

4-Amino-5-(4-bromobenzoyl)-3-(benzo[*d*]thiazol-2-yl)-2-[(2',3',4',6'-tetra-*O*-acetyl- β -D-galactopyranosyl)sulfanyl]thiophene

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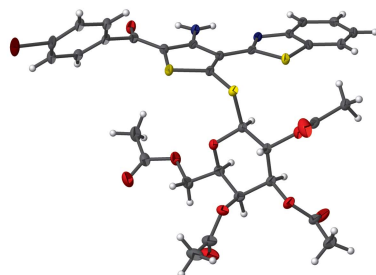
Keywords: benzothiazole; thiophene; galactose; crystal structure.

CCDC reference: 2167334

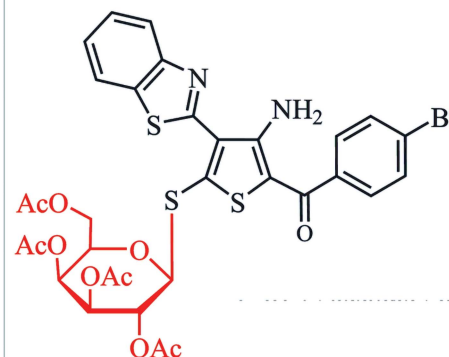
Structural data: full structural data are available from iucrdata.iucr.org^aChemistry Department, Faculty of Science, Helwan University, Cairo, Egypt, and ^bInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany.*Correspondence e-mail: p.jones@tu-bs.de

In the title compound, C₃₂H₂₉BrN₂O₁₀S₃, the benzothiazole and thiophene ring systems subtend an interplanar angle of 7.43 (12)°. The NH₂ group forms intramolecular hydrogen bonds to N_{thiazole} and O_{carbonyl}. The S_{galactose}—C_{thiophene} bond is short [1.759 (2) Å]. The molecules are connected to form ribbons parallel to the *b* axis by two 'weak' hydrogen bonds and a short N_{amino}···S_{galactose} contact.

3D view



Chemical scheme



Structure description

Benzothiazoles are the most widely applied class of heterocyclic compounds in medicinal chemistry, and benzothiazole derivatives have been employed in many pharmaceutical preparations (Bonde *et al.*, 2015), because they offer a variety of pharmacological properties useful in treating many diseases (Wang *et al.*, 2009). As clinical drugs, they often act with high therapeutic efficacy (Huang *et al.*, 2009). The broad pharmacological activities of benzothiazoles suggest that they are also important for developing future drugs (Rana *et al.*, 2008). Recently we have explored various novel synthetic methods to obtain benzothiazole derivatives (Azzam *et al.* 2017*a,b*, 2020*a,b,c*, 2021; Elgemeie *et al.*, 2000*a,b*; 2020*a*).

As a part of our current plan directed toward discovering synthetic methodologies for the preparation of *S*-glycosylated derivatives of heterocyclic nitrogen bases (Elgemeie *et al.*, 2017*a,b,c*), we have lately described the synthesis and biological activity of a series of heterocyclic *S*-glycosides that have promising cytotoxic activity (Abu-Zaied *et al.*, 2011, 2019*a,b*, 2020, 2021; Elgemeie *et al.*, 2009, 2018). We found that our reported dihydropyridine *S*-glycosides have a strong anti-*P*-glycoprotein effect against human tumor cells

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.703 (2)	S2—C12	1.733 (2)
S1—C5	1.731 (2)	S3—C2	1.759 (2)
S2—C6	1.762 (2)	S3—C31	1.819 (2)
C2—S1—C5	92.15 (12)	N1—C6—S2	115.18 (17)
C12—S2—C6	88.99 (12)	N1—C7—C12	114.8 (2)
C2—S3—C31	98.36 (11)	C7—C12—S2	109.94 (17)
C6—N1—C7	111.1 (2)		
O1—C31—C32—C33	53.1 (2)	C32—C33—C34—C35	48.1 (3)
C31—O1—C35—C34	69.4 (2)	C33—C34—C35—O1	−57.9 (3)
C31—C32—C33—C34	−45.9 (3)	C35—O1—C31—C32	−66.0 (2)

(Scala *et al.*, 1997). Consistent with these outcomes and our past research (Elgemeie *et al.*, 2015, 2016, 2019, 2020*b*), the purpose of the current study was to design and synthesize benzothiazole-based thiophene thioglycosides. The synthesis of our target benzothiazole-2-thiophene thioglycoside was carried out by the reaction of benzothiazole 2-thiophenethiol derivative **1** with 2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl bromide **2** in the presence of potassium hydroxide to give the corresponding benzothiazole-2-thiophene *S*-glycoside **3** in good yield (Fig. 1). It has been suggested that the *cis*-(α) sugars react *via* a simple S_N2 reaction to give the β -glycoside products such as **3** (Masoud *et al.*, 2017; Hammad *et al.*, 2018). The structure of **3** was confirmed based on the spectroscopic data (^{13}C NMR, ^1H NMR, and IR). The ^1H NMR spectrum of compound **3** showed the anomeric proton as a doublet at $\delta = 5.39$ p.p.m. with a spin–spin coupling constant ($J_{1',2'} = 8.8$ Hz) confirming the β -configuration. The other six protons of

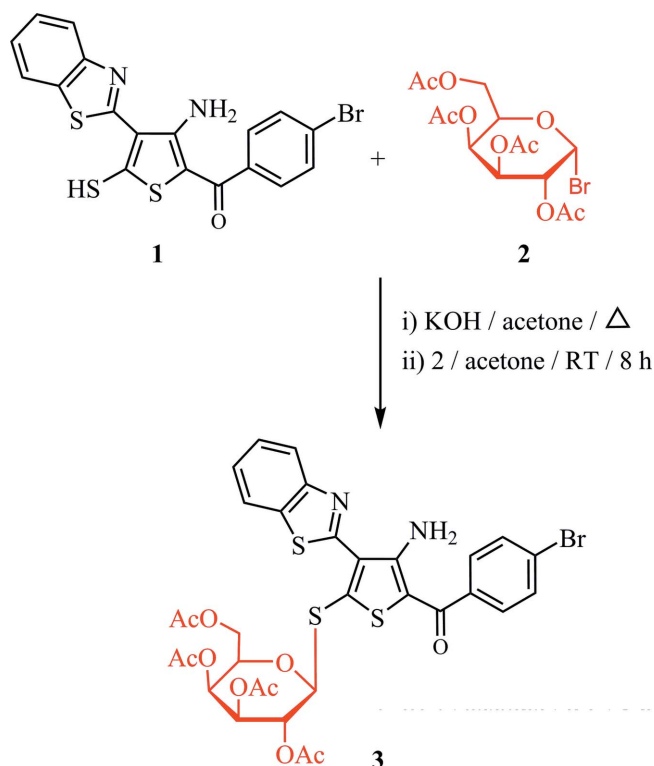


Figure 1
Reaction scheme.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H01 \cdots N1	0.86 (3)	2.12 (3)	2.746 (3)	129 (3)
N2—H02 \cdots O10	0.86 (3)	2.14 (3)	2.795 (3)	133 (3)
C31—H31 \cdots O6 ⁱ	1.00	2.34	3.290 (3)	158
C36—H36B \cdots O9 ⁱⁱ	0.99	2.33	3.294 (4)	164

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

galactose resonated at δ 4.00–5.30 p.p.m. In order to establish the structure of the product unambiguously, its crystal structure was determined and is reported here. To the best of our knowledge, this is the first reported X-ray structure of the new compound type benzothiazole-2-thiophene thioglycoside.

The structure of **3** is shown in Fig. 2. The dimensions of the benzothiazole moiety are as expected (a selection of molecular dimensions is presented in Table 1). The benzothiazole and thiophene ring systems are approximately coplanar [interplanar angle 7.43 (12) $^\circ$], a geometry that is reinforced by the two intramolecular hydrogen bonds from the NH_2 group to the thiazole nitrogen atom and the $\text{C}=\text{O}$ group (Table 2), whereas the bromophenyl and thiophene rings subtend an angle of 58.23 (6) $^\circ$. The intramolecular $\text{S}2\cdots\text{S}3$ contact is 3.1416 (8) Å.

The β configuration (equatorial position of the sulfur atom) at the anomeric carbon of the sugar (here C31) is confirmed, as is the axial configuration of the substituent at C34, characteristic of galactose. The galactose ring displays a slightly

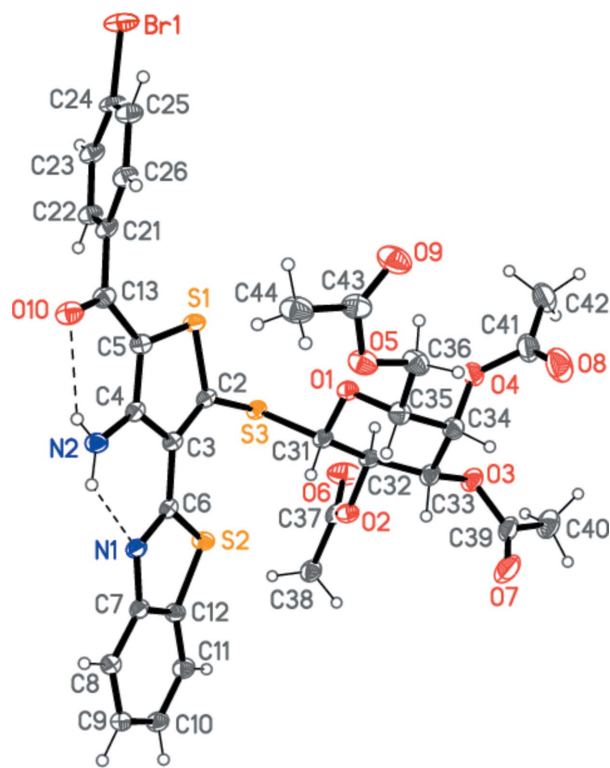


Figure 2
The molecule of **3** in the crystal. Ellipsoids represent 50% probability levels. The dashed lines indicate intramolecular hydrogen bonds.

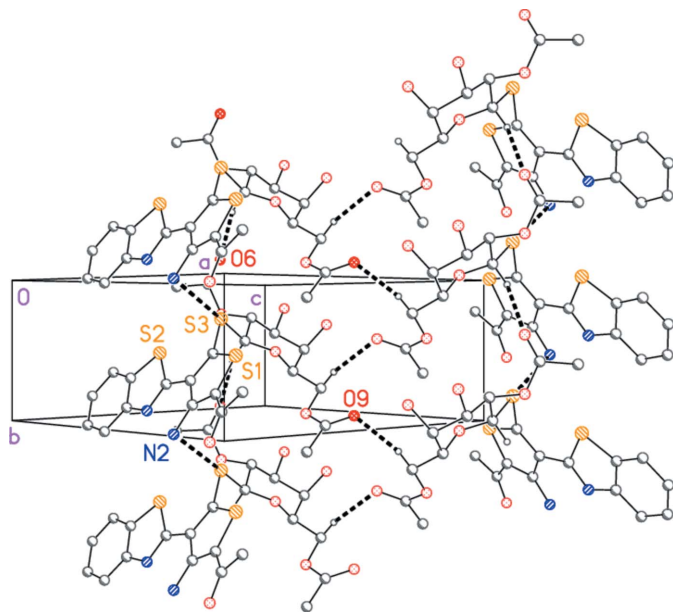


Figure 3
Crystal packing of **3** viewed perpendicular to $(10\bar{1})$ in the region $x \simeq 0.75$, $z \simeq 0.25$. For clarity, the following atoms/groups have been omitted: Hydrogen atoms not involved in ‘weak’ hydrogen bonding; two acetyl groups; the bromophenyl groups (except the *ipso* carbon atom). Dashed lines indicate hydrogen bonds or $N \cdots S$ contacts.

flattened chair conformation, with absolute torsion angles $< 50^\circ$ about C32–C33 and C33–C34. The configurations at C31–C35 are *S*, *R*, *S*, *R*, *R*, respectively. The S3–C31 bond is as expected longer than S3–C2, with values of 1.819 (2) and 1.759 (2) Å, respectively; the latter is significantly shorter than the values found for similar compounds in search of the Cambridge Structural Database (Groom *et al.*, 2016; performed using *CONQUEST* Version 2021.3.0) for purely organic galactose derivatives substituted with a sulfur atom at the anomeric carbon. There were 22 hits, of which two were axially substituted (NODQEC, Khair *et al.*, 1997; YINFUY, Smith *et al.*, 2013) and the remainder equatorially substituted. The 29 C–S bond lengths for the latter lay in the range 1.788–1.856, average 1.808 (13) Å. Restricting the analysis to the ten hits with an sp^2 carbon atom altered these values only marginally.

The N–H donor groups do not participate in intermolecular hydrogen bonding, but two short and acceptably linear C–H \cdots O contacts between the galactose moieties may be classed as ‘weak’ hydrogen bonds (Table 2). Additionally, a short contact $N2 \cdots S3$ of 3.249 (2) Å is observed (operator x , $1 + y$, z). The net effect is to form ribbons of molecules parallel to the b axis (Fig. 3).

Synthesis and crystallization

Thiophene thiol derivative **1** (2.23 g, 5 mmol) was dissolved in acetone (10 ml) containing 0.5 ml of aq. KOH (0.25 g, 5 mmol). The mixture was warmed to 50°C for 15 min. After cooling, a solution of 2,3,4,6-tetra-*O*-acetyl- β -D-galacto-

Table 3
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{32}\text{H}_{29}\text{BrN}_2\text{O}_{10}\text{S}_3$
M_r	777.66
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a , b , c (Å)	16.99261 (18), 6.02635 (7), 17.4076 (2)
β ($^\circ$)	107.8307 (12)
V (Å ³)	1696.97 (3)
Z	2
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	3.89
Crystal size (mm)	0.15 \times 0.06 \times 0.02
Data collection	
Diffractometer	XtaLAB Synergy
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2021)
T_{\min} , T_{\max}	0.781, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	107906, 7129, 7052
R_{int}	0.032
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.634
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.062, 1.04
No. of reflections	7129
No. of parameters	445
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.37, -0.72
Absolute structure	Flack x determined using 3095 quotients $[(I^-)-(I^+)]/[(I^+)+(I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.019 (7)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *XP* (Siemens, 1994) and *OLEX2* (Dolomanov *et al.*, 2009).

pyranosyl bromide **2** (2.05 g, 5 mmol) in acetone (10 ml) was added dropwise over 30 min. The reaction mixture was stirred at room temperature and monitored by TLC until the reaction was complete (8 h). The residue was washed with distilled water to remove KBr, then dried and crystallized from ethanol to produce compound **3** (Fig. 1).

Yellow solid, yield 65%, m.p. 403–405 K (EtOH); IR (KBr, cm^{-1}): ν 3406–3281 (NH₂), 2923 (ArCH), 1748 (4Ac-CO), 1720 (CO); ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.89, 1.91, 1.94, 2.01 (4 *s*, 12H, 4 \times OAc), 4.00–4.02 (*m*, 2H, H-6'), 4.32 (*t*, $J = 6.0$ Hz, 1H, H-5'), 5.15 (*t*, $J = 8.0$ Hz, 1H, H-4'), 5.25–5.30 (*m*, 2H, H-3', H-2'), 5.39 (*d*, $J = 8.8$ Hz, 1H, H-1'), 7.52 (*t*, $J = 7.4$ Hz, 1H, benzothiazole-H), 7.61 (*t*, $J = 7.4$ Hz, 1H, benzothiazole-H), 7.77–7.79 (*m*, 4H, Ar-H), 8.14 (*d*, $J = 7.6$ Hz, 1H, benzothiazole-H), 8.21 (*d*, $J = 8.0$ Hz, 1H, benzothiazole-H), 8.93 (*s*, *br*, D₂O exch., 2H, NH₂); Analysis: calculated for $\text{C}_{32}\text{H}_{29}\text{BrN}_2\text{O}_{10}\text{S}_3$ (777.68): C, 49.42; H, 3.76; N, 3.60; S, 12.37%. Found: C, 49.39; H, 3.73; N, 3.67; S, 12.40%.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Acknowledgements

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full crystallographic data

IUCrData (2022). 7, x220412 [https://doi.org/10.1107/S2414314622004126]

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Crystal data

$C_{32}H_{29}BrN_2O_{10}S_3$

$M_r = 777.66$

Monoclinic, $P2_1$

$a = 16.99261$ (18) Å

$b = 6.02635$ (7) Å

$c = 17.4076$ (2) Å

$\beta = 107.8307$ (12)°

$V = 1696.97$ (3) Å³

$Z = 2$

$F(000) = 796$

$D_x = 1.522$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 91570 reflections

$\theta = 2.7$ – 77.5 °

$\mu = 3.89$ mm⁻¹

$T = 100$ K

Lath, pale yellow

$0.15 \times 0.06 \times 0.02$ mm

Data collection

XtaLAB Synergy

diffractometer

Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2021)

$T_{\min} = 0.781$, $T_{\max} = 1.000$

107906 measured reflections

7129 independent reflections

7052 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 77.8$ °, $\theta_{\min} = 2.7$ °

$h = -21 \rightarrow 21$

$k = -7 \rightarrow 7$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.062$

$S = 1.04$

7129 reflections

445 parameters

2 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.6757P]$

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

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.72$ e Å⁻³

Absolute structure: Flack x determined using

3095 quotients $[(I^-)-(I^+)]/[(I^-)+(I^+)]$ (Parsons et al., 2013)

Absolute structure parameter: -0.019 (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.

Short contacts:

3.1416 (0.0008) S2 - S3 3.2493 (0.0021) N2 - S3_2

Operator \$2 : x,l+y,z

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

- 1.7949 (0.0074) x + 2.7373 (0.0043) y + 15.2223 (0.0070) z = 2.9267 (0.0054)

* 0.0402 (0.0013) C2 * -0.0135 (0.0017) N1 * -0.0086 (0.0019) C6 * -0.0308 (0.0020) C7 * -0.0016 (0.0018) C8 * 0.0379 (0.0020) C9 * 0.0338 (0.0019) C10 * -0.0142 (0.0018) C11 * -0.0432 (0.0020) C12

Rms deviation of fitted atoms = 0.0288

- 0.0073 (0.0162) x + 3.1508 (0.0048) y + 14.1284 (0.0110) z = 4.2446 (0.0123)

Angle to previous plane (with approximate esd) = 7.434 (0.118)

* 0.0061 (0.0010) S1 * 0.0046 (0.0013) C2 * -0.0152 (0.0014) C3 * 0.0207 (0.0014) C4 * -0.0162 (0.0013) C5 0.0201 (0.0033) S3 0.0387 (0.0033) N2 -0.1146 (0.0038) C13 0.0343 (0.0044) O10

Rms deviation of fitted atoms = 0.0140

5.5692 (0.0163) x + 2.3719 (0.0054) y - 15.9799 (0.0068) z = 5.2155 (0.0164)

Angle to previous plane (with approximate esd) = 58.230 (0.061)

* -0.0124 (0.0016) C21 * -0.0049 (0.0017) C22 * 0.0186 (0.0017) C23 * -0.0152 (0.0018) C24 * -0.0023 (0.0018) C25 * 0.0162 (0.0017) C26 -0.0309 (0.0037) C13 0.8520 (0.0040) O10 -0.1298 (0.0035) Br1

Rms deviation of fitted atoms = 0.0130

Refinement. The hydrogen atoms of the NH₂ group were refined freely, but with N—H distances restrained to be approximately equal (SADI). The methyl groups were refined as idealized rigid groups allowed to rotate but not tip, with C—H 0.98 Å and H—C—H 109.5°. Other hydrogens were included using a riding model starting from calculated positions (C—H_{aromatic} 0.95, C—H_{methylene} 0.99, C—H_{methine} 1.00 Å). The U(H) values were fixed at 1.5 or 1.2 times the equivalent U_{iso} value of the parent carbon atoms for methyl and non-methyl hydrogens respectively.

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

	x	y	z	U _{iso} */U _{eq}
Br1	1.17709 (2)	0.30260 (5)	0.13689 (2)	0.03408 (9)
S1	0.81796 (3)	0.50666 (10)	0.18829 (3)	0.01870 (11)
S2	0.51931 (3)	0.50194 (10)	0.15908 (3)	0.01913 (11)
S3	0.69078 (3)	0.27394 (9)	0.24112 (3)	0.01767 (11)
O1	0.76755 (10)	0.4911 (3)	0.37404 (9)	0.0193 (3)
O2	0.56621 (10)	0.2394 (3)	0.34351 (10)	0.0210 (3)
O3	0.64615 (12)	0.2015 (3)	0.51551 (11)	0.0263 (4)
O4	0.80626 (10)	0.3125 (3)	0.53459 (9)	0.0236 (3)
O5	0.85216 (11)	0.8993 (3)	0.41271 (12)	0.0287 (4)
O6	0.57638 (13)	-0.1299 (4)	0.33101 (15)	0.0391 (5)
O7	0.55812 (15)	0.4238 (4)	0.55315 (13)	0.0413 (5)
O8	0.86193 (15)	0.5092 (5)	0.64867 (13)	0.0468 (6)
O9	0.98997 (13)	0.9040 (4)	0.46564 (14)	0.0394 (5)
O10	0.85254 (11)	1.0388 (3)	0.07162 (11)	0.0243 (4)
N1	0.54299 (12)	0.8799 (3)	0.09717 (11)	0.0180 (4)
N2	0.69030 (12)	1.0127 (4)	0.07769 (12)	0.0196 (4)
H01	0.6390 (17)	1.048 (6)	0.0665 (18)	0.023 (8)*
H02	0.726 (2)	1.093 (6)	0.065 (2)	0.039 (10)*

C2	0.71837 (13)	0.4982 (4)	0.19001 (13)	0.0177 (4)
C3	0.67073 (14)	0.6741 (4)	0.14936 (13)	0.0167 (4)
C4	0.71933 (13)	0.8253 (4)	0.11822 (12)	0.0171 (4)
C5	0.80082 (14)	0.7495 (4)	0.13255 (13)	0.0188 (5)
C6	0.58211 (14)	0.7040 (4)	0.13374 (13)	0.0166 (4)
C7	0.45902 (14)	0.8671 (4)	0.08844 (13)	0.0174 (4)
C8	0.40068 (14)	1.0310 (4)	0.05402 (13)	0.0204 (5)
H8	0.416201	1.161819	0.031863	0.025*
C9	0.31929 (14)	0.9979 (5)	0.05296 (14)	0.0220 (5)
H9	0.278981	1.108347	0.030320	0.026*
C10	0.29589 (13)	0.8040 (5)	0.08480 (13)	0.0226 (5)
H10	0.240008	0.785287	0.083586	0.027*
C11	0.35290 (15)	0.6397 (4)	0.11791 (14)	0.0215 (5)
H11	0.336876	0.507638	0.138925	0.026*
C12	0.43461 (14)	0.6732 (4)	0.11962 (13)	0.0186 (4)
C13	0.86263 (14)	0.8523 (4)	0.10269 (14)	0.0196 (5)
C21	0.93984 (14)	0.7229 (4)	0.10924 (14)	0.0192 (5)
C22	0.93411 (14)	0.5116 (4)	0.07541 (14)	0.0214 (5)
H22	0.881300	0.450400	0.048610	0.026*
C23	1.00516 (15)	0.3892 (4)	0.08054 (15)	0.0221 (5)
H23	1.001565	0.247432	0.055855	0.026*
C24	1.08128 (14)	0.4797 (5)	0.12261 (15)	0.0241 (5)
C25	1.08860 (15)	0.6910 (5)	0.15573 (16)	0.0248 (5)
H25	1.141475	0.750716	0.183250	0.030*
C26	1.01739 (14)	0.8141 (5)	0.14802 (14)	0.0219 (5)
H26	1.021491	0.960444	0.169162	0.026*
C31	0.68674 (14)	0.4215 (4)	0.33099 (14)	0.0177 (4)
H31	0.649650	0.553540	0.315148	0.021*
C32	0.65357 (13)	0.2649 (4)	0.38322 (13)	0.0189 (5)
H32	0.682566	0.118429	0.390455	0.023*
C33	0.66127 (15)	0.3731 (4)	0.46429 (14)	0.0211 (5)
H33	0.617097	0.488234	0.456146	0.025*
C34	0.74480 (15)	0.4824 (4)	0.50439 (14)	0.0225 (5)
H34	0.740969	0.577656	0.550143	0.027*
C35	0.76617 (15)	0.6258 (4)	0.44166 (14)	0.0221 (5)
H35	0.722698	0.742486	0.422673	0.026*
C36	0.84913 (16)	0.7367 (5)	0.47261 (16)	0.0277 (5)
H36A	0.855276	0.809402	0.525127	0.033*
H36B	0.894073	0.626681	0.479826	0.033*
C37	0.53570 (15)	0.0359 (4)	0.31928 (14)	0.0222 (5)
C38	0.44510 (15)	0.0517 (5)	0.27487 (15)	0.0255 (5)
H38A	0.417097	0.130629	0.308282	0.038*
H38B	0.421897	-0.097856	0.263079	0.038*
H38C	0.437085	0.132674	0.224223	0.038*
C39	0.59276 (16)	0.2497 (5)	0.55765 (15)	0.0279 (6)
C40	0.5876 (2)	0.0572 (6)	0.61001 (17)	0.0354 (7)
H40A	0.578982	-0.079620	0.578079	0.053*
H40B	0.541162	0.079141	0.631549	0.053*

H40C	0.639093	0.045837	0.654741	0.053*
C41	0.86038 (18)	0.3428 (5)	0.60992 (15)	0.0326 (6)
C42	0.9152 (2)	0.1462 (6)	0.63644 (17)	0.0375 (7)
H42A	0.883168	0.022697	0.648177	0.056*
H42B	0.960362	0.183859	0.685145	0.056*
H42C	0.938204	0.102746	0.593438	0.056*
C43	0.92782 (16)	0.9685 (5)	0.41543 (17)	0.0283 (5)
C44	0.92423 (18)	1.1323 (5)	0.3502 (2)	0.0352 (6)
H44A	0.890426	1.072087	0.298245	0.053*
H44B	0.980271	1.161330	0.348046	0.053*
H44C	0.899639	1.270909	0.361338	0.053*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01892 (12)	0.02848 (15)	0.05928 (18)	0.00424 (11)	0.01851 (11)	0.00576 (13)
S1	0.0151 (2)	0.0187 (3)	0.0240 (2)	0.0015 (2)	0.00866 (19)	0.0033 (2)
S2	0.0149 (2)	0.0184 (3)	0.0248 (2)	-0.0013 (2)	0.00720 (19)	0.0027 (2)
S3	0.0188 (2)	0.0162 (3)	0.0201 (2)	0.0004 (2)	0.00916 (18)	0.0012 (2)
O1	0.0162 (7)	0.0215 (9)	0.0208 (7)	-0.0012 (7)	0.0064 (6)	-0.0001 (7)
O2	0.0178 (8)	0.0197 (9)	0.0268 (8)	-0.0013 (6)	0.0088 (6)	-0.0008 (6)
O3	0.0289 (9)	0.0290 (10)	0.0255 (8)	-0.0005 (8)	0.0151 (7)	0.0046 (7)
O4	0.0246 (8)	0.0248 (9)	0.0191 (7)	0.0013 (8)	0.0035 (6)	-0.0013 (7)
O5	0.0223 (9)	0.0254 (10)	0.0370 (10)	-0.0040 (7)	0.0071 (7)	0.0052 (8)
O6	0.0286 (10)	0.0248 (11)	0.0613 (13)	0.0015 (8)	0.0100 (9)	-0.0130 (9)
O7	0.0529 (14)	0.0450 (14)	0.0372 (11)	0.0105 (11)	0.0305 (10)	0.0039 (9)
O8	0.0534 (14)	0.0464 (14)	0.0312 (10)	0.0093 (12)	-0.0011 (9)	-0.0112 (10)
O9	0.0244 (10)	0.0413 (12)	0.0470 (12)	-0.0057 (9)	0.0030 (9)	0.0085 (10)
O10	0.0228 (8)	0.0182 (9)	0.0351 (9)	-0.0009 (7)	0.0136 (7)	0.0034 (7)
N1	0.0163 (9)	0.0204 (10)	0.0189 (8)	0.0004 (7)	0.0079 (7)	-0.0008 (7)
N2	0.0170 (9)	0.0187 (10)	0.0245 (9)	0.0019 (8)	0.0088 (7)	0.0051 (8)
C2	0.0165 (10)	0.0193 (11)	0.0194 (9)	-0.0007 (9)	0.0086 (8)	-0.0017 (9)
C3	0.0164 (10)	0.0167 (11)	0.0181 (10)	-0.0011 (8)	0.0071 (8)	-0.0014 (8)
C4	0.0177 (10)	0.0183 (11)	0.0166 (9)	-0.0018 (9)	0.0071 (8)	-0.0014 (9)
C5	0.0172 (10)	0.0188 (12)	0.0209 (10)	0.0000 (8)	0.0068 (8)	-0.0005 (8)
C6	0.0179 (11)	0.0180 (11)	0.0157 (9)	-0.0009 (8)	0.0079 (8)	-0.0008 (8)
C7	0.0157 (10)	0.0207 (12)	0.0167 (9)	-0.0014 (8)	0.0061 (8)	-0.0022 (8)
C8	0.0187 (11)	0.0239 (13)	0.0195 (10)	0.0021 (9)	0.0071 (8)	0.0024 (9)
C9	0.0180 (11)	0.0281 (13)	0.0201 (10)	0.0054 (10)	0.0063 (8)	0.0005 (10)
C10	0.0158 (9)	0.0303 (13)	0.0226 (10)	-0.0015 (11)	0.0073 (8)	-0.0014 (11)
C11	0.0173 (11)	0.0246 (13)	0.0240 (11)	-0.0039 (9)	0.0083 (9)	0.0001 (9)
C12	0.0160 (11)	0.0207 (12)	0.0191 (10)	-0.0002 (9)	0.0053 (8)	-0.0010 (9)
C13	0.0187 (10)	0.0193 (12)	0.0219 (10)	-0.0029 (8)	0.0076 (8)	-0.0023 (8)
C21	0.0190 (11)	0.0195 (11)	0.0227 (10)	-0.0026 (9)	0.0116 (9)	0.0016 (9)
C22	0.0182 (11)	0.0215 (12)	0.0267 (11)	-0.0021 (10)	0.0099 (9)	0.0004 (10)
C23	0.0211 (11)	0.0192 (11)	0.0299 (12)	-0.0015 (9)	0.0136 (9)	0.0003 (9)
C24	0.0159 (11)	0.0260 (13)	0.0346 (12)	0.0032 (10)	0.0138 (9)	0.0053 (11)
C25	0.0172 (11)	0.0260 (13)	0.0326 (13)	-0.0031 (10)	0.0097 (9)	-0.0001 (10)

C26	0.0210 (10)	0.0201 (12)	0.0266 (10)	-0.0026 (10)	0.0102 (9)	0.0007 (10)
C31	0.0165 (10)	0.0179 (11)	0.0200 (10)	-0.0003 (9)	0.0077 (8)	0.0010 (8)
C32	0.0162 (10)	0.0197 (13)	0.0223 (10)	-0.0010 (9)	0.0079 (8)	0.0010 (9)
C33	0.0224 (11)	0.0221 (12)	0.0215 (10)	-0.0003 (9)	0.0104 (9)	0.0028 (9)
C34	0.0242 (12)	0.0227 (12)	0.0210 (10)	0.0008 (10)	0.0075 (9)	-0.0019 (10)
C35	0.0222 (12)	0.0207 (12)	0.0228 (11)	-0.0014 (9)	0.0061 (9)	-0.0022 (9)
C36	0.0234 (12)	0.0269 (14)	0.0296 (12)	-0.0057 (10)	0.0035 (10)	0.0014 (10)
C37	0.0235 (12)	0.0234 (13)	0.0235 (11)	-0.0033 (10)	0.0128 (9)	-0.0038 (10)
C38	0.0216 (11)	0.0326 (15)	0.0242 (11)	-0.0063 (10)	0.0096 (9)	-0.0028 (10)
C39	0.0280 (12)	0.0387 (17)	0.0202 (11)	-0.0052 (11)	0.0122 (9)	-0.0025 (10)
C40	0.0403 (16)	0.0407 (18)	0.0300 (13)	-0.0078 (13)	0.0180 (12)	0.0024 (12)
C41	0.0381 (14)	0.0354 (17)	0.0215 (11)	0.0039 (12)	0.0050 (10)	-0.0017 (11)
C42	0.0414 (16)	0.0391 (17)	0.0253 (13)	0.0087 (13)	0.0002 (12)	-0.0012 (12)
C43	0.0227 (12)	0.0249 (13)	0.0361 (13)	-0.0042 (10)	0.0072 (10)	-0.0019 (11)
C44	0.0258 (13)	0.0321 (16)	0.0474 (16)	-0.0016 (12)	0.0109 (12)	0.0085 (13)

Geometric parameters (Å, °)

Br1—C24	1.898 (2)	C24—C25	1.388 (4)
S1—C2	1.703 (2)	C25—C26	1.390 (4)
S1—C5	1.731 (2)	C31—C32	1.532 (3)
S2—C6	1.762 (2)	C32—C33	1.523 (3)
S2—C12	1.733 (2)	C33—C34	1.526 (3)
S3—C2	1.759 (2)	C34—C35	1.521 (3)
S3—C31	1.819 (2)	C35—C36	1.503 (3)
O1—C31	1.412 (3)	C37—C38	1.499 (3)
O1—C35	1.436 (3)	C39—C40	1.494 (4)
O2—C32	1.441 (3)	C41—C42	1.490 (4)
O2—C37	1.348 (3)	C43—C44	1.492 (4)
O3—C33	1.439 (3)	N2—H01	0.86 (3)
O3—C39	1.361 (3)	N2—H02	0.86 (3)
O4—C34	1.442 (3)	C8—H8	0.9500
O4—C41	1.364 (3)	C9—H9	0.9500
O5—C36	1.443 (3)	C10—H10	0.9500
O5—C43	1.338 (3)	C11—H11	0.9500
O6—C37	1.196 (3)	C22—H22	0.9500
O7—C39	1.194 (4)	C23—H23	0.9500
O8—C41	1.205 (4)	C25—H25	0.9500
O9—C43	1.210 (3)	C26—H26	0.9500
O10—C13	1.237 (3)	C31—H31	1.0000
N1—C6	1.308 (3)	C32—H32	1.0000
N1—C7	1.390 (3)	C33—H33	1.0000
N2—C4	1.343 (3)	C34—H34	1.0000
C2—C3	1.389 (3)	C35—H35	1.0000
C3—C4	1.442 (3)	C36—H36A	0.9900
C3—C6	1.457 (3)	C36—H36B	0.9900
C4—C5	1.406 (3)	C38—H38A	0.9800
C5—C13	1.446 (3)	C38—H38B	0.9800

C7—C8	1.398 (3)	C38—H38C	0.9800
C7—C12	1.404 (3)	C40—H40A	0.9800
C8—C9	1.392 (3)	C40—H40B	0.9800
C9—C10	1.402 (4)	C40—H40C	0.9800
C10—C11	1.382 (4)	C42—H42A	0.9800
C11—C12	1.394 (3)	C42—H42B	0.9800
C13—C21	1.500 (3)	C42—H42C	0.9800
C21—C22	1.394 (4)	C44—H44A	0.9800
C21—C26	1.396 (3)	C44—H44B	0.9800
C22—C23	1.394 (3)	C44—H44C	0.9800
C23—C24	1.388 (3)		
C2—S1—C5	92.15 (12)	O4—C41—C42	111.4 (2)
C12—S2—C6	88.99 (12)	O8—C41—O4	122.8 (3)
C2—S3—C31	98.36 (11)	O8—C41—C42	125.7 (3)
C31—O1—C35	110.22 (17)	O5—C43—C44	111.4 (2)
C37—O2—C32	119.22 (19)	O9—C43—O5	122.8 (3)
C39—O3—C33	117.1 (2)	O9—C43—C44	125.8 (3)
C41—O4—C34	117.1 (2)	C4—N2—H01	121 (2)
C43—O5—C36	115.6 (2)	C4—N2—H02	116 (3)
C6—N1—C7	111.1 (2)	H01—N2—H02	123 (3)
S1—C2—S3	116.88 (14)	C9—C8—H8	120.8
C3—C2—S1	113.32 (18)	C7—C8—H8	120.8
C3—C2—S3	129.80 (17)	C8—C9—H9	119.5
C2—C3—C4	111.2 (2)	C10—C9—H9	119.5
C2—C3—C6	126.7 (2)	C11—C10—H10	119.5
C4—C3—C6	122.0 (2)	C9—C10—H10	119.5
N2—C4—C3	124.6 (2)	C10—C11—H11	120.9
N2—C4—C5	123.3 (2)	C12—C11—H11	120.9
C5—C4—C3	112.0 (2)	C21—C22—H22	119.7
C4—C5—S1	111.20 (17)	C23—C22—H22	119.7
C4—C5—C13	125.6 (2)	C24—C23—H23	120.8
C13—C5—S1	123.20 (18)	C22—C23—H23	120.8
N1—C6—S2	115.18 (17)	C24—C25—H25	120.5
N1—C6—C3	122.2 (2)	C26—C25—H25	120.5
C3—C6—S2	122.57 (18)	C25—C26—H26	120.0
N1—C7—C8	125.2 (2)	C21—C26—H26	120.0
N1—C7—C12	114.8 (2)	O1—C31—H31	109.8
C8—C7—C12	120.0 (2)	C32—C31—H31	109.8
C9—C8—C7	118.4 (2)	S3—C31—H31	109.8
C8—C9—C10	121.0 (2)	O2—C32—H32	111.2
C11—C10—C9	121.0 (2)	C33—C32—H32	111.2
C10—C11—C12	118.2 (2)	C31—C32—H32	111.2
C7—C12—S2	109.94 (17)	O3—C33—H33	108.5
C11—C12—S2	128.6 (2)	C32—C33—H33	108.5
C11—C12—C7	121.5 (2)	C34—C33—H33	108.5
O10—C13—C5	121.9 (2)	O4—C34—H34	109.5
O10—C13—C21	120.4 (2)	C35—C34—H34	109.5

C5—C13—C21	117.7 (2)	C33—C34—H34	109.5
C22—C21—C13	119.8 (2)	O1—C35—H35	108.8
C22—C21—C26	119.8 (2)	C36—C35—H35	108.8
C26—C21—C13	120.4 (2)	C34—C35—H35	108.8
C21—C22—C23	120.6 (2)	O5—C36—H36A	110.5
C24—C23—C22	118.4 (2)	C35—C36—H36A	110.5
C23—C24—Br1	118.1 (2)	O5—C36—H36B	110.5
C23—C24—C25	122.0 (2)	C35—C36—H36B	110.5
C25—C24—Br1	119.82 (19)	H36A—C36—H36B	108.7
C24—C25—C26	119.0 (2)	C37—C38—H38A	109.5
C25—C26—C21	120.1 (2)	C37—C38—H38B	109.5
O1—C31—S3	108.36 (15)	H38A—C38—H38B	109.5
O1—C31—C32	110.05 (18)	C37—C38—H38C	109.5
C32—C31—S3	109.08 (16)	H38A—C38—H38C	109.5
O2—C32—C31	107.04 (18)	H38B—C38—H38C	109.5
O2—C32—C33	105.88 (18)	C39—C40—H40A	109.5
C33—C32—C31	110.08 (19)	C39—C40—H40B	109.5
O3—C33—C32	106.6 (2)	H40A—C40—H40B	109.5
O3—C33—C34	110.14 (19)	C39—C40—H40C	109.5
C32—C33—C34	114.36 (19)	H40A—C40—H40C	109.5
O4—C34—C33	109.2 (2)	H40B—C40—H40C	109.5
O4—C34—C35	111.1 (2)	C41—C42—H42A	109.5
C35—C34—C33	108.05 (19)	C41—C42—H42B	109.5
O1—C35—C34	109.6 (2)	H42A—C42—H42B	109.5
O1—C35—C36	107.2 (2)	C41—C42—H42C	109.5
C36—C35—C34	113.5 (2)	H42A—C42—H42C	109.5
O5—C36—C35	106.3 (2)	H42B—C42—H42C	109.5
O2—C37—C38	109.8 (2)	C43—C44—H44A	109.5
O6—C37—O2	124.0 (2)	C43—C44—H44B	109.5
O6—C37—C38	126.1 (2)	H44A—C44—H44B	109.5
O3—C39—C40	109.7 (2)	C43—C44—H44C	109.5
O7—C39—O3	123.3 (2)	H44A—C44—H44C	109.5
O7—C39—C40	127.0 (3)	H44B—C44—H44C	109.5
Br1—C24—C25—C26	-176.89 (19)	C7—N1—C6—S2	1.4 (2)
S1—C2—C3—C4	-2.1 (2)	C7—N1—C6—C3	179.0 (2)
S1—C2—C3—C6	174.13 (19)	C7—C8—C9—C10	-0.7 (3)
S1—C5—C13—O10	-171.04 (18)	C8—C7—C12—S2	-179.43 (18)
S1—C5—C13—C21	10.0 (3)	C8—C7—C12—C11	-0.6 (3)
S3—C2—C3—C4	178.18 (17)	C8—C9—C10—C11	-0.2 (4)
S3—C2—C3—C6	-5.6 (4)	C9—C10—C11—C12	0.7 (4)
S3—C31—C32—O2	-73.6 (2)	C10—C11—C12—S2	178.28 (19)
S3—C31—C32—C33	171.81 (16)	C10—C11—C12—C7	-0.3 (4)
O1—C31—C32—O2	167.69 (18)	C12—S2—C6—N1	-1.70 (18)
O1—C31—C32—C33	53.1 (2)	C12—S2—C6—C3	-179.36 (19)
O1—C35—C36—O5	70.6 (3)	C12—C7—C8—C9	1.1 (3)
O2—C32—C33—O3	76.8 (2)	C13—C21—C22—C23	179.7 (2)
O2—C32—C33—C34	-161.3 (2)	C13—C21—C26—C25	178.3 (2)

O3—C33—C34—O4	47.2 (2)	C21—C22—C23—C24	2.3 (4)
O3—C33—C34—C35	168.1 (2)	C22—C21—C26—C25	-2.6 (4)
O4—C34—C35—O1	61.9 (2)	C22—C23—C24—Br1	174.97 (18)
O4—C34—C35—C36	-58.0 (3)	C22—C23—C24—C25	-3.3 (4)
O10—C13—C21—C22	-123.4 (3)	C23—C24—C25—C26	1.4 (4)
O10—C13—C21—C26	55.7 (3)	C24—C25—C26—C21	1.6 (4)
N1—C7—C8—C9	-177.1 (2)	C26—C21—C22—C23	0.6 (3)
N1—C7—C12—S2	-1.1 (2)	C31—S3—C2—S1	105.40 (14)
N1—C7—C12—C11	177.7 (2)	C31—S3—C2—C3	-74.9 (2)
N2—C4—C5—S1	178.69 (18)	C31—O1—C35—C34	69.4 (2)
N2—C4—C5—C13	-3.7 (4)	C31—O1—C35—C36	-166.9 (2)
C2—S1—C5—C4	1.97 (18)	C31—C32—C33—O3	-167.85 (18)
C2—S1—C5—C13	-175.7 (2)	C31—C32—C33—C34	-45.9 (3)
C2—S3—C31—O1	-66.64 (17)	C32—O2—C37—O6	2.7 (3)
C2—S3—C31—C32	173.56 (15)	C32—O2—C37—C38	-176.21 (19)
C2—C3—C4—N2	-178.6 (2)	C32—C33—C34—O4	-72.8 (2)
C2—C3—C4—C5	3.6 (3)	C32—C33—C34—C35	48.1 (3)
C2—C3—C6—S2	-4.9 (3)	C33—O3—C39—O7	0.9 (4)
C2—C3—C6—N1	177.6 (2)	C33—O3—C39—C40	-177.5 (2)
C3—C4—C5—S1	-3.5 (2)	C33—C34—C35—O1	-57.9 (3)
C3—C4—C5—C13	174.1 (2)	C33—C34—C35—C36	-177.7 (2)
C4—C3—C6—S2	170.96 (17)	C34—O4—C41—O8	-5.0 (4)
C4—C3—C6—N1	-6.5 (3)	C34—O4—C41—C42	174.8 (2)
C4—C5—C13—O10	11.6 (4)	C34—C35—C36—O5	-168.2 (2)
C4—C5—C13—C21	-167.4 (2)	C35—O1—C31—S3	174.79 (15)
C5—S1—C2—S3	179.85 (14)	C35—O1—C31—C32	-66.0 (2)
C5—S1—C2—C3	0.13 (18)	C36—O5—C43—O9	-1.6 (4)
C5—C13—C21—C22	55.6 (3)	C36—O5—C43—C44	178.8 (2)
C5—C13—C21—C26	-125.3 (2)	C37—O2—C32—C31	119.2 (2)
C6—S2—C12—C7	1.47 (17)	C37—O2—C32—C33	-123.3 (2)
C6—S2—C12—C11	-177.2 (2)	C39—O3—C33—C32	-132.7 (2)
C6—N1—C7—C8	178.1 (2)	C39—O3—C33—C34	102.8 (2)
C6—N1—C7—C12	-0.2 (3)	C41—O4—C34—C33	-136.2 (2)
C6—C3—C4—N2	4.9 (3)	C41—O4—C34—C35	104.8 (3)
C6—C3—C4—C5	-172.8 (2)	C43—O5—C36—C35	-160.4 (2)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H01 \cdots N1	0.86 (3)	2.12 (3)	2.746 (3)	129 (3)
N2—H02 \cdots O10	0.86 (3)	2.14 (3)	2.795 (3)	133 (3)
C11—H11 \cdots Br1 ⁱ	0.95	2.97	3.710 (2)	135
C31—H31 \cdots O6 ⁱⁱ	1.00	2.34	3.290 (3)	158
C35—H35 \cdots O6 ⁱⁱ	1.00	2.62	3.532 (3)	151
C36—H36B \cdots O9 ⁱⁱⁱ	0.99	2.33	3.294 (4)	164

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