290 (4)	0.0043 (3)	0.0032 (3)	-0.0045 (3)
C12	0.0266 (14)	0.0253 (13)	0.0267 (14)	-0.0014 (11)	0.0058 (12)	0.0007 (12)
C13	0.0337 (16)	0.0343 (15)	0.0331 (16)	-0.0093 (13)	-0.0005 (13)	-0.0047 (14)
C14	0.0425 (18)	0.0461 (18)	0.0305 (16)	-0.0013 (14)	0.0000 (14)	-0.0137 (15)
C15	0.0437 (18)	0.0420 (17)	0.0408 (18)	0.0018 (15)	0.0044 (15)	-0.0170 (15)
C16	0.0303 (14)	0.0295 (14)	0.0287 (15)	0.0027 (12)	0.0052 (12)	-0.0028 (13)
C17	0.0276 (14)	0.0231 (12)	0.0225 (14)	-0.0007 (11)	0.0038 (11)	0.0016 (11)
C18	0.0262 (14)	0.0297 (15)	0.0225 (14)	0.0023 (11)	0.0032 (12)	0.0017 (11)
C19	0.062 (2)	0.048 (2)	0.061 (2)	-0.0282 (18)	0.004 (2)	-0.0068 (19)
C20	0.0333 (17)	0.060 (2)	0.0387 (19)	0.0004 (16)	-0.0078 (14)	-0.0049 (17)
C21	0.0418 (18)	0.0429 (18)	0.0472 (19)	0.0173 (15)	0.0028 (16)	-0.0068 (16)
C22	0.0396 (18)	0.0499 (19)	0.0433 (19)	-0.0023 (15)	0.0206 (16)	-0.0042 (16)
N3	0.0218 (11)	0.0306 (13)	0.0210 (12)	0.0003 (10)	0.0015 (9)	-0.0004 (10)
N4	0.0286 (14)	0.0594 (17)	0.0277 (15)	0.0047 (13)	0.0038 (12)	-0.0121 (13)
S2	0.0230 (3)	0.0361 (4)	0.0287 (4)	0.0008 (3)	0.0053 (3)	0.0016 (3)
C26	0.0268 (14)	0.0289 (14)	0.0248 (14)	0.0020 (12)	0.0021 (12)	-0.0022 (12)
C25	0.0281 (15)	0.0363 (15)	0.0243 (15)	-0.0015 (12)	0.0031 (12)	-0.0019 (13)
C24	0.0250 (14)	0.0386 (16)	0.0256 (15)	0.0016 (12)	0.0025 (12)	-0.0064 (13)
C23	0.0279 (15)	0.0321 (14)	0.0251 (15)	-0.0012 (12)	0.0045 (12)	-0.0019 (13)
O1	0.0275 (10)	0.0581 (14)	0.0274 (11)	-0.0050 (10)	0.0029 (8)	-0.0178 (11)
O2	0.0259 (12)	0.109 (2)	0.0368 (13)	-0.0003 (13)	0.0035 (10)	-0.0313 (14)
O3	0.0263 (11)	0.0618 (16)	0.0273 (12)	-0.0077 (10)	0.0022 (9)	-0.0105 (10)
O4	0.0280 (11)	0.0919 (19)	0.0312 (12)	-0.0076 (12)	0.0084 (10)	-0.0186 (13)

Geometric parameters (\AA , $^\circ$)

C1—C6	1.349 (4)	C13—C19	1.530 (4)
C1—C2	1.506 (4)	C13—C20	1.538 (5)
C1—S1	1.754 (3)	C13—C14	1.538 (4)
C2—C8	1.515 (5)	C14—C15	1.528 (5)
C2—C9	1.531 (5)	C14—H14A	0.9900
C2—C3A	1.537 (6)	C14—H14B	0.9900
C2—C3B	1.589 (10)	C15—C16	1.536 (4)
C3A—C4A	1.544 (9)	C15—H15A	0.9900

C3A—H3A1	0.9900	C15—H15B	0.9900
C3A—H3A2	0.9900	C16—C17	1.512 (4)
C4A—C5	1.581 (6)	C16—C22	1.532 (4)
C4A—H4A1	0.9900	C16—C21	1.536 (4)
C4A—H4A2	0.9900	C17—N3	1.395 (4)
C3B—C4B	1.499 (14)	C18—N3	1.321 (3)
C3B—H3B1	0.9900	C18—N4	1.337 (4)
C3B—H3B2	0.9900	C18—S2	1.728 (3)
C4B—C5	1.519 (8)	C19—H19A	0.9800
C4B—H4B1	0.9900	C19—H19B	0.9800
C4B—H4B2	0.9900	C19—H19C	0.9800
C5—C6	1.502 (4)	C20—H20A	0.9800
C5—C10	1.520 (4)	C20—H20B	0.9800
C5—C11	1.525 (5)	C20—H20C	0.9800
C6—N1	1.394 (3)	C21—H21A	0.9800
C7—N2	1.319 (4)	C21—H21B	0.9800
C7—N1	1.325 (3)	C21—H21C	0.9800
C7—S1	1.726 (3)	C22—H22A	0.9800
C8—H8A	0.9800	C22—H22B	0.9800
C8—H8B	0.9800	C22—H22C	0.9800
C8—H8C	0.9800	N3—H4N	0.87 (8)
C9—H9A	0.9800	N4—H5N	0.82 (4)
C9—H9B	0.9800	N4—H6N	0.92 (4)
C9—H9C	0.9800	C26—O4	1.228 (3)
C10—H10A	0.9800	C26—O3	1.283 (4)
C10—H10B	0.9800	C26—C25	1.496 (4)
C10—H10C	0.9800	C25—C24	1.521 (4)
C11—H11A	0.9800	C25—H25A	0.9900
C11—H11B	0.9800	C25—H25B	0.9900
C11—H11C	0.9800	C24—C23	1.515 (4)
N1—H1N	0.93 (3)	C24—H24A	0.9900
N2—H2N	0.89 (4)	C24—H24B	0.9900
N2—H3N	0.82 (4)	C23—O2	1.249 (4)
C12—C17	1.348 (4)	C23—O1	1.252 (3)
C12—C13	1.503 (4)	O3—H1O	0.82 (10)
C12—S2	1.753 (3)		
C6—C1—C2	127.6 (3)	C17—C12—S2	109.8 (2)
C6—C1—S1	110.5 (2)	C13—C12—S2	123.0 (2)
C2—C1—S1	122.0 (2)	C12—C13—C19	110.5 (3)
C1—C2—C8	110.5 (3)	C12—C13—C20	110.2 (3)
C1—C2—C9	109.6 (3)	C19—C13—C20	109.1 (3)
C8—C2—C9	107.7 (3)	C12—C13—C14	106.4 (2)
C1—C2—C3A	106.1 (3)	C19—C13—C14	111.6 (3)
C8—C2—C3A	120.8 (4)	C20—C13—C14	109.1 (3)
C9—C2—C3A	101.6 (4)	C15—C14—C13	112.5 (3)
C1—C2—C3B	104.4 (4)	C15—C14—H14A	109.1
C8—C2—C3B	94.5 (5)	C13—C14—H14A	109.1

C9—C2—C3B	128.7 (5)	C15—C14—H14B	109.1
C2—C3A—C4A	110.5 (5)	C13—C14—H14B	109.1
C2—C3A—H3A1	109.6	H14A—C14—H14B	107.8
C4A—C3A—H3A1	109.6	C14—C15—C16	113.7 (3)
C2—C3A—H3A2	109.6	C14—C15—H15A	108.8
C4A—C3A—H3A2	109.6	C16—C15—H15A	108.8
H3A1—C3A—H3A2	108.1	C14—C15—H15B	108.8
C3A—C4A—C5	110.5 (5)	C16—C15—H15B	108.8
C3A—C4A—H4A1	109.5	H15A—C15—H15B	107.7
C5—C4A—H4A1	109.5	C17—C16—C22	109.9 (2)
C3A—C4A—H4A2	109.5	C17—C16—C21	110.3 (2)
C5—C4A—H4A2	109.5	C22—C16—C21	109.3 (3)
H4A1—C4A—H4A2	108.1	C17—C16—C15	107.6 (2)
C4B—C3B—C2	113.6 (8)	C22—C16—C15	111.0 (3)
C4B—C3B—H3B1	108.8	C21—C16—C15	108.7 (3)
C2—C3B—H3B1	108.8	C12—C17—N3	114.6 (2)
C4B—C3B—H3B2	108.8	C12—C17—C16	124.7 (2)
C2—C3B—H3B2	108.8	N3—C17—C16	120.7 (2)
H3B1—C3B—H3B2	107.7	N3—C18—N4	123.8 (3)
C3B—C4B—C5	114.1 (8)	N3—C18—S2	113.0 (2)
C3B—C4B—H4B1	108.7	N4—C18—S2	123.2 (2)
C5—C4B—H4B1	108.7	C13—C19—H19A	109.5
C3B—C4B—H4B2	108.7	C13—C19—H19B	109.5
C5—C4B—H4B2	108.7	H19A—C19—H19B	109.5
H4B1—C4B—H4B2	107.6	C13—C19—H19C	109.5
C6—C5—C4B	109.0 (4)	H19A—C19—H19C	109.5
C6—C5—C10	110.2 (2)	H19B—C19—H19C	109.5
C4B—C5—C10	122.0 (4)	C13—C20—H20A	109.5
C6—C5—C11	110.4 (3)	C13—C20—H20B	109.5
C4B—C5—C11	95.9 (5)	H20A—C20—H20B	109.5
C10—C5—C11	108.3 (3)	C13—C20—H20C	109.5
C6—C5—C4A	105.6 (3)	H20A—C20—H20C	109.5
C10—C5—C4A	101.6 (3)	H20B—C20—H20C	109.5
C11—C5—C4A	120.2 (4)	C16—C21—H21A	109.5
C1—C6—N1	113.4 (2)	C16—C21—H21B	109.5
C1—C6—C5	124.8 (3)	H21A—C21—H21B	109.5
N1—C6—C5	121.7 (2)	C16—C21—H21C	109.5
N2—C7—N1	124.0 (3)	H21A—C21—H21C	109.5
N2—C7—S1	123.7 (2)	H21B—C21—H21C	109.5
N1—C7—S1	112.3 (2)	C16—C22—H22A	109.5
C2—C8—H8A	109.5	C16—C22—H22B	109.5
C2—C8—H8B	109.5	H22A—C22—H22B	109.5
H8A—C8—H8B	109.5	C16—C22—H22C	109.5
C2—C8—H8C	109.5	H22A—C22—H22C	109.5
H8A—C8—H8C	109.5	H22B—C22—H22C	109.5
H8B—C8—H8C	109.5	C18—N3—C17	112.5 (2)
C2—C9—H9A	109.5	C18—N3—H4N	121 (4)
C2—C9—H9B	109.5	C17—N3—H4N	127 (4)

H9A—C9—H9B	109.5	C18—N4—H5N	115 (3)
C2—C9—H9C	109.5	C18—N4—H6N	115 (2)
H9A—C9—H9C	109.5	H5N—N4—H6N	118 (3)
H9B—C9—H9C	109.5	C18—S2—C12	90.03 (13)
C5—C10—H10A	109.5	O4—C26—O3	122.7 (3)
C5—C10—H10B	109.5	O4—C26—C25	121.1 (3)
H10A—C10—H10B	109.5	O3—C26—C25	116.1 (2)
C5—C10—H10C	109.5	C26—C25—C24	114.4 (2)
H10A—C10—H10C	109.5	C26—C25—H25A	108.7
H10B—C10—H10C	109.5	C24—C25—H25A	108.7
C5—C11—H11A	109.5	C26—C25—H25B	108.7
C5—C11—H11B	109.5	C24—C25—H25B	108.7
H11A—C11—H11B	109.5	H25A—C25—H25B	107.6
C5—C11—H11C	109.5	C23—C24—C25	114.6 (2)
H11A—C11—H11C	109.5	C23—C24—H24A	108.6
H11B—C11—H11C	109.5	C25—C24—H24A	108.6
C7—N1—C6	113.7 (2)	C23—C24—H24B	108.6
C7—N1—H1N	118.6 (18)	C25—C24—H24B	108.6
C6—N1—H1N	127.6 (18)	H24A—C24—H24B	107.6
C7—N2—H2N	120 (2)	O2—C23—O1	124.5 (3)
C7—N2—H3N	117 (3)	O2—C23—C24	118.2 (2)
H2N—N2—H3N	121 (4)	O1—C23—C24	117.3 (2)
C7—S1—C1	90.11 (13)	C26—O3—H1O	117 (5)
C17—C12—C13	127.2 (3)		
C6—C1—C2—C8	117.8 (4)	N1—C7—S1—C1	0.3 (2)
S1—C1—C2—C8	-61.8 (3)	C6—C1—S1—C7	0.1 (2)
C6—C1—C2—C9	-123.7 (3)	C2—C1—S1—C7	179.7 (2)
S1—C1—C2—C9	56.7 (3)	C17—C12—C13—C19	105.9 (4)
C6—C1—C2—C3A	-14.8 (5)	S2—C12—C13—C19	-74.9 (3)
S1—C1—C2—C3A	165.7 (3)	C17—C12—C13—C20	-133.5 (3)
C6—C1—C2—C3B	17.2 (6)	S2—C12—C13—C20	45.7 (3)
S1—C1—C2—C3B	-162.3 (5)	C17—C12—C13—C14	-15.3 (4)
C1—C2—C3A—C4A	47.7 (6)	S2—C12—C13—C14	163.9 (2)
C8—C2—C3A—C4A	-78.9 (5)	C12—C13—C14—C15	45.6 (3)
C9—C2—C3A—C4A	162.2 (5)	C19—C13—C14—C15	-74.9 (3)
C2—C3A—C4A—C5	-70.2 (6)	C20—C13—C14—C15	164.5 (3)
C1—C2—C3B—C4B	-46.1 (9)	C13—C14—C15—C16	-63.9 (4)
C8—C2—C3B—C4B	-158.7 (8)	C14—C15—C16—C17	42.2 (3)
C9—C2—C3B—C4B	84.4 (9)	C14—C15—C16—C22	-78.1 (3)
C2—C3B—C4B—C5	62.4 (12)	C14—C15—C16—C21	161.6 (3)
C3B—C4B—C5—C6	-40.4 (10)	C13—C12—C17—N3	177.9 (3)
C3B—C4B—C5—C10	89.8 (8)	S2—C12—C17—N3	-1.4 (3)
C3B—C4B—C5—C11	-154.4 (8)	C13—C12—C17—C16	-1.9 (4)
C3A—C4A—C5—C6	49.7 (6)	S2—C12—C17—C16	178.8 (2)
C3A—C4A—C5—C10	164.7 (5)	C22—C16—C17—C12	110.0 (3)
C3A—C4A—C5—C11	-75.9 (5)	C21—C16—C17—C12	-129.4 (3)
C2—C1—C6—N1	-179.9 (3)	C15—C16—C17—C12	-11.0 (4)

S1—C1—C6—N1	-0.4 (3)	C22—C16—C17—N3	-69.8 (3)
C2—C1—C6—C5	-0.4 (5)	C21—C16—C17—N3	50.8 (3)
S1—C1—C6—C5	179.2 (2)	C15—C16—C17—N3	169.2 (3)
C4B—C5—C6—C1	10.6 (6)	N4—C18—N3—C17	-177.9 (3)
C10—C5—C6—C1	-125.7 (3)	S2—C18—N3—C17	-0.6 (3)
C11—C5—C6—C1	114.7 (3)	C12—C17—N3—C18	1.3 (3)
C4A—C5—C6—C1	-16.8 (4)	C16—C17—N3—C18	-178.9 (2)
C4B—C5—C6—N1	-169.9 (5)	N3—C18—S2—C12	-0.2 (2)
C10—C5—C6—N1	53.8 (4)	N4—C18—S2—C12	177.2 (3)
C11—C5—C6—N1	-65.8 (4)	C17—C12—S2—C18	0.9 (2)
C4A—C5—C6—N1	162.8 (4)	C13—C12—S2—C18	-178.4 (2)
N2—C7—N1—C6	178.3 (3)	O4—C26—C25—C24	4.3 (4)
S1—C7—N1—C6	-0.5 (3)	O3—C26—C25—C24	-174.1 (3)
C1—C6—N1—C7	0.6 (3)	C26—C25—C24—C23	170.2 (3)
C5—C6—N1—C7	-179.0 (2)	C25—C24—C23—O2	-18.9 (4)
N2—C7—S1—C1	-178.5 (3)	C25—C24—C23—O1	163.5 (3)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1N...O1	0.93 (3)	1.70 (3)	2.632 (3)	175 (3)
N2—H2N...O4 ⁱ	0.89 (4)	1.98 (4)	2.779 (3)	149 (3)
N2—H3N...O2	0.82 (4)	1.89 (4)	2.716 (4)	176 (4)
N3—H4N...O3	0.87 (8)	1.73 (8)	2.594 (3)	166 (6)
N4—H5N...O2 ⁱⁱ	0.82 (4)	2.07 (4)	2.804 (4)	148 (4)
N4—H6N...O4	0.92 (4)	1.93 (4)	2.842 (4)	169 (3)
O3—H1O...N3	0.82 (10)	1.78 (10)	2.594 (3)	174 (8)

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