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4-Bromo-3-methylanilinium perchlorate
18-crown-6 clathrate

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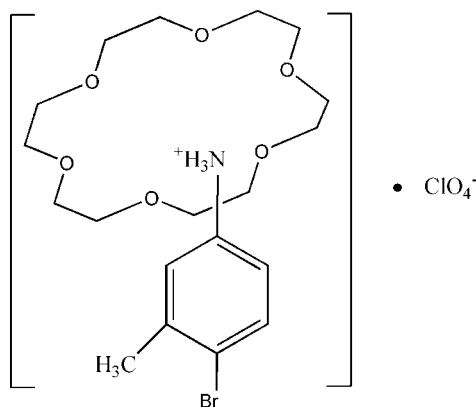
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å;
R factor = 0.060; wR factor = 0.157; data-to-parameter ratio = 19.6.

The reaction of 4-bromo-3-methylanilinium perchlorate and 18-crown-6 in methanol solution yielded the title compound, $\text{C}_7\text{H}_9\text{BrN}^+\cdot\text{ClO}_4^-\cdot\text{C}_{12}\text{H}_{24}\text{O}_6$. The protonated 4-bromo-3-methylamine unit contains one $-\text{NH}_3^+$ substituent, resulting in a 1:1 supramolecular rotator-stator structure, $(\text{C}_7\text{H}_9\text{Br}-\text{NH}_3^+)(18\text{-crown-6})$, through three bifurcated $\text{N}-\text{H}\cdots(\text{O},\text{O})$ hydrogen bonds between the ammonium group of the cation and the O atoms of the crown ether molecule.

Related literature

For the structures of similar crown ether clathrates, see: Akutagawa *et al.* (2002); Ge & Zhao (2010*a,b*); Guo & Zhao (2010); Zhao (2010); Zhao & Qu (2010*a,b*). The title compound was prepared as part of a study of ferroelectric materials. For their properties, see: Fu *et al.* (2007); Zhang *et al.* (2009); Ye *et al.* (2009).



Experimental

Crystal data

 $\text{C}_7\text{H}_9\text{BrN}^+\cdot\text{ClO}_4^-\cdot\text{C}_{12}\text{H}_{24}\text{O}_6$ $M_r = 550.81$

Monoclinic, $P2_1/c$
 $a = 11.967$ (2) Å
 $b = 13.446$ (3) Å
 $c = 15.677$ (3) Å
 $\beta = 94.05$ (3)°
 $V = 2516.3$ (9) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.79$ mm⁻¹
 $T = 296$ K
 $0.40 \times 0.30 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.530$, $T_{\max} = 0.699$

25007 measured reflections
5665 independent reflections
4005 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.066$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.157$
 $S = 1.09$
5665 reflections

289 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.41$ e Å⁻³
 $\Delta\rho_{\min} = -0.98$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1A}\cdots\text{O8}$ | 0.89 | 2.22 | 2.905 (4) | 134 |
| $\text{N1}-\text{H1A}\cdots\text{O9}$ | 0.89 | 2.19 | 2.966 (4) | 145 |
| $\text{N1}-\text{H1B}\cdots\text{O5}$ | 0.89 | 2.19 | 2.955 (4) | 144 |
| $\text{N1}-\text{H1B}\cdots\text{O10}$ | 0.89 | 2.22 | 2.912 (4) | 134 |
| $\text{N1}-\text{H1E}\cdots\text{O6}$ | 0.89 | 2.29 | 2.970 (4) | 133 |
| $\text{N1}-\text{H1E}\cdots\text{O7}$ | 0.89 | 2.12 | 2.893 (4) | 145 |

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors are grateful to the starter fund of Southeast University for financial support to purchase the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2260).

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supplementary materials

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4-Bromo-3-methylanilinium perchlorate 18-crown-6 clathrate

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Comment

There is currently a great deal of interest in crown ethers because of their ability to form non-covalent, H-bonding complexes with ammonium cations both in solid and in solution (Akutagawa *et al.*, 2002; Ge *et al.*, 2010a,b; Guo *et al.*, 2010; Zhao *et al.*, 2010a,b). Not only the size of the crown ether, but also the nature of the ammonium cation ($-\text{NH}_4^+$, RNH_3^+ , R_2NH_2^+ , *etc*) can influence on the stoichiometry and stability of these host-guest complexes. The host molecules combine with the guest species by intermolecular interaction, and if the host molecule possess some specific sites, it is easy to realise high selectivity in ion or molecular recognitions. 18-Crown-6 have the highest affinity for ammonium cation RNH_3^+ , while most studies of 18-crown-6 and its derivatives invariably showed a 1:1 stoichiometry with RNH_3^+ cations.

Dielectric permittivity of the title compound is tested to systematically investigate the ferroelectric phase transitions materials (Ye *et al.*, 2009; Zhang *et al.*, 2009). The title compound has no dielectric anomaly with the value of 5 and 8 under 1M Hz in the temperature from 80 to 433 K (the compound m.p.> 453 K), suggesting that the compound should be no distinct phase transition occurred within the measured temperature range.

The title compound is composed of cationic $[\text{C}_7\text{H}_9\text{NBr}(18\text{-Crown-6})]^+$ and one single anionic $[\text{ClO}_4]^-$ anions (Fig. 1). Supramolecular rotators was assembled between protonated 4-bromo-3-methylanilinium $[\text{C}_7\text{H}_6\text{Br}-\text{NH}_3]^+$ and 18-crown-6 by hydrogen-bonding. The ammonium moieties of ($-\text{NH}_3^+$) cations were interacted with the oxygen atom of crown ethers through six simple $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding, forming 1:1 supramolecular rotator-stator structures.

The macrocycle adopts a conformation with approximate D_{3d} symmetry, with all $\text{O}-\text{C}-\text{C}-\text{O}$ torsion angles being *gauche* and alternating in sign, and all $\text{C}-\text{O}-\text{C}-\text{C}$ torsion angles being *trans*. The $\text{C}-\text{N}$ bonds of $[\text{C}_7\text{H}_6\text{Br}-\text{NH}_3]^+$ were almost perpendicular to the mean oxygen planes of crown ethers.

Supramolecular cation structure, $[\text{C}_7\text{H}_9\text{NBr}(18\text{-Crown-6})]^+$, were introduced as counter cations to $[\text{ClO}_4]^-$ anions. Cl has a flattened tetrahedral coordination by four O^{2-} ions [range of *cis*-bond angles = 108.4 (2)–110.3 (2) °; $\text{dav}(\text{Cl}-\text{O}) = 1.426$ (3)–1.457 (3) Å].

The title compound was stabilized by intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, but no intermolecular hydrogen bond was observed. The intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding length are within the usual range: 2.893 (4) and 2.970 (4) Å.

Experimental

$\text{C}_7\text{H}_8\text{NBr}$. HClO_4 (2 mmol, 0.57 g) and 18-crown-6 (2 mmol, 0.528 g) were dissolved in 40 ml methanol solution. The precipitate was filtered out. Two days later, single crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of methanol solution at 0°C.

Refinement

All the C—H hydrogen atoms were calculated geometrically, with C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H respectively, and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl H and $x = 1.2$ for all other H atoms.

All the N—H hydrogen atoms were calculated geometrically. The positions of the H atoms of the nitrogen atoms were refined using a riding model with N—H = 0.89 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$.

Figures

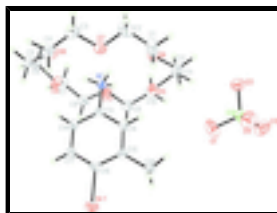


Fig. 1. The title molecules with the atomic numbering scheme. The displacement ellipsoids are drawn at the 30% probability level.

4-Bromo-3-methylanilinium perchlorate–18-crown-6 (1/1)

Crystal data

$\text{C}_7\text{H}_9\text{BrN}^+\cdot\text{ClO}_4^-\cdot\text{C}_{12}\text{H}_{24}\text{O}_6$

$M_r = 550.81$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 11.967(2) \text{ \AA}$

$b = 13.446(3) \text{ \AA}$

$c = 15.677(3) \text{ \AA}$

$\beta = 94.05(3)^\circ$

$V = 2516.3(9) \text{ \AA}^3$

$Z = 4$

$F(000) = 1144$

$D_x = 1.454 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 20001 reflections

$\theta = 3.0\text{--}27.3^\circ$

$\mu = 1.79 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Prism, colorless

$0.40 \times 0.30 \times 0.20 \text{ mm}$

Data collection

Rigaku SCXmini
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: $28.5714 \text{ pixels mm}^{-1}$

CCD_Profile_fitting scans

Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)

$T_{\text{min}} = 0.530$, $T_{\text{max}} = 0.699$

25007 measured reflections

5665 independent reflections

4005 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.066$

$\theta_{\text{max}} = 27.3^\circ$, $\theta_{\text{min}} = 3.0^\circ$

$h = -15 \rightarrow 15$

$k = -17 \rightarrow 17$

$l = -20 \rightarrow 20$

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.060$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.157$ | H-atom parameters constrained |
| $S = 1.09$ | $w = 1/[\sigma^2(F_o^2) + (0.0769P)^2 + 0.8528P]$ |
| 5665 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 289 parameters | $(\Delta/\sigma)_{\max} = 0.001$ |
| 0 restraints | $\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\min} = -0.98 \text{ e } \text{\AA}^{-3}$ |

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|--------------|--------------|----------------------------------|
| Br1 | 0.19928 (4) | 1.01458 (3) | -0.00712 (3) | 0.06334 (18) |
| O8 | 0.0452 (2) | 0.60635 (19) | 0.30049 (15) | 0.0495 (6) |
| N1 | 0.2459 (2) | 0.72782 (19) | 0.29922 (16) | 0.0367 (6) |
| H1A | 0.1796 | 0.7195 | 0.3206 | 0.055* |
| H1B | 0.2937 | 0.7545 | 0.3389 | 0.055* |
| H1E | 0.2719 | 0.6692 | 0.2833 | 0.055* |
| O9 | 0.0542 (2) | 0.78578 (18) | 0.39854 (15) | 0.0499 (6) |
| C15 | 0.3203 (3) | 0.8828 (2) | 0.1107 (2) | 0.0370 (7) |
| C16 | 0.2147 (3) | 0.9217 (2) | 0.08602 (19) | 0.0398 (7) |
| O6 | 0.4462 (2) | 0.59829 (19) | 0.29366 (17) | 0.0551 (7) |
| O5 | 0.4715 (2) | 0.78411 (19) | 0.37212 (16) | 0.0518 (6) |
| O7 | 0.2319 (2) | 0.53548 (19) | 0.21645 (17) | 0.0554 (7) |
| O10 | 0.2751 (2) | 0.84908 (18) | 0.45312 (16) | 0.0506 (6) |
| C13 | 0.2336 (3) | 0.7946 (2) | 0.22444 (19) | 0.0332 (7) |
| C17 | 0.1196 (3) | 0.8976 (3) | 0.1282 (2) | 0.0453 (8) |
| H17A | 0.0503 | 0.9242 | 0.1098 | 0.054* |
| C18 | 0.1292 (3) | 0.8336 (2) | 0.1982 (2) | 0.0415 (8) |
| H18A | 0.0664 | 0.8171 | 0.2270 | 0.050* |

supplementary materials

| | | | | |
|------|-------------|-------------|--------------|-------------|
| C14 | 0.3275 (3) | 0.8187 (2) | 0.1809 (2) | 0.0398 (7) |
| H14A | 0.3966 | 0.7914 | 0.1990 | 0.048* |
| C11 | 0.5624 (3) | 0.7135 (3) | 0.3751 (3) | 0.0545 (10) |
| H11A | 0.5601 | 0.6721 | 0.4256 | 0.065* |
| H11B | 0.6335 | 0.7484 | 0.3781 | 0.065* |
| C6 | -0.0296 (3) | 0.7105 (3) | 0.4065 (2) | 0.0537 (9) |
| H6A | -0.0976 | 0.7405 | 0.4250 | 0.064* |
| H6B | -0.0033 | 0.6619 | 0.4490 | 0.064* |
| C10 | 0.4740 (3) | 0.8459 (3) | 0.4471 (3) | 0.0600 (10) |
| H10A | 0.5406 | 0.8872 | 0.4499 | 0.072* |
| H10B | 0.4766 | 0.8045 | 0.4979 | 0.072* |
| C7 | 0.0804 (3) | 0.8360 (3) | 0.4778 (2) | 0.0562 (10) |
| H7A | 0.1013 | 0.7881 | 0.5224 | 0.067* |
| H7B | 0.0155 | 0.8726 | 0.4944 | 0.067* |
| C19 | 0.4241 (3) | 0.9087 (3) | 0.0644 (3) | 0.0580 (10) |
| H19A | 0.4878 | 0.8747 | 0.0911 | 0.087* |
| H19B | 0.4366 | 0.9792 | 0.0673 | 0.087* |
| H19C | 0.4132 | 0.8887 | 0.0056 | 0.087* |
| C8 | 0.1762 (3) | 0.9065 (3) | 0.4666 (3) | 0.0579 (10) |
| H8A | 0.1585 | 0.9496 | 0.4180 | 0.070* |
| H8B | 0.1891 | 0.9476 | 0.5172 | 0.070* |
| C3 | 0.1271 (4) | 0.4814 (3) | 0.2176 (3) | 0.0600 (10) |
| H3A | 0.1286 | 0.4386 | 0.2675 | 0.072* |
| H3B | 0.1164 | 0.4401 | 0.1670 | 0.072* |
| C5 | -0.0538 (3) | 0.6604 (3) | 0.3215 (2) | 0.0517 (9) |
| H5A | -0.1164 | 0.6149 | 0.3244 | 0.062* |
| H5B | -0.0733 | 0.7096 | 0.2778 | 0.062* |
| C4 | 0.0330 (3) | 0.5545 (3) | 0.2200 (2) | 0.0539 (9) |
| H4A | 0.0356 | 0.6014 | 0.1731 | 0.065* |
| H4B | -0.0383 | 0.5201 | 0.2144 | 0.065* |
| C9 | 0.3713 (3) | 0.9105 (3) | 0.4438 (3) | 0.0583 (10) |
| H9A | 0.3780 | 0.9592 | 0.4895 | 0.070* |
| H9B | 0.3633 | 0.9457 | 0.3897 | 0.070* |
| C12 | 0.5517 (3) | 0.6502 (3) | 0.2967 (3) | 0.0573 (10) |
| H12A | 0.5554 | 0.6914 | 0.2462 | 0.069* |
| H12B | 0.6128 | 0.6027 | 0.2978 | 0.069* |
| C1 | 0.4329 (4) | 0.5300 (4) | 0.2234 (4) | 0.0794 (15) |
| H1C | 0.4969 | 0.4856 | 0.2243 | 0.095* |
| H1D | 0.4290 | 0.5664 | 0.1698 | 0.095* |
| C2 | 0.3278 (4) | 0.4705 (3) | 0.2295 (4) | 0.0794 (15) |
| H2A | 0.3239 | 0.4185 | 0.1866 | 0.095* |
| H2B | 0.3280 | 0.4395 | 0.2854 | 0.095* |
| Cl2 | 0.75937 (7) | 0.70425 (7) | 0.09959 (6) | 0.0485 (2) |
| O2 | 0.7570 (3) | 0.6235 (2) | 0.15986 (19) | 0.0709 (8) |
| O1 | 0.6613 (3) | 0.7637 (3) | 0.1044 (3) | 0.0979 (12) |
| O4 | 0.7607 (3) | 0.6624 (3) | 0.01394 (19) | 0.0784 (9) |
| O3 | 0.8582 (3) | 0.7636 (3) | 0.1177 (2) | 0.0849 (10) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Br1 | 0.0687 (3) | 0.0700 (3) | 0.0526 (3) | 0.0157 (2) | 0.0132 (2) | 0.02676 (19) |
| O8 | 0.0416 (13) | 0.0607 (16) | 0.0458 (13) | -0.0055 (11) | -0.0003 (11) | -0.0053 (11) |
| N1 | 0.0388 (14) | 0.0358 (14) | 0.0359 (14) | -0.0015 (11) | 0.0058 (11) | 0.0020 (11) |
| O9 | 0.0502 (14) | 0.0543 (15) | 0.0469 (14) | -0.0092 (11) | 0.0152 (11) | -0.0020 (11) |
| C15 | 0.0384 (17) | 0.0343 (16) | 0.0393 (17) | 0.0015 (13) | 0.0110 (14) | -0.0005 (13) |
| C16 | 0.052 (2) | 0.0352 (17) | 0.0332 (16) | 0.0051 (14) | 0.0053 (14) | 0.0025 (13) |
| O6 | 0.0451 (14) | 0.0589 (16) | 0.0627 (16) | 0.0068 (12) | 0.0125 (12) | -0.0091 (13) |
| O5 | 0.0417 (14) | 0.0535 (15) | 0.0588 (16) | 0.0012 (11) | -0.0066 (12) | 0.0054 (12) |
| O7 | 0.0568 (16) | 0.0443 (14) | 0.0657 (17) | 0.0002 (12) | 0.0081 (13) | -0.0090 (12) |
| O10 | 0.0548 (15) | 0.0390 (13) | 0.0585 (16) | -0.0048 (11) | 0.0074 (12) | -0.0054 (11) |
| C13 | 0.0372 (16) | 0.0302 (15) | 0.0326 (15) | -0.0003 (12) | 0.0049 (13) | 0.0004 (12) |
| C17 | 0.0337 (17) | 0.053 (2) | 0.050 (2) | 0.0103 (15) | 0.0032 (15) | 0.0062 (16) |
| C18 | 0.0326 (17) | 0.0468 (19) | 0.0459 (18) | 0.0020 (14) | 0.0089 (14) | 0.0067 (15) |
| C14 | 0.0338 (17) | 0.0399 (18) | 0.0461 (18) | 0.0050 (14) | 0.0054 (14) | 0.0034 (14) |
| C11 | 0.0356 (19) | 0.056 (2) | 0.072 (3) | -0.0006 (16) | 0.0029 (18) | 0.019 (2) |
| C6 | 0.044 (2) | 0.064 (2) | 0.056 (2) | -0.0041 (17) | 0.0191 (17) | 0.0041 (18) |
| C10 | 0.053 (2) | 0.050 (2) | 0.073 (3) | -0.0102 (18) | -0.016 (2) | -0.007 (2) |
| C7 | 0.065 (3) | 0.059 (2) | 0.047 (2) | -0.0005 (19) | 0.0175 (18) | -0.0075 (17) |
| C19 | 0.047 (2) | 0.061 (2) | 0.068 (3) | 0.0070 (18) | 0.0247 (19) | 0.015 (2) |
| C8 | 0.066 (3) | 0.051 (2) | 0.058 (2) | 0.0028 (19) | 0.0092 (19) | -0.0115 (18) |
| C3 | 0.072 (3) | 0.046 (2) | 0.062 (3) | -0.0129 (19) | 0.003 (2) | -0.0103 (18) |
| C5 | 0.0389 (19) | 0.057 (2) | 0.059 (2) | -0.0073 (17) | 0.0030 (17) | 0.0075 (18) |
| C4 | 0.059 (2) | 0.058 (2) | 0.045 (2) | -0.0166 (19) | -0.0031 (17) | -0.0041 (17) |
| C9 | 0.056 (2) | 0.045 (2) | 0.073 (3) | -0.0110 (18) | -0.004 (2) | -0.0066 (18) |
| C12 | 0.0360 (19) | 0.073 (3) | 0.064 (2) | 0.0088 (18) | 0.0142 (17) | 0.013 (2) |
| C1 | 0.065 (3) | 0.084 (3) | 0.091 (4) | 0.021 (2) | 0.015 (3) | -0.035 (3) |
| C2 | 0.080 (3) | 0.051 (3) | 0.107 (4) | 0.008 (2) | 0.003 (3) | -0.032 (3) |
| C12 | 0.0381 (4) | 0.0543 (5) | 0.0526 (5) | 0.0011 (4) | -0.0005 (4) | 0.0077 (4) |
| O2 | 0.075 (2) | 0.0661 (19) | 0.0713 (19) | -0.0057 (15) | 0.0047 (15) | 0.0206 (15) |
| O1 | 0.074 (2) | 0.105 (3) | 0.114 (3) | 0.043 (2) | 0.002 (2) | -0.002 (2) |
| O4 | 0.080 (2) | 0.101 (3) | 0.0551 (18) | -0.0078 (19) | 0.0068 (15) | -0.0074 (16) |
| O3 | 0.074 (2) | 0.097 (2) | 0.081 (2) | -0.0366 (19) | -0.0162 (17) | 0.0177 (18) |

Geometric parameters (Å, °)

| | | | |
|---------|-----------|----------|-----------|
| Br1—C16 | 1.921 (3) | C6—H6B | 0.9700 |
| O8—C4 | 1.440 (4) | C10—C9 | 1.503 (5) |
| O8—C5 | 1.448 (4) | C10—H10A | 0.9700 |
| N1—C13 | 1.476 (4) | C10—H10B | 0.9700 |
| N1—H1A | 0.8900 | C7—C8 | 1.507 (5) |
| N1—H1B | 0.8900 | C7—H7A | 0.9700 |
| N1—H1E | 0.8900 | C7—H7B | 0.9700 |
| O9—C7 | 1.430 (4) | C19—H19A | 0.9600 |
| O9—C6 | 1.437 (4) | C19—H19B | 0.9600 |
| C15—C14 | 1.396 (4) | C19—H19C | 0.9600 |

supplementary materials

| | | | |
|--------------|-----------|---------------|-----------|
| C15—C16 | 1.397 (4) | C8—H8A | 0.9700 |
| C15—C19 | 1.523 (4) | C8—H8B | 0.9700 |
| C16—C17 | 1.393 (5) | C3—C4 | 1.497 (6) |
| O6—C1 | 1.435 (5) | C3—H3A | 0.9700 |
| O6—C12 | 1.440 (4) | C3—H3B | 0.9700 |
| O5—C10 | 1.437 (5) | C5—H5A | 0.9700 |
| O5—C11 | 1.442 (4) | C5—H5B | 0.9700 |
| O7—C2 | 1.445 (5) | C4—H4A | 0.9700 |
| O7—C3 | 1.451 (5) | C4—H4B | 0.9700 |
| O10—C9 | 1.432 (4) | C9—H9A | 0.9700 |
| O10—C8 | 1.440 (4) | C9—H9B | 0.9700 |
| C13—C18 | 1.390 (4) | C12—H12A | 0.9700 |
| C13—C14 | 1.394 (4) | C12—H12B | 0.9700 |
| C17—C18 | 1.393 (4) | C1—C2 | 1.498 (7) |
| C17—H17A | 0.9300 | C1—H1C | 0.9700 |
| C18—H18A | 0.9300 | C1—H1D | 0.9700 |
| C14—H14A | 0.9300 | C2—H2A | 0.9700 |
| C11—C12 | 1.493 (6) | C2—H2B | 0.9700 |
| C11—H11A | 0.9700 | C12—O1 | 1.426 (3) |
| C11—H11B | 0.9700 | C12—O3 | 1.439 (3) |
| C6—C5 | 1.503 (5) | C12—O2 | 1.441 (3) |
| C6—H6A | 0.9700 | C12—O4 | 1.457 (3) |
| C4—O8—C5 | 114.1 (3) | C15—C19—H19C | 109.5 |
| C13—N1—H1A | 109.5 | H19A—C19—H19C | 109.5 |
| C13—N1—H1B | 109.5 | H19B—C19—H19C | 109.5 |
| H1A—N1—H1B | 109.5 | O10—C8—C7 | 108.7 (3) |
| C13—N1—H1E | 109.5 | O10—C8—H8A | 110.0 |
| H1A—N1—H1E | 109.5 | C7—C8—H8A | 110.0 |
| H1B—N1—H1E | 109.5 | O10—C8—H8B | 110.0 |
| C7—O9—C6 | 111.6 (3) | C7—C8—H8B | 110.0 |
| C14—C15—C16 | 117.0 (3) | H8A—C8—H8B | 108.3 |
| C14—C15—C19 | 120.6 (3) | O7—C3—C4 | 108.9 (3) |
| C16—C15—C19 | 122.3 (3) | O7—C3—H3A | 109.9 |
| C17—C16—C15 | 122.3 (3) | C4—C3—H3A | 109.9 |
| C17—C16—Br1 | 118.3 (2) | O7—C3—H3B | 109.9 |
| C15—C16—Br1 | 119.4 (2) | C4—C3—H3B | 109.9 |
| C1—O6—C12 | 112.7 (3) | H3A—C3—H3B | 108.3 |
| C10—O5—C11 | 112.5 (3) | O8—C5—C6 | 108.5 (3) |
| C2—O7—C3 | 112.0 (3) | O8—C5—H5A | 110.0 |
| C9—O10—C8 | 112.4 (3) | C6—C5—H5A | 110.0 |
| C18—C13—C14 | 120.5 (3) | O8—C5—H5B | 110.0 |
| C18—C13—N1 | 120.1 (3) | C6—C5—H5B | 110.0 |
| C14—C13—N1 | 119.4 (3) | H5A—C5—H5B | 108.4 |
| C18—C17—C16 | 119.5 (3) | O8—C4—C3 | 108.0 (3) |
| C18—C17—H17A | 120.2 | O8—C4—H4A | 110.1 |
| C16—C17—H17A | 120.2 | C3—C4—H4A | 110.1 |
| C13—C18—C17 | 119.2 (3) | O8—C4—H4B | 110.1 |
| C13—C18—H18A | 120.4 | C3—C4—H4B | 110.1 |
| C17—C18—H18A | 120.4 | H4A—C4—H4B | 108.4 |

| | | | |
|-----------------|------------|---------------|-------------|
| C13—C14—C15 | 121.4 (3) | O10—C9—C10 | 108.9 (3) |
| C13—C14—H14A | 119.3 | O10—C9—H9A | 109.9 |
| C15—C14—H14A | 119.3 | C10—C9—H9A | 109.9 |
| O5—C11—C12 | 109.2 (3) | O10—C9—H9B | 109.9 |
| O5—C11—H11A | 109.8 | C10—C9—H9B | 109.9 |
| C12—C11—H11A | 109.8 | H9A—C9—H9B | 108.3 |
| O5—C11—H11B | 109.8 | O6—C12—C11 | 109.1 (3) |
| C12—C11—H11B | 109.8 | O6—C12—H12A | 109.9 |
| H11A—C11—H11B | 108.3 | C11—C12—H12A | 109.9 |
| O9—C6—C5 | 109.3 (3) | O6—C12—H12B | 109.9 |
| O9—C6—H6A | 109.8 | C11—C12—H12B | 109.9 |
| C5—C6—H6A | 109.8 | H12A—C12—H12B | 108.3 |
| O9—C6—H6B | 109.8 | O6—C1—C2 | 109.9 (4) |
| C5—C6—H6B | 109.8 | O6—C1—H1C | 109.7 |
| H6A—C6—H6B | 108.3 | C2—C1—H1C | 109.7 |
| O5—C10—C9 | 109.7 (3) | O6—C1—H1D | 109.7 |
| O5—C10—H10A | 109.7 | C2—C1—H1D | 109.7 |
| C9—C10—H10A | 109.7 | H1C—C1—H1D | 108.2 |
| O5—C10—H10B | 109.7 | O7—C2—C1 | 109.3 (4) |
| C9—C10—H10B | 109.7 | O7—C2—H2A | 109.8 |
| H10A—C10—H10B | 108.2 | C1—C2—H2A | 109.8 |
| O9—C7—C8 | 108.5 (3) | O7—C2—H2B | 109.8 |
| O9—C7—H7A | 110.0 | C1—C2—H2B | 109.8 |
| C8—C7—H7A | 110.0 | H2A—C2—H2B | 108.3 |
| O9—C7—H7B | 110.0 | O1—C12—O3 | 110.3 (2) |
| C8—C7—H7B | 110.0 | O1—C12—O2 | 109.5 (2) |
| H7A—C7—H7B | 108.4 | O3—C12—O2 | 110.04 (19) |
| C15—C19—H19A | 109.5 | O1—C12—O4 | 109.1 (2) |
| C15—C19—H19B | 109.5 | O3—C12—O4 | 109.5 (2) |
| H19A—C19—H19B | 109.5 | O2—C12—O4 | 108.4 (2) |
| C14—C15—C16—C17 | -0.6 (5) | C6—O9—C7—C8 | 174.6 (3) |
| C19—C15—C16—C17 | 179.8 (3) | C9—O10—C8—C7 | -178.6 (3) |
| C14—C15—C16—Br1 | 177.5 (2) | O9—C7—C8—O10 | -67.0 (4) |
| C19—C15—C16—Br1 | -2.1 (4) | C2—O7—C3—C4 | 169.7 (4) |
| C15—C16—C17—C18 | 0.7 (5) | C4—O8—C5—C6 | 180.0 (3) |
| Br1—C16—C17—C18 | -177.4 (3) | O9—C6—C5—O8 | 66.3 (4) |
| C14—C13—C18—C17 | -0.5 (5) | C5—O8—C4—C3 | -164.9 (3) |
| N1—C13—C18—C17 | 179.1 (3) | O7—C3—C4—O8 | -66.0 (4) |
| C16—C17—C18—C13 | -0.2 (5) | C8—O10—C9—C10 | 169.2 (3) |
| C18—C13—C14—C15 | 0.6 (5) | O5—C10—C9—O10 | 68.3 (4) |
| N1—C13—C14—C15 | -178.9 (3) | C1—O6—C12—C11 | -175.7 (4) |
| C16—C15—C14—C13 | -0.1 (5) | O5—C11—C12—O6 | -60.0 (4) |
| C19—C15—C14—C13 | 179.6 (3) | C12—O6—C1—C2 | 173.7 (4) |
| C10—O5—C11—C12 | 178.1 (3) | C3—O7—C2—C1 | 177.2 (4) |
| C7—O9—C6—C5 | 180.0 (3) | O6—C1—C2—O7 | 67.1 (5) |
| C11—O5—C10—C9 | -174.4 (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—H1B...O5 | 0.89 | 2.19 | 2.955 (4) | 144 |
| N1—H1E...O6 | 0.89 | 2.29 | 2.970 (4) | 133 |
| N1—H1E...O7 | 0.89 | 2.12 | 2.893 (4) | 145 |
| N1—H1A...O8 | 0.89 | 2.22 | 2.905 (4) | 134 |
| N1—H1A...O9 | 0.89 | 2.19 | 2.966 (4) | 145 |
| N1—H1B...O10 | 0.89 | 2.22 | 2.912 (4) | 134 |

Fig. 1

