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# 3-{3,5-Bis[(2-butoxyethoxy)carbonyl]-2,6-dimethyl-1,4-dihydropyridin-4-yl}-1-[(3,4,5-trimethoxybenzoyl)methyl]-pyridinium bromide

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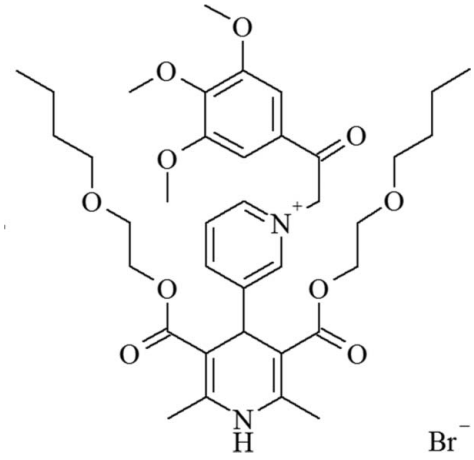
Key indicators: single-crystal X-ray study; $T$ = 190 K; mean $\sigma$(C–C) = 0.004 Å; disorder in main residue; $R$ factor = 0.056; $wR$ factor = 0.127; data-to-parameter ratio = 18.8.

In the title salt, $C_{37}H_{51}N_2O_{10}^{+}\cdot Br^{-}$, the 1,4-dihydropyridine (1,4-DHP) ring adopts a slighly puckered boat conformation. The N and opposite C atoms deviate from the least-squares plane calculated through the four other ring atoms by 0.068 (5) and 0.224 (5) Å, respectively. The orientation of both C=O groups is similar (*cis* with respect to the double bonds of 1,4-DHP. The pyridinium ring has an axial orientation with respect to the1,4-DHP ring and is almost perpendicular to the least-squares plane of the 1,4-DHP ring, making a dihedral angle of 89.2 (3)°. The molecule has a compact shape due to the parallel orientation of the long-chain substituents. One of the butoxy groups was fond to be disordered (occupancy ratio 0.70:0.30). In the crystal, the bromide anion accepts a weak hydrogen bond from the N—H group of a neighboring 1,4-DHP ring.

## Related literature

For general information on the relationship between 1,4-dihydropyridine ring substituents and pharmaceutical effects, see: Hasko & Pacher (2008); Niebauer & Robinson (2006); Ruiz *et al.* (2012); Swarnalatha *et al.* (2011). For the synthesis of the DHP 3-pyridyl derivative, see: Saini *et al.* (2008).



## Experimental

### Crystal data

$C_{37}H_{51}N_2O_{10}^{+}\cdot Br^{-}$
$M_r$ = 763.71
Triclinic, $P\overline{1}$
$a$ = 8.9501 (2) Å
$b$ = 12.4741 (3) Å
$c$ = 17.6994 (5) Å
$\alpha$ = 93.057 (1)°
$\beta$ = 91.658 (1)°
$\gamma$ = 108.024 (1)°
$V$ = 1874.25 (8) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.16 mm$^{-1}$
$T$ = 190 K
0.32 × 0.18 × 0.16 mm

### Data collection

Nonius KappaCCD diffractometer
13618 measured reflections
8822 independent reflections
6509 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.035

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.127
$S$ = 1.03
8822 reflections
469 parameters
4 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.15 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.41 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···Br1$^{i}$ | 0.86 | 2.61 | 3.421 (2) | 157 |

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

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97*.

The study was supported by the Latvian National Research programme 2010–2013 'Development of prevention, treatment, diagnostic means and practices, and biomedicine technologies for improvement of public health'.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VM2184).

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# supporting information

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## 3-{3,5-Bis[(2-butoxyethoxy)carbonyl]-2,6-dimethyl-1,4-dihydropyridin-4-yl}-1-[(3,4,5-trimethoxybenzoyl)methyl]pyridinium bromide

**Imants Bisenieks, Anatoly Mishnev, Imanta Bruvere and Brigita Vigante**

### S1. Comment

Nowadays considerable attention is paid to the synthesis of 1,4-dihydropyridine (1,4-DHP) derivatives because of their wide spectrum of biological activity. Slight variations in 1,4-DHP ring substituents can result in considerable changes in pharmacological effects (Swarnalatha *et al.*, 2011). 1,4-Dihydropyridines are considered as privileged structures, because these compounds are capable to bind to multiple receptors with high affinity (Ruiz *et al.*, 2012).

It was found that the concentration of adenosine, the natural ligand of the $A_{2A}$ receptor, changes in the ischemia, hypoxia and inflammation conditions (Hasko & Pacher, 2008). The $A_{2A}$ receptor is believed to play a role in cardioprotection, inflammation, stroke and certain central nervous system disorders (Niebauer & Robinson, 2006). We were looking for molecules based on 1,4-DHP able to bind $A_{2A}$ adenosine receptors and possessing enhanced water solubility.

Fig. 1 shows a view of the crystal structure of the title compound. For the disordered butoxy fragment only atoms with the higher occupation factor are shown. In the crystal structure, the 1,4-DHP ring adopts a slightly puckered boat conformation. Atoms N1 and C4 deviate from the least-squares plane calculated through the four other ring atoms by 0.068 (5) Å and 0.224 (5) Å, respectively. The orientation of both C=O groups is *cis* with respect to the double bonds of 1,4-DHP. The pyridinium ring has an axial orientation with respect to the 1,4-DHP ring and is almost perpendicular to the least-squares average plane of the 1,4-DHP ring with a dihedral angle between both planes of 89.2 (3)°. The molecule has a compact shape with all long chain substituents oriented approximately in one direction. All bonds in the substituents at the 3 and 5 position of 1,4-DHP have *trans* orientation except for bonds C29B—C30B and C33—C34 (gau*che*$^-$). The bromine anion forms a weak hydrogen bond with N1—H1 of a neighboring 1,4-DHP ring. The distance between the bromine ion and the positively charged N2 atom is 4.185 (5) Å.

### S2. Experimental

First the DHP 3-pyridyl derivative was obtained by means of the Hantzsch method as described by Saini *et al.* (2008). After the structure confirmation the intermediate (1 mmol) was added to *α*-bromo-(3,4,5-trimethoxy)-acetophenone (1 mmol) in 30 ml acetone. Reaction mixture was boiled for 24 h, and after completion (monitored by TLC) cooled to ambient temperature. This procedure gives the title compound pyridinium salt as block crystals, suitable for X-ray analysis. $^1$H-NMR (400 MHz, DMSO-$d_6$), $\delta$/p.p.m.: 9.08 (m, 1H, py-2-H), 8.78–8.82 (m, 1H, py-6-H), 8.46 (d, 1H, $J$=8.0 Hz, py-4-H), 7.71–7.77(m, 2H, py-5-H and N—H), 7.46 (s, 2H, Ph-2,6-H), 6.95 (m, 2H, $N^+CH_2$), 5.16(s, 1H, 4-H), 4.17 (t, 4H, $J$=4.8 Hz, $COOCH_2CH_2$), 3.98 (s, 6H,Ar—H), 3.92 (s, 3H, Ar-4-$OCH_3$), 3.52–3.62 (m, 4H, 3,5-$COOCH_2CH_2$),3.36–3.45 (m, 4H, 3,5-$CH_2CH_2CH_2CH_3$), 2.46 (s, 6H, 2,6-$CH_3$),1.46–1.53(m, 4H, 3,5-$CH_2CH_2CH_2CH_3$), 1.25–1,35 (m, 4H,3,5-$CH_2CH_2CH_2CH_3$), 0.85–0.89 (t, 6H, $J$=7.6 Hz,3,5-$CH_2CH_2CH_2CH_3$); MS (ESI) m/$z$: 684 $[M—Br]^+$; Anal. Calcd for $C_{37}H_{51}BrN_2O_{10}$: C, 58.19; H, 6.73; N, 3.67; found: C, 58.11; H, 6.76; N, 3.61.

## S3. Refinement

The H-atoms were included in the refinement at calculated positions (N—H = 0.86 Å, C—H = 0.93 to 0.98 Å) and treated using a riding-model approximation as implemented in *SHELXL97* software. Disorder was detected in the butoxy group with occupancies of 0.7 for atoms C28, C29, C30 and C31 and 0.3 for C28B, C29B, C30B and C31B. The maximum difference density is rather high (1.15 e Å$^{-3}$) because of Fourier series truncation errors expected for a structure containing a heavy atom Br.

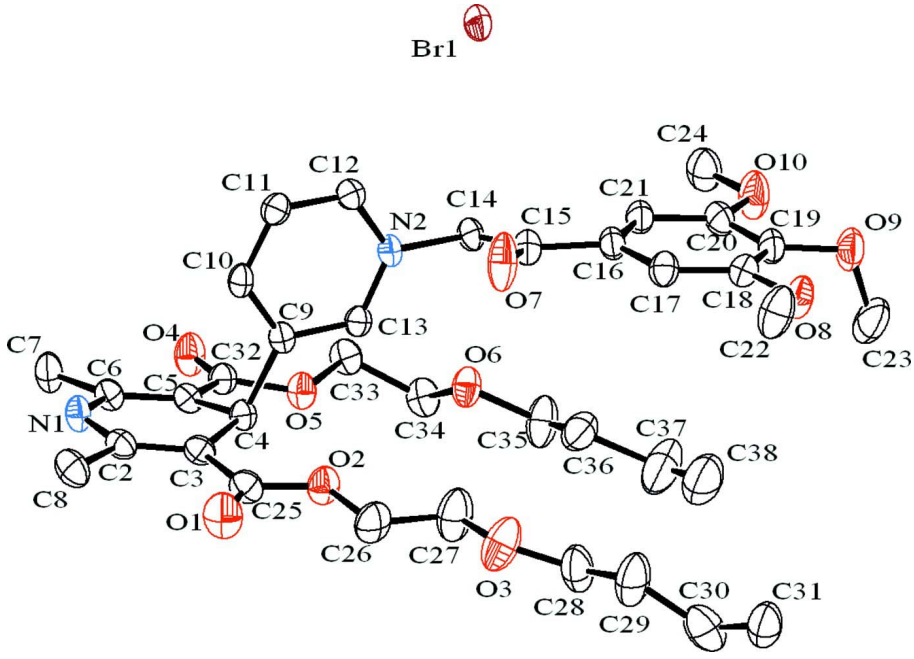


**Figure 1**

The molecular structure of the title compound showing 50% probability elipsoids. No hydrogen atoms shown for clarity. For the disordered butoxy fragment only atoms with the higher occupation factor are shown (C28 - C31).

### 3-{3,5-Bis[(2-butoxyethoxy)carbonyl]-2,6-dimethyl-1,4-dihydropyridin-4-yl}- 1-[(3,4,5-trimethoxybenzoyl)methyl]pyridinium bromide

*Crystal data*

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$M_r = 763.71$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.9501$ (2) Å
$b = 12.4741$ (3) Å
$c = 17.6994$ (5) Å
$\alpha = 93.057$ (1)°
$\beta = 91.658$ (1)°
$\gamma = 108.024$ (1)°
$V = 1874.25$ (8) Å$^3$
$Z = 2$
$F(000) = 804$
$D_x = 1.353$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 20441 reflections
$\theta = 1.0$–$27.9$°
$\mu = 1.16$ mm$^{-1}$
$T = 190$ K
Block, colourless
0.32 × 0.18 × 0.16 mm

*Data collection*

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
CCD scans
13618 measured reflections
8822 independent reflections
6509 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.8°$, $\theta_{min} = 2.1°$
$h = -11 \rightarrow 11$
$k = -16 \rightarrow 16$
$l = -23 \rightarrow 23$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.127$
$S = 1.03$
8822 reflections
469 parameters
4 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 2.P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.15$ e Å$^{-3}$
$\Delta\rho_{min} = -0.41$ e Å$^{-3}$

*Special details*

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

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Br1 | 0.37986 (4) | 0.16649 (2) | 0.524390 (18) | 0.03630 (11) | |
| O5 | −0.0812 (2) | 0.54844 (16) | 0.61743 (11) | 0.0294 (4) | |
| O6 | −0.1497 (2) | 0.35179 (17) | 0.69842 (12) | 0.0354 (5) | |
| N2 | 0.2738 (3) | 0.43048 (18) | 0.64368 (12) | 0.0233 (5) | |
| O8 | 0.2588 (3) | 0.03534 (18) | 0.93630 (12) | 0.0410 (5) | |
| O4 | −0.1071 (2) | 0.62698 (18) | 0.50837 (12) | 0.0377 (5) | |
| O10 | −0.0811 (3) | −0.10148 (19) | 0.72532 (13) | 0.0512 (6) | |
| O2 | 0.2910 (3) | 0.71278 (18) | 0.81572 (11) | 0.0362 (5) | |
| N1 | 0.2834 (3) | 0.90617 (19) | 0.59677 (14) | 0.0310 (5) | |
| H1 | 0.3253 | 0.9628 | 0.5704 | 0.037* | |
| O9 | 0.0265 (3) | −0.12535 (18) | 0.86279 (13) | 0.0474 (6) | |
| O1 | 0.4524 (3) | 0.8906 (2) | 0.82333 (13) | 0.0491 (6) | |
| C32 | −0.0378 (3) | 0.6335 (2) | 0.56916 (15) | 0.0264 (6) | |
| O7 | 0.4044 (3) | 0.3582 (2) | 0.75908 (14) | 0.0528 (7) | |
| C10 | 0.4047 (3) | 0.6509 (2) | 0.61258 (15) | 0.0263 (6) | |
| H10 | 0.4495 | 0.7258 | 0.6015 | 0.032* | |
| C13 | 0.2062 (3) | 0.5076 (2) | 0.66831 (15) | 0.0243 (6) | |

| | | | | |
|---|---|---|---|---|
| H13 | 0.1170 | 0.4854 | 0.6965 | 0.029* |
| C4 | 0.1812 (3) | 0.7049 (2) | 0.67322 (15) | 0.0243 (6) |
| H4 | 0.1025 | 0.6725 | 0.7099 | 0.029* |
| C5 | 0.0976 (3) | 0.7251 (2) | 0.60136 (15) | 0.0248 (6) |
| C14 | 0.2046 (3) | 0.3118 (2) | 0.66100 (16) | 0.0264 (6) |
| H14A | 0.2135 | 0.2628 | 0.6181 | 0.032* |
| H14B | 0.0939 | 0.2967 | 0.6701 | 0.032* |
| C6 | 0.1559 (3) | 0.8212 (2) | 0.56498 (16) | 0.0279 (6) |
| C16 | 0.2225 (3) | 0.1752 (2) | 0.76203 (16) | 0.0285 (6) |
| C12 | 0.4066 (3) | 0.4596 (2) | 0.60494 (15) | 0.0261 (6) |
| H12 | 0.4516 | 0.4050 | 0.5887 | 0.031* |
| C11 | 0.4746 (3) | 0.5706 (2) | 0.58965 (16) | 0.0277 (6) |
| H11 | 0.5674 | 0.5918 | 0.5640 | 0.033* |
| C15 | 0.2887 (3) | 0.2872 (2) | 0.73052 (17) | 0.0309 (6) |
| C9 | 0.2681 (3) | 0.6197 (2) | 0.65203 (14) | 0.0229 (5) |
| C33 | −0.1872 (3) | 0.4421 (2) | 0.58642 (17) | 0.0312 (6) |
| H33A | −0.1295 | 0.4009 | 0.5576 | 0.037* |
| H33B | −0.2663 | 0.4550 | 0.5527 | 0.037* |
| C2 | 0.3479 (3) | 0.9060 (2) | 0.66820 (16) | 0.0283 (6) |
| C21 | 0.1014 (3) | 0.0893 (2) | 0.72309 (17) | 0.0304 (6) |
| H21 | 0.0643 | 0.0996 | 0.6753 | 0.036* |
| O3 | 0.3297 (3) | 0.5876 (3) | 0.98920 (14) | 0.0642 (8) |
| C17 | 0.2812 (3) | 0.1598 (2) | 0.83288 (17) | 0.0310 (6) |
| H17 | 0.3636 | 0.2168 | 0.8576 | 0.037* |
| C34 | −0.2639 (3) | 0.3750 (3) | 0.64977 (18) | 0.0346 (7) |
| H34A | −0.3208 | 0.4167 | 0.6785 | 0.041* |
| H34B | −0.3389 | 0.3045 | 0.6294 | 0.041* |
| C7 | 0.0949 (4) | 0.8480 (3) | 0.49096 (17) | 0.0372 (7) |
| H7A | 0.1144 | 0.7999 | 0.4509 | 0.056* |
| H7B | 0.1474 | 0.9255 | 0.4818 | 0.056* |
| H7C | −0.0162 | 0.8359 | 0.4928 | 0.056* |
| C19 | 0.0922 (4) | −0.0265 (2) | 0.82862 (17) | 0.0358 (7) |
| C25 | 0.3563 (4) | 0.8138 (3) | 0.78638 (17) | 0.0326 (6) |
| C20 | 0.0376 (4) | −0.0115 (2) | 0.75696 (17) | 0.0352 (7) |
| C3 | 0.2964 (3) | 0.8140 (2) | 0.70859 (15) | 0.0269 (6) |
| C8 | 0.4740 (4) | 1.0140 (2) | 0.69322 (19) | 0.0386 (7) |
| H8A | 0.4357 | 1.0542 | 0.7319 | 0.058* |
| H8B | 0.5024 | 1.0598 | 0.6508 | 0.058* |
| H8C | 0.5647 | 0.9972 | 0.7129 | 0.058* |
| C26 | 0.3417 (4) | 0.7075 (3) | 0.89303 (17) | 0.0438 (8) |
| H26A | 0.3135 | 0.7627 | 0.9255 | 0.053* |
| H26B | 0.4550 | 0.7240 | 0.8971 | 0.053* |
| C18 | 0.2157 (4) | 0.0586 (3) | 0.86639 (16) | 0.0323 (6) |
| C24 | −0.1484 (4) | −0.0902 (3) | 0.65342 (19) | 0.0461 (8) |
| H24A | −0.1965 | −0.0314 | 0.6577 | 0.069* |
| H24B | −0.2264 | −0.1602 | 0.6366 | 0.069* |
| H24C | −0.0675 | −0.0715 | 0.6174 | 0.069* |
| C36 | −0.1104 (4) | 0.2827 (3) | 0.81904 (19) | 0.0467 (9) |

| | | | | | |
|---|---|---|---|---|---|
| H36A | −0.0652 | 0.3591 | 0.8414 | 0.056* | |
| H36B | −0.0256 | 0.2582 | 0.7991 | 0.056* | |
| C22 | 0.3969 (4) | 0.1114 (3) | 0.9727 (2) | 0.0550 (10) | |
| H22A | 0.4852 | 0.1150 | 0.9423 | 0.083* | |
| H22B | 0.4143 | 0.0857 | 1.0213 | 0.083* | |
| H22C | 0.3849 | 0.1852 | 0.9791 | 0.083* | |
| C23 | −0.1099 (5) | −0.1226 (3) | 0.9026 (2) | 0.0635 (12) | |
| H23A | −0.1531 | −0.1927 | 0.9258 | 0.095* | |
| H23B | −0.1872 | −0.1118 | 0.8676 | 0.095* | |
| H23C | −0.0808 | −0.0615 | 0.9409 | 0.095* | |
| C35 | −0.2229 (4) | 0.2823 (3) | 0.7565 (2) | 0.0519 (9) | |
| H32A | −0.2704 | 0.2055 | 0.7352 | 0.062* | |
| H32B | −0.3060 | 0.3089 | 0.7763 | 0.062* | |
| C27 | 0.2631 (5) | 0.5922 (3) | 0.9163 (2) | 0.0582 (10) | |
| H27A | 0.1505 | 0.5784 | 0.9182 | 0.070* | |
| H27B | 0.2819 | 0.5362 | 0.8810 | 0.070* | |
| C37 | −0.1891 (6) | 0.2048 (5) | 0.8804 (3) | 0.0757 (13) | |
| H37A | −0.2754 | 0.2289 | 0.8989 | 0.091* | |
| H37B | −0.2336 | 0.1288 | 0.8574 | 0.091* | |
| C38 | −0.0868 (6) | 0.2013 (5) | 0.9449 (3) | 0.0794 (14) | |
| H38A | −0.1465 | 0.1517 | 0.9804 | 0.119* | |
| H38B | −0.0429 | 0.2759 | 0.9688 | 0.119* | |
| H38C | −0.0035 | 0.1741 | 0.9279 | 0.119* | |
| C28 | 0.2319 (8) | 0.5017 (5) | 1.0321 (3) | 0.0560 (15) | 0.70 |
| H28A | 0.1895 | 0.4332 | 0.9995 | 0.067* | 0.70 |
| H28B | 0.1442 | 0.5254 | 1.0490 | 0.067* | 0.70 |
| C29 | 0.3162 (9) | 0.4762 (6) | 1.0992 (3) | 0.0622 (18) | 0.70 |
| H29A | 0.3861 | 0.5469 | 1.1224 | 0.075* | 0.70 |
| H29B | 0.3811 | 0.4313 | 1.0818 | 0.075* | 0.70 |
| C30 | 0.2131 (9) | 0.4145 (6) | 1.1593 (4) | 0.0618 (18) | 0.70 |
| H30A | 0.1629 | 0.4647 | 1.1840 | 0.074* | 0.70 |
| H30B | 0.1310 | 0.3505 | 1.1353 | 0.074* | 0.70 |
| C31 | 0.3027 (7) | 0.3732 (4) | 1.2181 (3) | 0.0540 (14) | 0.70 |
| H31A | 0.2320 | 0.3353 | 1.2550 | 0.081* | 0.70 |
| H31B | 0.3832 | 0.4363 | 1.2426 | 0.081* | 0.70 |
| H31C | 0.3501 | 0.3217 | 1.1942 | 0.081* | 0.70 |
| C28B | 0.300 (2) | 0.4835 (14) | 1.0220 (10) | 0.090* | 0.30 |
| H28C | 0.3490 | 0.4347 | 0.9949 | 0.108* | 0.30 |
| H28D | 0.1879 | 0.4450 | 1.0234 | 0.108* | 0.30 |
| C29B | 0.376 (2) | 0.5201 (13) | 1.1025 (9) | 0.062 (5)* | 0.30 |
| H29C | 0.4893 | 0.5497 | 1.0998 | 0.074* | 0.30 |
| H29D | 0.3390 | 0.5795 | 1.1247 | 0.074* | 0.30 |
| C30B | 0.334 (2) | 0.4200 (13) | 1.1518 (9) | 0.071 (4)* | 0.30 |
| H30C | 0.3348 | 0.3528 | 1.1218 | 0.086* | 0.30 |
| H30D | 0.4134 | 0.4333 | 1.1927 | 0.086* | 0.30 |
| C31B | 0.177 (3) | 0.400 (3) | 1.1845 (16) | 0.100* | 0.30 |
| H31D | 0.1543 | 0.3340 | 1.2134 | 0.150* | 0.30 |
| H31E | 0.0983 | 0.3877 | 1.1443 | 0.150* | 0.30 |

| | | | | | |
|---|---|---|---|---|---|
| H31F | 0.1777 | 0.4640 | 1.2168 | 0.150* | 0.30 |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0452 (2) | 0.02315 (15) | 0.03853 (18) | 0.00647 (12) | 0.00596 (13) | 0.00699 (11) |
| O5 | 0.0275 (10) | 0.0252 (10) | 0.0299 (10) | 0.0006 (8) | −0.0061 (8) | 0.0031 (8) |
| O6 | 0.0267 (11) | 0.0348 (12) | 0.0421 (12) | 0.0041 (9) | 0.0009 (9) | 0.0138 (9) |
| N2 | 0.0235 (12) | 0.0192 (11) | 0.0251 (11) | 0.0036 (9) | −0.0029 (9) | 0.0043 (9) |
| O8 | 0.0500 (14) | 0.0376 (12) | 0.0297 (11) | 0.0037 (10) | −0.0017 (10) | 0.0126 (9) |
| O4 | 0.0413 (12) | 0.0334 (11) | 0.0328 (11) | 0.0039 (10) | −0.0123 (9) | 0.0072 (9) |
| O10 | 0.0711 (17) | 0.0278 (12) | 0.0394 (13) | −0.0068 (11) | −0.0079 (12) | 0.0053 (10) |
| O2 | 0.0437 (12) | 0.0343 (12) | 0.0262 (11) | 0.0063 (10) | −0.0071 (9) | 0.0024 (9) |
| N1 | 0.0343 (13) | 0.0214 (12) | 0.0345 (13) | 0.0036 (10) | 0.0003 (11) | 0.0076 (10) |
| O9 | 0.0687 (16) | 0.0267 (11) | 0.0385 (13) | 0.0011 (11) | 0.0061 (11) | 0.0095 (9) |
| O1 | 0.0562 (15) | 0.0393 (13) | 0.0401 (13) | 0.0007 (11) | −0.0164 (11) | −0.0043 (10) |
| C32 | 0.0262 (14) | 0.0264 (14) | 0.0263 (14) | 0.0077 (12) | −0.0006 (11) | 0.0030 (11) |
| O7 | 0.0429 (14) | 0.0422 (14) | 0.0581 (15) | −0.0104 (11) | −0.0206 (12) | 0.0251 (11) |
| C10 | 0.0277 (14) | 0.0211 (13) | 0.0261 (14) | 0.0013 (11) | −0.0014 (11) | 0.0052 (11) |
| C13 | 0.0237 (14) | 0.0246 (14) | 0.0236 (13) | 0.0061 (11) | −0.0013 (11) | 0.0036 (11) |
| C4 | 0.0235 (14) | 0.0223 (13) | 0.0260 (14) | 0.0056 (11) | −0.0010 (11) | 0.0029 (11) |
| C5 | 0.0246 (14) | 0.0219 (13) | 0.0276 (14) | 0.0075 (11) | −0.0016 (11) | 0.0001 (11) |
| C14 | 0.0238 (14) | 0.0185 (13) | 0.0336 (15) | 0.0017 (11) | −0.0001 (11) | 0.0035 (11) |
| C6 | 0.0304 (15) | 0.0246 (14) | 0.0299 (15) | 0.0102 (12) | −0.0010 (12) | 0.0027 (11) |
| C16 | 0.0279 (15) | 0.0243 (14) | 0.0352 (16) | 0.0092 (12) | 0.0052 (12) | 0.0095 (12) |
| C12 | 0.0248 (14) | 0.0252 (14) | 0.0283 (14) | 0.0079 (11) | −0.0007 (11) | 0.0022 (11) |
| C11 | 0.0231 (14) | 0.0285 (14) | 0.0291 (15) | 0.0043 (11) | 0.0024 (11) | 0.0044 (11) |
| C15 | 0.0285 (15) | 0.0290 (15) | 0.0346 (16) | 0.0073 (13) | 0.0007 (12) | 0.0083 (12) |
| C9 | 0.0252 (14) | 0.0200 (13) | 0.0210 (13) | 0.0041 (11) | −0.0066 (10) | 0.0007 (10) |
| C33 | 0.0272 (15) | 0.0258 (14) | 0.0356 (16) | 0.0022 (12) | −0.0060 (12) | −0.0013 (12) |
| C2 | 0.0287 (15) | 0.0223 (14) | 0.0327 (15) | 0.0069 (12) | 0.0006 (12) | −0.0016 (11) |
| C21 | 0.0352 (16) | 0.0246 (14) | 0.0303 (15) | 0.0069 (12) | 0.0029 (12) | 0.0056 (11) |
| O3 | 0.0659 (18) | 0.082 (2) | 0.0400 (14) | 0.0141 (16) | −0.0042 (12) | 0.0262 (14) |
| C17 | 0.0261 (15) | 0.0301 (15) | 0.0351 (16) | 0.0053 (12) | 0.0011 (12) | 0.0072 (12) |
| C34 | 0.0265 (15) | 0.0303 (16) | 0.0421 (18) | 0.0024 (12) | −0.0052 (13) | 0.0029 (13) |
| C7 | 0.0472 (19) | 0.0268 (15) | 0.0349 (17) | 0.0071 (14) | −0.0043 (14) | 0.0089 (13) |
| C19 | 0.0495 (19) | 0.0229 (14) | 0.0328 (16) | 0.0068 (14) | 0.0066 (14) | 0.0066 (12) |
| C25 | 0.0335 (16) | 0.0304 (15) | 0.0329 (16) | 0.0097 (13) | −0.0038 (13) | −0.0024 (13) |
| C20 | 0.0442 (18) | 0.0212 (14) | 0.0363 (17) | 0.0048 (13) | 0.0032 (14) | 0.0005 (12) |
| C3 | 0.0276 (14) | 0.0246 (14) | 0.0272 (14) | 0.0072 (12) | −0.0023 (11) | −0.0030 (11) |
| C8 | 0.0358 (17) | 0.0247 (15) | 0.0508 (19) | 0.0040 (13) | −0.0024 (14) | −0.0016 (14) |
| C26 | 0.054 (2) | 0.050 (2) | 0.0262 (16) | 0.0135 (17) | −0.0073 (14) | 0.0052 (14) |
| C18 | 0.0379 (17) | 0.0318 (16) | 0.0285 (15) | 0.0115 (13) | 0.0054 (12) | 0.0066 (12) |
| C24 | 0.053 (2) | 0.0328 (17) | 0.044 (2) | 0.0022 (16) | −0.0047 (16) | 0.0020 (15) |
| C36 | 0.044 (2) | 0.060 (2) | 0.0438 (19) | 0.0244 (18) | 0.0135 (16) | 0.0187 (17) |
| C22 | 0.048 (2) | 0.064 (2) | 0.043 (2) | 0.0007 (19) | −0.0078 (16) | 0.0201 (18) |
| C23 | 0.081 (3) | 0.043 (2) | 0.049 (2) | −0.009 (2) | 0.023 (2) | 0.0077 (17) |
| C35 | 0.040 (2) | 0.044 (2) | 0.061 (2) | −0.0057 (16) | 0.0009 (17) | 0.0230 (17) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C27 | 0.069 (3) | 0.057 (2) | 0.040 (2) | 0.006 (2) | −0.0143 (18) | 0.0160 (17) |
| C37 | 0.070 (3) | 0.095 (4) | 0.067 (3) | 0.025 (3) | 0.020 (2) | 0.043 (3) |
| C38 | 0.095 (4) | 0.092 (4) | 0.066 (3) | 0.043 (3) | 0.026 (3) | 0.038 (3) |
| C28 | 0.091 (5) | 0.037 (3) | 0.037 (3) | 0.015 (3) | −0.010 (3) | 0.008 (2) |
| C29 | 0.079 (5) | 0.059 (4) | 0.042 (3) | 0.010 (4) | −0.009 (3) | 0.020 (3) |
| C30 | 0.072 (5) | 0.036 (3) | 0.074 (5) | 0.013 (3) | −0.004 (3) | −0.004 (3) |
| C31 | 0.075 (4) | 0.042 (3) | 0.037 (3) | 0.006 (3) | −0.001 (3) | 0.007 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O5—C32 | 1.367 (3) | C7—H7C | 0.9600 |
| O5—C33 | 1.441 (3) | C19—C20 | 1.388 (4) |
| O6—C35 | 1.422 (4) | C19—C18 | 1.396 (4) |
| O6—C34 | 1.424 (4) | C25—C3 | 1.463 (4) |
| N2—C13 | 1.347 (3) | C8—H8A | 0.9600 |
| N2—C12 | 1.349 (3) | C8—H8B | 0.9600 |
| N2—C14 | 1.470 (3) | C8—H8C | 0.9600 |
| O8—C18 | 1.358 (4) | C26—C27 | 1.479 (5) |
| O8—C22 | 1.417 (4) | C26—H26A | 0.9700 |
| O4—C32 | 1.212 (3) | C26—H26B | 0.9700 |
| O10—C20 | 1.365 (4) | C24—H24A | 0.9600 |
| O10—C24 | 1.424 (4) | C24—H24B | 0.9600 |
| O2—C25 | 1.353 (4) | C24—H24C | 0.9600 |
| O2—C26 | 1.440 (4) | C36—C35 | 1.473 (5) |
| N1—C2 | 1.375 (4) | C36—C37 | 1.534 (5) |
| N1—C6 | 1.376 (4) | C36—H36A | 0.9700 |
| N1—H1 | 0.8600 | C36—H36B | 0.9700 |
| O9—C19 | 1.373 (4) | C22—H22A | 0.9600 |
| O9—C23 | 1.435 (5) | C22—H22B | 0.9600 |
| O1—C25 | 1.215 (4) | C22—H22C | 0.9600 |
| C32—C5 | 1.460 (4) | C23—H23A | 0.9600 |
| O7—C15 | 1.211 (4) | C23—H23B | 0.9600 |
| C10—C9 | 1.384 (4) | C23—H23C | 0.9600 |
| C10—C11 | 1.386 (4) | C35—H32A | 0.9700 |
| C10—H10 | 0.9300 | C35—H32B | 0.9700 |
| C13—C9 | 1.385 (4) | C27—H27A | 0.9700 |
| C13—H13 | 0.9300 | C27—H27B | 0.9700 |
| C4—C3 | 1.520 (4) | C37—C38 | 1.452 (6) |
| C4—C5 | 1.528 (4) | C37—H37A | 0.9700 |
| C4—C9 | 1.537 (4) | C37—H37B | 0.9700 |
| C4—H4 | 0.9800 | C38—H38A | 0.9600 |
| C5—C6 | 1.356 (4) | C38—H38B | 0.9600 |
| C14—C15 | 1.518 (4) | C38—H38C | 0.9600 |
| C14—H14A | 0.9700 | C28—C29 | 1.490 (8) |
| C14—H14B | 0.9700 | C28—H28A | 0.9700 |
| C6—C7 | 1.498 (4) | C28—H28B | 0.9700 |
| C16—C17 | 1.391 (4) | C29—C30 | 1.510 (9) |
| C16—C21 | 1.399 (4) | C29—H29A | 0.9700 |

| | | | |
|---|---|---|---|
| C16—C15 | 1.485 (4) | C29—H29B | 0.9700 |
| C12—C11 | 1.375 (4) | C30—C31 | 1.501 (9) |
| C12—H12 | 0.9300 | C30—H30A | 0.9700 |
| C11—H11 | 0.9300 | C30—H30B | 0.9700 |
| C33—C34 | 1.489 (4) | C31—H31A | 0.9600 |
| C33—H33A | 0.9700 | C31—H31B | 0.9600 |
| C33—H33B | 0.9700 | C31—H31C | 0.9600 |
| C2—C3 | 1.349 (4) | C28B—C29B | 1.544 (17) |
| C2—C8 | 1.501 (4) | C28B—H28C | 0.9700 |
| C21—C20 | 1.387 (4) | C28B—H28D | 0.9700 |
| C21—H21 | 0.9300 | C29B—C30B | 1.520 (16) |
| O3—C28B | 1.404 (15) | C29B—H29C | 0.9700 |
| O3—C27 | 1.417 (4) | C29B—H29D | 0.9700 |
| O3—C28 | 1.427 (6) | C30B—C31B | 1.486 (17) |
| C17—C18 | 1.390 (4) | C30B—H30C | 0.9700 |
| C17—H17 | 0.9300 | C30B—H30D | 0.9700 |
| C34—H34A | 0.9700 | C31B—H31D | 0.9600 |
| C34—H34B | 0.9700 | C31B—H31E | 0.9600 |
| C7—H7A | 0.9600 | C31B—H31F | 0.9600 |
| C7—H7B | 0.9600 | | |

| | | | |
|---|---|---|---|
| C32—O5—C33 | 116.7 (2) | C27—C26—H26A | 110.1 |
| C35—O6—C34 | 111.0 (2) | O2—C26—H26B | 110.1 |
| C13—N2—C12 | 121.7 (2) | C27—C26—H26B | 110.1 |
| C13—N2—C14 | 119.6 (2) | H26A—C26—H26B | 108.4 |
| C12—N2—C14 | 118.7 (2) | O8—C18—C17 | 124.9 (3) |
| C18—O8—C22 | 117.6 (3) | O8—C18—C19 | 115.4 (3) |
| C20—O10—C24 | 118.0 (3) | C17—C18—C19 | 119.8 (3) |
| C25—O2—C26 | 114.4 (2) | O10—C24—H24A | 109.5 |
| C2—N1—C6 | 124.0 (2) | O10—C24—H24B | 109.5 |
| C2—N1—H1 | 118.0 | H24A—C24—H24B | 109.5 |
| C6—N1—H1 | 118.0 | O10—C24—H24C | 109.5 |
| C19—O9—C23 | 111.4 (3) | H24A—C24—H24C | 109.5 |
| O4—C32—O5 | 121.2 (2) | H24B—C24—H24C | 109.5 |
| O4—C32—C5 | 128.1 (3) | C35—C36—C37 | 111.8 (3) |
| O5—C32—C5 | 110.7 (2) | C35—C36—H36A | 109.3 |
| C9—C10—C11 | 120.0 (3) | C37—C36—H36A | 109.3 |
| C9—C10—H10 | 120.0 | C35—C36—H36B | 109.3 |
| C11—C10—H10 | 120.0 | C37—C36—H36B | 109.3 |
| N2—C13—C9 | 120.7 (2) | H36A—C36—H36B | 107.9 |
| N2—C13—H13 | 119.7 | O8—C22—H22A | 109.5 |
| C9—C13—H13 | 119.7 | O8—C22—H22B | 109.5 |
| C3—C4—C5 | 111.6 (2) | H22A—C22—H22B | 109.5 |
| C3—C4—C9 | 110.2 (2) | O8—C22—H22C | 109.5 |
| C5—C4—C9 | 108.0 (2) | H22A—C22—H22C | 109.5 |
| C3—C4—H4 | 109.0 | H22B—C22—H22C | 109.5 |
| C5—C4—H4 | 109.0 | O9—C23—H23A | 109.5 |
| C9—C4—H4 | 109.0 | O9—C23—H23B | 109.5 |

| | | | |
|---|---|---|---|
| C6—C5—C32 | 120.9 (2) | H23A—C23—H23B | 109.5 |
| C6—C5—C4 | 120.8 (2) | O9—C23—H23C | 109.5 |
| C32—C5—C4 | 118.0 (2) | H23A—C23—H23C | 109.5 |
| N2—C14—C15 | 110.2 (2) | H23B—C23—H23C | 109.5 |
| N2—C14—H14A | 109.6 | O6—C35—C36 | 112.1 (3) |
| C15—C14—H14A | 109.6 | O6—C35—H32A | 109.2 |
| N2—C14—H14B | 109.6 | C36—C35—H32A | 109.2 |
| C15—C14—H14B | 109.6 | O6—C35—H32B | 109.2 |
| H14A—C14—H14B | 108.1 | C36—C35—H32B | 109.2 |
| C5—C6—N1 | 119.6 (3) | H32A—C35—H32B | 107.9 |
| C5—C6—C7 | 126.7 (3) | O3—C27—C26 | 105.7 (3) |
| N1—C6—C7 | 113.7 (2) | O3—C27—H27A | 110.6 |
| C17—C16—C21 | 121.1 (3) | C26—C27—H27A | 110.6 |
| C17—C16—C15 | 117.7 (3) | O3—C27—H27B | 110.6 |
| C21—C16—C15 | 121.2 (3) | C26—C27—H27B | 110.6 |
| N2—C12—C11 | 119.4 (2) | H27A—C27—H27B | 108.7 |
| N2—C12—H12 | 120.3 | C38—C37—C36 | 115.5 (4) |
| C11—C12—H12 | 120.3 | C38—C37—H37A | 108.4 |
| C12—C11—C10 | 119.9 (3) | C36—C37—H37A | 108.4 |
| C12—C11—H11 | 120.1 | C38—C37—H37B | 108.4 |
| C10—C11—H11 | 120.1 | C36—C37—H37B | 108.4 |
| O7—C15—C16 | 122.1 (3) | H37A—C37—H37B | 107.5 |
| O7—C15—C14 | 120.1 (3) | C37—C38—H38A | 109.5 |
| C16—C15—C14 | 117.7 (2) | C37—C38—H38B | 109.5 |
| C10—C9—C13 | 118.3 (2) | H38A—C38—H38B | 109.5 |
| C10—C9—C4 | 121.3 (2) | C37—C38—H38C | 109.5 |
| C13—C9—C4 | 120.4 (2) | H38A—C38—H38C | 109.5 |
| O5—C33—C34 | 108.9 (2) | H38B—C38—H38C | 109.5 |
| O5—C33—H33A | 109.9 | O3—C28—C29 | 113.3 (5) |
| C34—C33—H33A | 109.9 | O3—C28—H28A | 108.9 |
| O5—C33—H33B | 109.9 | C29—C28—H28A | 108.9 |
| C34—C33—H33B | 109.9 | O3—C28—H28B | 108.9 |
| H33A—C33—H33B | 108.3 | C29—C28—H28B | 108.9 |
| C3—C2—N1 | 120.0 (2) | H28A—C28—H28B | 107.7 |
| C3—C2—C8 | 126.3 (3) | C28—C29—C30 | 115.8 (6) |
| N1—C2—C8 | 113.7 (3) | C28—C29—H29A | 108.3 |
| C20—C21—C16 | 118.9 (3) | C30—C29—H29A | 108.3 |
| C20—C21—H21 | 120.5 | C28—C29—H29B | 108.3 |
| C16—C21—H21 | 120.5 | C30—C29—H29B | 108.3 |
| C28B—O3—C27 | 119.8 (8) | H29A—C29—H29B | 107.4 |
| C28B—O3—C28 | 30.1 (8) | C31—C30—C29 | 112.9 (6) |
| C27—O3—C28 | 113.2 (3) | C31—C30—H30A | 109.0 |
| C18—C17—C16 | 119.4 (3) | C29—C30—H30A | 109.0 |
| C18—C17—H17 | 120.3 | C31—C30—H30B | 109.0 |
| C16—C17—H17 | 120.3 | C29—C30—H30B | 109.0 |
| O6—C34—C33 | 110.7 (2) | H30A—C30—H30B | 107.8 |
| O6—C34—H34A | 109.5 | C30—C31—H31A | 109.5 |
| C33—C34—H34A | 109.5 | C30—C31—H31B | 109.5 |

| | | | |
|---|---|---|---|
| O6—C34—H34B | 109.5 | H31A—C31—H31B | 109.5 |
| C33—C34—H34B | 109.5 | C30—C31—H31C | 109.5 |
| H34A—C34—H34B | 108.1 | H31A—C31—H31C | 109.5 |
| C6—C7—H7A | 109.5 | H31B—C31—H31C | 109.5 |
| C6—C7—H7B | 109.5 | O3—C28B—C29B | 101.9 (12) |
| H7A—C7—H7B | 109.5 | O3—C28B—H28C | 111.4 |
| C6—C7—H7C | 109.5 | C29B—C28B—H28C | 111.4 |
| H7A—C7—H7C | 109.5 | O3—C28B—H28D | 111.4 |
| H7B—C7—H7C | 109.5 | C29B—C28B—H28D | 111.4 |
| O9—C19—C20 | 120.4 (3) | H28C—C28B—H28D | 109.3 |
| O9—C19—C18 | 119.3 (3) | C30B—C29B—C28B | 110.1 (13) |
| C20—C19—C18 | 120.3 (3) | C30B—C29B—H29C | 109.6 |
| O1—C25—O2 | 120.9 (3) | C28B—C29B—H29C | 109.6 |
| O1—C25—C3 | 127.7 (3) | C30B—C29B—H29D | 109.6 |
| O2—C25—C3 | 111.4 (2) | C28B—C29B—H29D | 109.6 |
| O10—C20—C21 | 124.7 (3) | H29C—C29B—H29D | 108.2 |
| O10—C20—C19 | 114.8 (3) | C31B—C30B—C29B | 112.6 (17) |
| C21—C20—C19 | 120.5 (3) | C31B—C30B—H30C | 109.1 |
| C2—C3—C25 | 121.1 (3) | C29B—C30B—H30C | 109.1 |
| C2—C3—C4 | 121.0 (2) | C31B—C30B—H30D | 109.1 |
| C25—C3—C4 | 117.8 (2) | C29B—C30B—H30D | 109.1 |
| C2—C8—H8A | 109.5 | H30C—C30B—H30D | 107.8 |
| C2—C8—H8B | 109.5 | C30B—C31B—H31D | 109.5 |
| H8A—C8—H8B | 109.5 | C30B—C31B—H31E | 109.5 |
| C2—C8—H8C | 109.5 | H31D—C31B—H31E | 109.5 |
| H8A—C8—H8C | 109.5 | C30B—C31B—H31F | 109.5 |
| H8B—C8—H8C | 109.5 | H31D—C31B—H31F | 109.5 |
| O2—C26—C27 | 107.9 (3) | H31E—C31B—H31F | 109.5 |
| O2—C26—H26A | 110.1 | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···Br1$^{i}$ | 0.86 | 2.61 | 3.421 (2) | 157 |

Symmetry code: (i) *x*, *y*+1, *z*.