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# Ethanaminium 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate methanol monosolvate

**Jian Li**

Department of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, People's Republic of China
Correspondence e-mail: ljwfu@163.com

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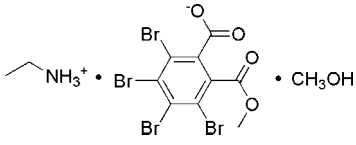
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.011 Å; $R$ factor = 0.042; $wR$ factor = 0.068; data-to-parameter ratio = 16.5.

In the crystal structure of the title compound, $C_2H_8N^+\cdot C_9H_3Br_4O_4^-\cdot CH_4O$, intermolecular N—H···O and O—H···O hydrogen bonds link the components into chains along [001]. Additional stabilization is supplied by weak C—H···O and C—H···Br interactions.

## Related literature

For a related structure, see: Liang (2008).




## Experimental

### Crystal data

$C_2H_8N^+\cdot C_9H_3Br_4O_4^-\cdot CH_4O$
$M_r$ = 572.89
Monoclinic, $P2_1/c$
$a$ = 9.4651 (8) Å
$b$ = 25.6544 (19) Å
$c$ = 8.3365 (6) Å
$\beta$ = 112.787 (1)°
$V$ = 1866.3 (2) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 8.64 mm$^{-1}$
$T$ = 298 K
0.40 × 0.35 × 0.33 mm

### Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min}$ = 0.130, $T_{max}$ = 0.163
9436 measured reflections
3295 independent reflections
1454 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.086

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.068
$S$ = 0.99
3295 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.49 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.51 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$A$···O4$^{i}$ | 0.89 | 1.94 | 2.772 (9) | 155 |
| N1—H1$B$···O5 | 0.89 | 1.92 | 2.810 (9) | 174 |
| N1—H1$C$···O3$^{ii}$ | 0.89 | 1.99 | 2.871 (7) | 170 |
| N1—H1$C$···O4$^{ii}$ | 0.89 | 2.58 | 3.249 (8) | 132 |
| O5—H5···O3 | 0.82 | 1.90 | 2.705 (8) | 165 |
| C10—H10$A$···Br3$^{iii}$ | 0.97 | 2.92 | 3.736 (8) | 143 |
| C11—H11$B$···O2$^{iv}$ | 0.96 | 2.47 | 3.357 (10) | 153 |

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5189).

## References

Bruker (1997). *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Liang, Z.-P. (2008). *Acta Cryst.* E**64**, o2416.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

# supporting information

*Acta Cryst.* (2011). E**67**, o200 [https://doi.org/10.1107/S1600536810052591]

## Ethanaminium 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate methanol monosolvate

**Jian Li**

### S1. Comment

4,5,6,7-Tetrabromo-2-ethylisoindoline-1,3-dione is an important flame retardant. 2-(Methoxycarbonyl)-3,4,5,6-tetrabromobenzoic acid is an intermediate in the sytnthesis of this flame retardant. In this paper, the structure of the title compound is reported. The asymmetric unit of the title compound (I) contains one ethanaminium cation, one 2-(methoxycarbonyl)-3,4,5,6-tetrabromobenzoate anion and one methanol solvent molecule (Fig. 1). The bond lengths and angles agree with those in ethane-1,2-diaminium 2-(methoxycarbonyl)-3,4,5,6-tetrabromo benzoate methanol solvate (Liang, 2008). In the crystal structure, intermolecular N—H···O and O—H···O hydrogen bonds link the components of the structure into one-dimensional chains along [001](see fig. 2). Additional stabilization is supplied by weak C—H···O and C—H···Br interactions.

### S2. Experimental

A mixture of 4,5,6,7-tetrabromoisobenzofuran-1,3-dione (4.64 g, 0.01 mol) and methanol (15 ml) was refluxed for 0.5 h. And then ethanamine (0.45 g, 0.01 mol) was added to the above solution, and mixed for 10 min at room temperature. The solution was kept at room temperature for 3 d. Natural evaporation gave colourless single crystals of the title compound, suitable for X-ray analysis.

### S3. Refinement

H atoms were initially located from difference maps and then refined in a riding model with C—H = 0.96–0.97 Å, N—H = 0.89 Å, O-H = 0.82Å and $U_{iso}$(H) = 1.2$U_{eq}$(C) or 1.5$U_{eq}$(O, N, methyl C).

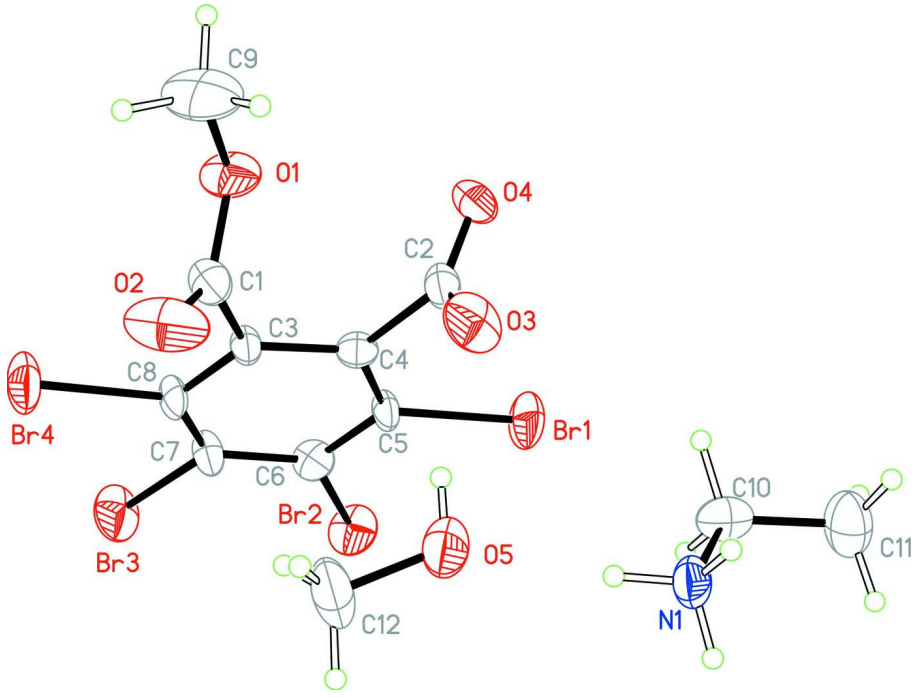


**Figure 1**

The asymmetric unit of (I), drawn with 30% probability ellipsoids.

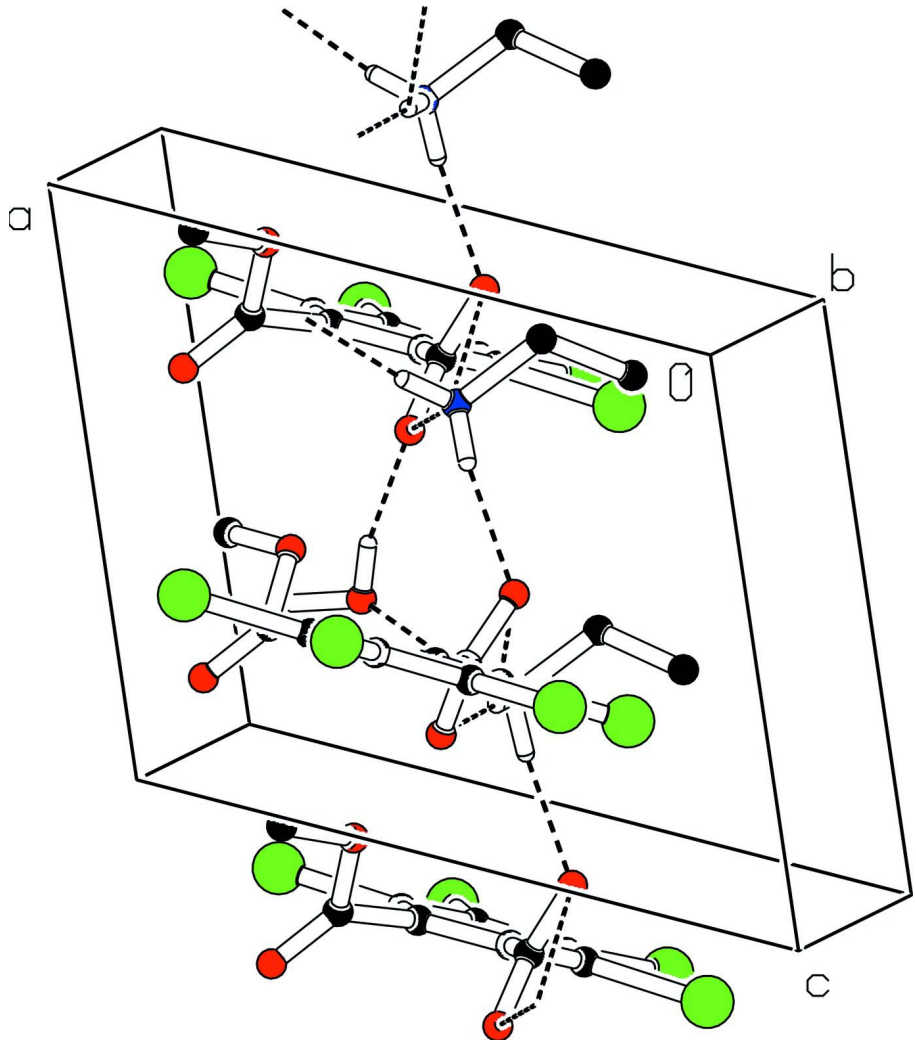


**Figure 2**

The crystal packing of (I). Hydrogen bonds are indicated by dashed lines.

## Ethanaminium 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate methanol monosolvate

*Crystal data*

$C_2H_8N^+·C_9H_3Br_4O_4^-·CH_4O$
$M_r$ = 572.89
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a$ = 9.4651 (8) Å
$b$ = 25.6544 (19) Å
$c$ = 8.3365 (6) Å
$\beta$ = 112.787 (1)°
$V$ = 1866.3 (2) Å$^3$
$Z$ = 4
$F(000)$ = 1096
$D_x$ = 2.039 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 1513 reflections
$\theta$ = 2.3–20.6°
$\mu$ = 8.64 mm$^{-1}$
$T$ = 298 K
Block, colorless
0.40 × 0.35 × 0.33 mm

*Data collection*

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min}$ = 0.130, $T_{max}$ = 0.163
9436 measured reflections
3295 independent reflections
1454 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.086
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 2.3°
$h = -9 \rightarrow 11$
$k = -30 \rightarrow 30$
$l = -9 \rightarrow 8$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.068
$S$ = 0.99
3295 reflections
200 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0024P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.49 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.51 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.32729 (8) | 0.90633 (3) | 0.26426 (13) | 0.0702 (3) |
| Br2 | 0.40752 (9) | 1.03175 (3) | 0.25156 (12) | 0.0705 (3) |
| Br3 | 0.73585 (10) | 1.06551 (3) | 0.23297 (14) | 0.0807 (3) |
| Br4 | 0.98266 (9) | 0.97499 (3) | 0.23443 (13) | 0.0773 (3) |
| N1 | 0.5436 (6) | 0.7996 (2) | 0.8034 (8) | 0.0546 (19) |
| H1A | 0.5376 | 0.8133 | 0.8986 | 0.082* |
| H1B | 0.6186 | 0.8151 | 0.7820 | 0.082* |
| H1C | 0.5631 | 0.7656 | 0.8196 | 0.082* |
| O1 | 0.8313 (6) | 0.8333 (2) | 0.1273 (8) | 0.0672 (18) |
| O2 | 0.9937 (7) | 0.8565 (2) | 0.3871 (9) | 0.101 (3) |
| O3 | 0.6431 (6) | 0.8063 (2) | 0.3863 (8) | 0.076 (2) |
| O4 | 0.4945 (6) | 0.8125 (2) | 0.1079 (8) | 0.0713 (19) |
| O5 | 0.7663 (7) | 0.8481 (2) | 0.7090 (7) | 0.104 (2) |
| H5 | 0.7413 | 0.8383 | 0.6081 | 0.157* |
| C1 | 0.8783 (9) | 0.8620 (3) | 0.2667 (14) | 0.050 (3) |
| C2 | 0.5820 (10) | 0.8306 (3) | 0.2499 (14) | 0.050 (3) |

| | | | | |
|---|---|---|---|---|
| C3 | 0.7630 (7) | 0.9042 (3) | 0.2521 (9) | 0.0369 (19) |
| C4 | 0.6200 (8) | 0.8886 (3) | 0.2517 (9) | 0.040 (2) |
| C5 | 0.5158 (7) | 0.9276 (3) | 0.2534 (9) | 0.040 (2) |
| C6 | 0.5515 (7) | 0.9794 (3) | 0.2527 (9) | 0.047 (2) |
| C7 | 0.6915 (8) | 0.9947 (3) | 0.2450 (10) | 0.045 (2) |
| C8 | 0.7960 (7) | 0.9565 (3) | 0.2469 (9) | 0.040 (2) |
| C9 | 0.9329 (9) | 0.7886 (3) | 0.1323 (11) | 0.097 (3) |
| H9A | 1.0367 | 0.8006 | 0.1685 | 0.146* |
| H9B | 0.9010 | 0.7734 | 0.0185 | 0.146* |
| H9C | 0.9266 | 0.7629 | 0.2131 | 0.146* |
| C10 | 0.3935 (9) | 0.8076 (3) | 0.6508 (10) | 0.056 (2) |
| H10A | 0.3730 | 0.8447 | 0.6333 | 0.068* |
| H10B | 0.4018 | 0.7937 | 0.5466 | 0.068* |
| C11 | 0.2643 (8) | 0.7820 (3) | 0.6773 (10) | 0.081 (3) |
| H11A | 0.2763 | 0.7449 | 0.6766 | 0.121* |
| H11B | 0.1697 | 0.7919 | 0.5854 | 0.121* |
| H11C | 0.2630 | 0.7926 | 0.7872 | 0.121* |
| C12 | 0.8988 (9) | 0.8774 (3) | 0.7572 (12) | 0.104 (4) |
| H12A | 0.9141 | 0.8959 | 0.8627 | 0.155* |
| H12B | 0.8899 | 0.9019 | 0.6667 | 0.155* |
| H12C | 0.9844 | 0.8548 | 0.7757 | 0.155* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0399 (5) | 0.0808 (7) | 0.1016 (9) | −0.0038 (5) | 0.0403 (6) | 0.0061 (6) |
| Br2 | 0.0615 (6) | 0.0617 (6) | 0.0956 (8) | 0.0286 (5) | 0.0386 (6) | 0.0063 (6) |
| Br3 | 0.0898 (7) | 0.0337 (5) | 0.1331 (10) | −0.0058 (5) | 0.0592 (7) | −0.0010 (6) |
| Br4 | 0.0455 (6) | 0.0699 (7) | 0.1306 (10) | −0.0122 (5) | 0.0496 (6) | −0.0070 (6) |
| N1 | 0.061 (5) | 0.042 (4) | 0.072 (6) | −0.011 (3) | 0.039 (4) | 0.000 (4) |
| O1 | 0.057 (4) | 0.063 (4) | 0.077 (5) | 0.027 (3) | 0.022 (4) | −0.014 (4) |
| O2 | 0.068 (4) | 0.114 (6) | 0.085 (6) | 0.048 (4) | −0.011 (4) | −0.033 (4) |
| O3 | 0.101 (5) | 0.044 (4) | 0.070 (5) | −0.006 (3) | 0.020 (4) | 0.019 (4) |
| O4 | 0.094 (5) | 0.062 (4) | 0.062 (5) | −0.038 (3) | 0.035 (4) | −0.021 (4) |
| O5 | 0.101 (5) | 0.150 (6) | 0.074 (6) | −0.064 (4) | 0.048 (4) | −0.018 (4) |
| C1 | 0.036 (6) | 0.042 (6) | 0.072 (9) | 0.003 (5) | 0.020 (6) | −0.009 (6) |
| C2 | 0.047 (6) | 0.036 (6) | 0.075 (9) | −0.006 (5) | 0.035 (6) | −0.005 (6) |
| C3 | 0.031 (4) | 0.028 (4) | 0.057 (6) | −0.003 (4) | 0.023 (4) | −0.005 (5) |
| C4 | 0.043 (5) | 0.032 (5) | 0.043 (6) | 0.007 (4) | 0.017 (5) | −0.002 (4) |
| C5 | 0.026 (4) | 0.038 (5) | 0.060 (6) | −0.007 (4) | 0.021 (4) | −0.004 (5) |
| C6 | 0.035 (5) | 0.045 (6) | 0.058 (6) | 0.014 (4) | 0.016 (5) | −0.001 (4) |
| C7 | 0.032 (5) | 0.033 (5) | 0.068 (6) | −0.003 (4) | 0.019 (5) | 0.003 (4) |
| C8 | 0.016 (4) | 0.041 (5) | 0.062 (6) | −0.001 (4) | 0.014 (4) | −0.002 (5) |
| C9 | 0.090 (7) | 0.080 (7) | 0.106 (9) | 0.045 (6) | 0.022 (6) | −0.025 (6) |
| C10 | 0.077 (6) | 0.046 (6) | 0.040 (6) | 0.018 (5) | 0.015 (6) | 0.009 (5) |
| C11 | 0.052 (6) | 0.097 (7) | 0.085 (8) | −0.013 (5) | 0.017 (6) | 0.016 (6) |
| C12 | 0.082 (7) | 0.100 (8) | 0.144 (10) | −0.050 (6) | 0.060 (7) | −0.030 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C5 | 1.902 (6) | C3—C4 | 1.411 (8) |
| Br2—C6 | 1.911 (6) | C4—C5 | 1.410 (8) |
| Br3—C7 | 1.876 (6) | C5—C6 | 1.370 (8) |
| Br4—C8 | 1.871 (6) | C6—C7 | 1.408 (7) |
| N1—C10 | 1.509 (8) | C7—C8 | 1.389 (8) |
| N1—H1A | 0.8900 | C9—H9A | 0.9600 |
| N1—H1B | 0.8900 | C9—H9B | 0.9600 |
| N1—H1C | 0.8900 | C9—H9C | 0.9600 |
| O1—C1 | 1.301 (9) | C10—C11 | 1.478 (8) |
| O1—C9 | 1.487 (7) | C10—H10A | 0.9700 |
| O2—C1 | 1.171 (9) | C10—H10B | 0.9700 |
| O3—C2 | 1.227 (9) | C11—H11A | 0.9600 |
| O4—C2 | 1.241 (9) | C11—H11B | 0.9600 |
| O5—C12 | 1.381 (7) | C11—H11C | 0.9600 |
| O5—H5 | 0.8200 | C12—H12A | 0.9600 |
| C1—C3 | 1.507 (9) | C12—H12B | 0.9600 |
| C2—C4 | 1.530 (9) | C12—H12C | 0.9600 |
| C3—C8 | 1.381 (7) | | |

| | | | |
|---|---|---|---|
| C10—N1—H1A | 109.5 | C6—C7—Br3 | 120.5 (5) |
| C10—N1—H1B | 109.5 | C3—C8—C7 | 121.2 (6) |
| H1A—N1—H1B | 109.5 | C3—C8—Br4 | 118.6 (5) |
| C10—N1—H1C | 109.5 | C7—C8—Br4 | 120.2 (5) |
| H1A—N1—H1C | 109.5 | O1—C9—H9A | 109.5 |
| H1B—N1—H1C | 109.5 | O1—C9—H9B | 109.5 |
| C1—O1—C9 | 114.7 (6) | H9A—C9—H9B | 109.5 |
| C12—O5—H5 | 109.5 | O1—C9—H9C | 109.5 |
| O2—C1—O1 | 125.5 (8) | H9A—C9—H9C | 109.5 |
| O2—C1—C3 | 124.2 (9) | H9B—C9—H9C | 109.5 |
| O1—C1—C3 | 110.4 (7) | C11—C10—N1 | 112.1 (6) |
| O3—C2—O4 | 126.6 (8) | C11—C10—H10A | 109.2 |
| O3—C2—C4 | 117.4 (8) | N1—C10—H10A | 109.2 |
| O4—C2—C4 | 116.0 (8) | C11—C10—H10B | 109.2 |
| C8—C3—C4 | 120.3 (6) | N1—C10—H10B | 109.2 |
| C8—C3—C1 | 122.3 (6) | H10A—C10—H10B | 107.9 |
| C4—C3—C1 | 117.4 (6) | C10—C11—H11A | 109.5 |
| C5—C4—C3 | 118.2 (6) | C10—C11—H11B | 109.5 |
| C5—C4—C2 | 121.9 (7) | H11A—C11—H11B | 109.5 |
| C3—C4—C2 | 119.9 (6) | C10—C11—H11C | 109.5 |
| C6—C5—C4 | 121.0 (6) | H11A—C11—H11C | 109.5 |
| C6—C5—Br1 | 121.0 (5) | H11B—C11—H11C | 109.5 |
| C4—C5—Br1 | 118.0 (5) | O5—C12—H12A | 109.5 |
| C5—C6—C7 | 120.6 (6) | O5—C12—H12B | 109.5 |
| C5—C6—Br2 | 120.3 (5) | H12A—C12—H12B | 109.5 |
| C7—C6—Br2 | 119.0 (6) | O5—C12—H12C | 109.5 |
| C8—C7—C6 | 118.8 (6) | H12A—C12—H12C | 109.5 |

| | | | |
|---|---|---|---|
| C8—C7—Br3 | 120.8 (5) | H12B—C12—H12C | 109.5 |
| | | | |
| C9—O1—C1—O2 | 3.5 (13) | C2—C4—C5—Br1 | 2.8 (10) |
| C9—O1—C1—C3 | −176.8 (6) | C4—C5—C6—C7 | 1.9 (11) |
| O2—C1—C3—C8 | 64.3 (12) | Br1—C5—C6—C7 | 179.9 (5) |
| O1—C1—C3—C8 | −115.3 (8) | C4—C5—C6—Br2 | 179.1 (5) |
| O2—C1—C3—C4 | −112.9 (10) | Br1—C5—C6—Br2 | −2.9 (9) |
| O1—C1—C3—C4 | 67.5 (9) | C5—C6—C7—C8 | −3.2 (11) |
| C8—C3—C4—C5 | −2.7 (10) | Br2—C6—C7—C8 | 179.6 (6) |
| C1—C3—C4—C5 | 174.6 (7) | C5—C6—C7—Br3 | 177.0 (6) |
| C8—C3—C4—C2 | 177.5 (7) | Br2—C6—C7—Br3 | −0.2 (8) |
| C1—C3—C4—C2 | −5.3 (11) | C4—C3—C8—C7 | 1.4 (11) |
| O3—C2—C4—C5 | −104.5 (9) | C1—C3—C8—C7 | −175.7 (8) |
| O4—C2—C4—C5 | 77.2 (10) | C4—C3—C8—Br4 | −176.4 (5) |
| O3—C2—C4—C3 | 75.3 (10) | C1—C3—C8—Br4 | 6.4 (11) |
| O4—C2—C4—C3 | −103.0 (8) | C6—C7—C8—C3 | 1.5 (11) |
| C3—C4—C5—C6 | 1.0 (10) | Br3—C7—C8—C3 | −178.7 (5) |
| C2—C4—C5—C6 | −179.1 (7) | C6—C7—C8—Br4 | 179.3 (5) |
| C3—C4—C5—Br1 | −177.0 (5) | Br3—C7—C8—Br4 | −0.9 (9) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···O4$^{i}$ | 0.89 | 1.94 | 2.772 (9) | 155 |
| N1—H1*B*···O5 | 0.89 | 1.92 | 2.810 (9) | 174 |
| N1—H1*C*···O3$^{ii}$ | 0.89 | 1.99 | 2.871 (7) | 170 |
| N1—H1*C*···O4$^{ii}$ | 0.89 | 2.58 | 3.249 (8) | 132 |
| O5—H5···O3 | 0.82 | 1.90 | 2.705 (8) | 165 |
| C10—H10*A*···Br3$^{iii}$ | 0.97 | 2.92 | 3.736 (8) | 143 |
| C11—H11*B*···O2$^{iv}$ | 0.96 | 2.47 | 3.357 (10) | 153 |

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*, −*y*+3/2, *z*+1/2; (iii) −*x*+1, −*y*+2, −*z*+1; (iv) *x*−1, *y*, *z*.