# organic papers

# 1-Chloro-3,4-dinitrobenzene–1,4-dioxane (1/1)

## Sarah A. Barnett,* Juliette Pradon, Thomas C. Lewis and Derek A. Tocher

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, England

Correspondence e-mail:
sarah.barnett@ucl.ac.uk

## Key indicators

Single-crystal X-ray study
$T$ = 150 K
Mean $\sigma$(C–C) = 0.002 Å
$R$ factor = 0.031
$wR$ factor = 0.084
Data-to-parameter ratio = 12.3

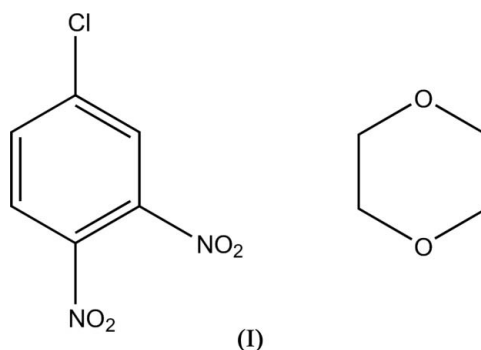For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The solvate structure of 1-chloro-3,4-dinitrobenzene with 1,4-dioxane, $C_6H_3ClN_2O_4 \cdot C_4H_8N_2$, is reported. Alternating molecules of 3,4-dinitro-1-chlorobenzene and 1,4-dioxane are linked by C—H···O hydrogen bonds into a continuous two-dimensional sheet.

## Comment

The title compound, (I), was produced during an experimental crystallization polymorph screen on 1-chloro-3,4-dinitrobenzene (3,4-DNCB). Compound (I) crystallizes in the space group $P\bar{1}$ with one molecule of 3,4-DNCB and one molecule of 1,4-dioxane in the asymmetric unit (Fig. 1).



The crystal structure of (I) is characterized by alternating molecules of 3,4-DNCB and 1,4-dioxane, linked by a series of C—H···O hydrogen bonds (Table 1) into a continuous two-dimensional sheet which lies parallel to the $(11\bar{1})$ plane (Fig. 2). Alternating 3,4-DNCB molecules and 1,4-dioxane are linked by pairwise C—H···O hydrogen bonds, forming a chain
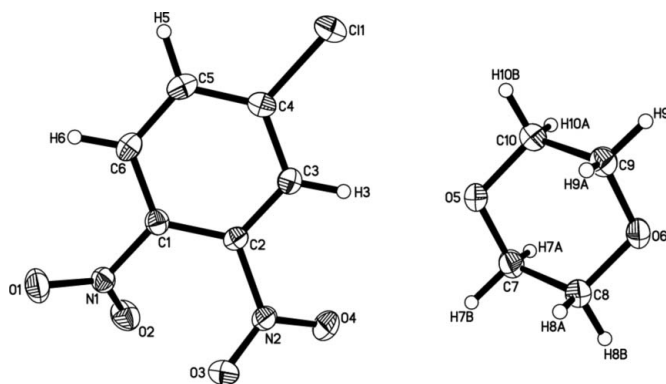


**Figure 1**
The structure of the asymmetric unit of (I), showing the numbering scheme used. Displacement ellipsoids are drawn at the 50% probability level.
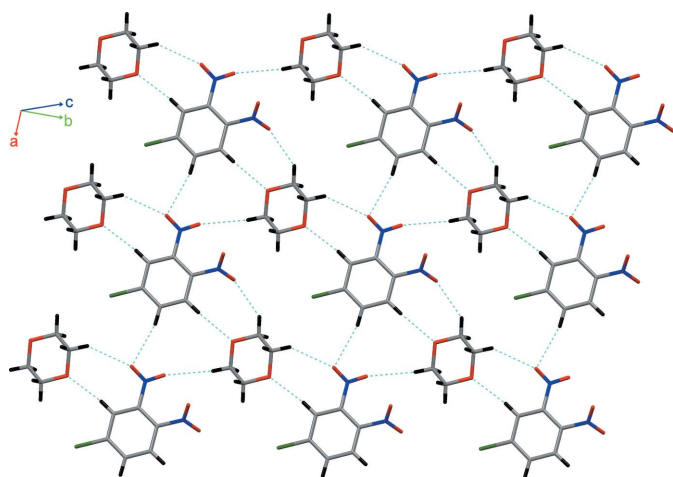
**Figure 2**
The two-dimensional network formed by compound (I), showing the intermolecular interactions as thin pale-blue lines. Key: C grey, N blue, O red, Cl green and H black.
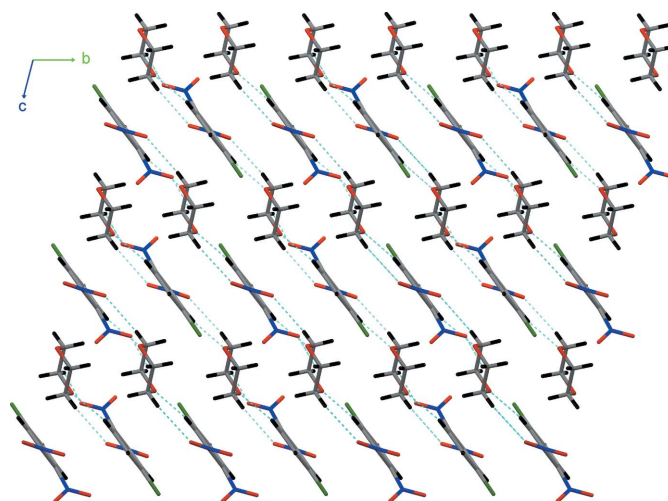


**Figure 3**
Packing diagram, showing the stacking of the sheets. C—H···O interactions are shown as thin pale-blue lines. Key: C grey, N blue, O red, Cl green and H black.

which runs parallel to the body diagonal (111). These chains are then hydrogen-bonded together, forming a sheet *via* two C—H···O interactions between two 3,4-DNCB molecules and one C—H···O interaction between the 3,4-DNCB molecule and a 1,4-dioxane molecule of the adjacent chain. Viewing the crystal structure down the *a* axis reveals that there are alternating layers of 3,4-DNCB and 1,4-dioxane (Fig. 3).

## Experimental

The title compound was recrystallized from 1,4-dioxane solution by slow evaporation at 298 K.

### Crystal data

$C_6H_3ClN_2O_4 \cdot C_4H_8O_2$
$M_r = 290.66$
Triclinic, $P\bar{1}$
$a = 8.2976$ (12) Å
$b = 8.7112$ (13) Å
$c = 8.8015$ (13) Å
$\alpha = 103.661$ (2)°
$\beta = 103.909$ (2)°
$\gamma = 91.718$ (2)°
$V = 597.52$ (15) Å$^3$

$Z = 2$
$D_x = 1.616$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3669 reflections
$\theta = 2.5–28.2°$
$\mu = 0.35$ mm$^{-1}$
$T = 150$ (2) K
Block, yellow
$0.86 \times 0.67 \times 0.45$ mm

### Data collection

Bruker SMART APEX diffractometer
Narrow–frame $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.738$, $T_{max} = 0.856$
4424 measured reflections

2650 independent reflections
2529 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 28.2°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.084$
$S = 1.07$
2647 reflections
216 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.1587P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å$^{-3}$
$\Delta\rho_{min} = -0.32$ e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C3—H3···O5 | 0.938 (15) | 2.331 (15) | 3.2553 (14) | 168.3 (13) |
| C5—H5···O4$^i$ | 0.969 (17) | 2.697 (18) | 3.6166 (16) | 158.7 (13) |
| C6—H6···O6$^{ii}$ | 0.949 (15) | 2.468 (15) | 3.4017 (14) | 168.1 (12) |
| C7—H7B···O4 | 0.990 (17) | 2.624 (17) | 3.4618 (16) | 142.5 (13) |
| C8—H8B···O1$^{iii}$ | 0.996 (19) | 2.446 (18) | 3.2604 (16) | 138.6 (13) |
| C9—H9B···O3$^{iv}$ | 0.951 (18) | 2.649 (18) | 3.5930 (16) | 172.3 (14) |

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

H atoms were located in a difference Fourier map and refined freely [C—H = 0.938 (15)–0.996 (19) Å]. The three reflections with the greatest discrepancies were omitted from the refinement.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

## References

Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SMART* (Version 5.625), *SAINT* (Version 6.22) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M. K., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Sheldrick, G. M. (1997). *SHELXS97 & SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

# supporting information

## 1-Chloro-3,4-dinitrobenzene–1,4-dioxane (1/1)

### Sarah A. Barnett, Juliette Pradon, Thomas C. Lewis and Derek A. Tocher

**4-Chloro-1,2-dinitrobenzene–1,4-dioxane (1/1)**

*Crystal data*

| | |
|---|---|
| $C_6H_3ClN_2O_4 \cdot C_4H_8O_2$ | $Z = 2$ |
| $M_r = 290.66$ | $F(000) = 300$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.616$ Mg m$^{-3}$ |
| $a = 8.2976$ (12) Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $b = 8.7112$ (13) Å | Cell parameters from 3669 reflections |
| $c = 8.8015$ (13) Å | $\theta = 2.5$–28.2° |
| $\alpha = 103.661$ (2)° | $\mu = 0.35$ mm$^{-1}$ |
| $\beta = 103.909$ (2)° | $T = 150$ K |
| $\gamma = 91.718$ (2)° | Block, yellow |
| $V = 597.52$ (15) Å$^3$ | $0.86 \times 0.67 \times 0.45$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART APEX diffractometer | 4424 measured reflections |
| Radiation source: fine-focus sealed tube | 2650 independent reflections |
| Graphite monochromator | 2529 reflections with $I > 2\sigma(I)$ |
| Narrow–frame $\omega$ scans | $R_{int} = 0.014$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2001) | $\theta_{max} = 28.2°$, $\theta_{min} = 2.4°$ |
| | $h = -10 \rightarrow 10$ |
| | $k = -11 \rightarrow 11$ |
| $T_{min} = 0.738$, $T_{max} = 0.856$ | $l = -11 \rightarrow 11$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: Difference Fourier synthesis |
| Least-squares matrix: full | Hydrogen site location: Found from delta-F |
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | All H-atom parameters refined |
| $wR(F^2) = 0.084$ | $w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.1587P]$ |
| $S = 1.07$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 2647 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 216 parameters | $\Delta\rho_{max} = 0.36$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.32$ e Å$^{-3}$ |
| Primary atom site location: Direct methods | |

*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 (Å$^2$)*

|  | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.01692 (14) | 0.14991 (13) | 0.38735 (13) | 0.0189 (2) |
| C2 | 0.13820 (13) | 0.25986 (13) | 0.49998 (13) | 0.0182 (2) |
| C3 | 0.09882 (14) | 0.37166 (13) | 0.62157 (13) | 0.0198 (2) |
| H3 | 0.1791 (19) | 0.4482 (18) | 0.6968 (18) | 0.024 (4)* |
| C4 | −0.06714 (14) | 0.36928 (13) | 0.62793 (13) | 0.0205 (2) |
| C5 | −0.18948 (14) | 0.25951 (15) | 0.51873 (14) | 0.0233 (2) |
| H5 | −0.304 (2) | 0.262 (2) | 0.526 (2) | 0.035 (4)* |
| C6 | −0.14693 (14) | 0.14773 (14) | 0.39675 (14) | 0.0218 (2) |
| H6 | −0.2275 (19) | 0.0712 (18) | 0.3186 (18) | 0.022 (3)* |
| Cl1 | −0.11770 (4) | 0.50731 (4) | 0.78178 (4) | 0.02978 (11) |
| N1 | 0.05511 (12) | 0.04236 (11) | 0.24729 (11) | 0.0204 (2) |
| O1 | −0.00297 (12) | −0.09537 (10) | 0.21122 (11) | 0.0300 (2) |
| O2 | 0.13920 (12) | 0.09876 (11) | 0.17386 (10) | 0.0295 (2) |
| N2 | 0.31546 (12) | 0.25335 (12) | 0.50183 (11) | 0.0217 (2) |
| O3 | 0.36588 (11) | 0.12279 (11) | 0.46586 (11) | 0.0301 (2) |
| O4 | 0.40217 (11) | 0.37924 (11) | 0.54379 (12) | 0.0318 (2) |
| C7 | 0.50812 (15) | 0.71687 (15) | 0.86037 (14) | 0.0265 (3) |
| H7A | 0.512 (2) | 0.821 (2) | 0.8349 (19) | 0.034 (4)* |
| H7B | 0.533 (2) | 0.635 (2) | 0.772 (2) | 0.036 (4)* |
| C8 | 0.62967 (15) | 0.72245 (16) | 1.01944 (15) | 0.0264 (3) |
| H8A | 0.6304 (19) | 0.6196 (19) | 1.0408 (18) | 0.026 (4)* |
| H8B | 0.746 (2) | 0.756 (2) | 1.020 (2) | 0.040 (4)* |
| C9 | 0.42101 (16) | 0.79512 (16) | 1.15303 (14) | 0.0273 (3) |
| H9A | 0.414 (2) | 0.695 (2) | 1.1806 (18) | 0.029 (4)* |
| H9B | 0.398 (2) | 0.875 (2) | 1.237 (2) | 0.039 (4)* |
| C10 | 0.29983 (16) | 0.78846 (16) | 0.99319 (15) | 0.0272 (3) |
| H10A | 0.297 (2) | 0.891 (2) | 0.970 (2) | 0.037 (4)* |
| H10B | 0.186 (2) | 0.757 (2) | 0.991 (2) | 0.035 (4)* |
| O5 | 0.34241 (11) | 0.67501 (10) | 0.86581 (10) | 0.0258 (2) |
| O6 | 0.58807 (11) | 0.83433 (11) | 1.14873 (10) | 0.0273 (2) |

*Atomic displacement parameters (Å$^2$)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0205 (5) | 0.0180 (5) | 0.0177 (5) | 0.0016 (4) | 0.0039 (4) | 0.0044 (4) |
| C2 | 0.0155 (5) | 0.0194 (5) | 0.0203 (5) | 0.0011 (4) | 0.0046 (4) | 0.0058 (4) |
| C3 | 0.0193 (5) | 0.0190 (5) | 0.0204 (5) | 0.0002 (4) | 0.0045 (4) | 0.0046 (4) |
| C4 | 0.0223 (5) | 0.0211 (5) | 0.0207 (5) | 0.0051 (4) | 0.0083 (4) | 0.0068 (4) |
| C5 | 0.0170 (5) | 0.0298 (6) | 0.0248 (5) | 0.0025 (4) | 0.0055 (4) | 0.0099 (5) |
| C6 | 0.0179 (5) | 0.0246 (6) | 0.0211 (5) | −0.0012 (4) | 0.0014 (4) | 0.0067 (4) |

| | | | | | |
|---|---|---|---|---|---|
| Cl1 | 0.02999 (17) | 0.03041 (18) | 0.02956 (17) | 0.00620 (12) | 0.01481 (12) | 0.00096 (12) |
| N1 | 0.0198 (4) | 0.0199 (5) | 0.0190 (4) | 0.0023 (3) | 0.0018 (3) | 0.0031 (4) |
| O1 | 0.0339 (5) | 0.0195 (4) | 0.0312 (4) | −0.0023 (3) | 0.0049 (4) | 0.0000 (3) |
| O2 | 0.0367 (5) | 0.0284 (5) | 0.0260 (4) | 0.0016 (4) | 0.0151 (4) | 0.0047 (3) |
| N2 | 0.0168 (4) | 0.0261 (5) | 0.0198 (4) | 0.0005 (4) | 0.0047 (3) | 0.0017 (4) |
| O3 | 0.0229 (4) | 0.0300 (5) | 0.0334 (5) | 0.0083 (3) | 0.0067 (4) | 0.0005 (4) |
| O4 | 0.0217 (4) | 0.0307 (5) | 0.0390 (5) | −0.0074 (4) | 0.0089 (4) | 0.0010 (4) |
| C7 | 0.0261 (6) | 0.0276 (6) | 0.0228 (5) | −0.0011 (5) | 0.0077 (5) | −0.0002 (5) |
| C8 | 0.0224 (6) | 0.0268 (6) | 0.0258 (6) | 0.0001 (5) | 0.0058 (4) | −0.0009 (5) |
| C9 | 0.0252 (6) | 0.0327 (7) | 0.0218 (5) | −0.0001 (5) | 0.0070 (5) | 0.0017 (5) |
| C10 | 0.0240 (6) | 0.0301 (6) | 0.0242 (6) | 0.0034 (5) | 0.0061 (5) | 0.0002 (5) |
| O5 | 0.0224 (4) | 0.0267 (4) | 0.0223 (4) | −0.0012 (3) | 0.0034 (3) | −0.0027 (3) |
| O6 | 0.0239 (4) | 0.0292 (5) | 0.0225 (4) | −0.0033 (3) | 0.0045 (3) | −0.0036 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C6 | 1.3816 (16) | N2—O3 | 1.2210 (14) |
| C1—C2 | 1.3881 (15) | C7—O5 | 1.4267 (14) |
| C1—N1 | 1.4691 (14) | C7—C8 | 1.5052 (18) |
| C2—C3 | 1.3768 (15) | C7—H7A | 0.982 (17) |
| C2—N2 | 1.4700 (14) | C7—H7B | 0.990 (17) |
| C3—C4 | 1.3913 (15) | C8—O6 | 1.4314 (14) |
| C3—H3 | 0.938 (15) | C8—H8A | 0.958 (16) |
| C4—C5 | 1.3811 (16) | C8—H8B | 0.996 (19) |
| C4—Cl1 | 1.7291 (11) | C9—O6 | 1.4292 (15) |
| C5—C6 | 1.3908 (17) | C9—C10 | 1.5071 (17) |
| C5—H5 | 0.969 (17) | C9—H9A | 0.962 (17) |
| C6—H6 | 0.949 (15) | C9—H9B | 0.951 (18) |
| N1—O1 | 1.2184 (13) | C10—O5 | 1.4306 (14) |
| N1—O2 | 1.2215 (13) | C10—H10A | 0.964 (18) |
| N2—O4 | 1.2208 (13) | C10—H10B | 0.973 (17) |
| | | | |
| C6—C1—C2 | 120.56 (10) | O5—C7—H7A | 108.9 (10) |
| C6—C1—N1 | 117.89 (10) | C8—C7—H7A | 110.4 (10) |
| C2—C1—N1 | 121.33 (10) | O5—C7—H7B | 107.0 (10) |
| C3—C2—C1 | 121.33 (10) | C8—C7—H7B | 110.9 (10) |
| C3—C2—N2 | 117.30 (9) | H7A—C7—H7B | 109.0 (13) |
| C1—C2—N2 | 121.19 (10) | O6—C8—C7 | 110.89 (10) |
| C2—C3—C4 | 117.37 (10) | O6—C8—H8A | 109.6 (9) |
| C2—C3—H3 | 122.1 (9) | C7—C8—H8A | 110.3 (9) |
| C4—C3—H3 | 120.5 (9) | O6—C8—H8B | 106.8 (10) |
| C5—C4—C3 | 122.32 (10) | C7—C8—H8B | 111.9 (10) |
| C5—C4—Cl1 | 119.85 (9) | H8A—C8—H8B | 107.3 (14) |
| C3—C4—Cl1 | 117.82 (9) | O6—C9—C10 | 111.09 (10) |
| C4—C5—C6 | 119.34 (10) | O6—C9—H9A | 109.7 (10) |
| C4—C5—H5 | 120.1 (10) | C10—C9—H9A | 110.3 (9) |
| C6—C5—H5 | 120.6 (10) | O6—C9—H9B | 106.5 (11) |
| C1—C6—C5 | 119.06 (10) | C10—C9—H9B | 110.7 (11) |

| | | | |
|---|---|---|---|
| C1—C6—H6 | 119.0 (9) | H9A—C9—H9B | 108.3 (14) |
| C5—C6—H6 | 121.9 (9) | O5—C10—C9 | 110.50 (10) |
| O1—N1—O2 | 125.13 (10) | O5—C10—H10A | 110.2 (10) |
| O1—N1—C1 | 117.35 (9) | C9—C10—H10A | 110.8 (11) |
| O2—N1—C1 | 117.50 (9) | O5—C10—H10B | 106.6 (10) |
| O4—N2—O3 | 124.94 (10) | C9—C10—H10B | 113.0 (10) |
| O4—N2—C2 | 117.27 (10) | H10A—C10—H10B | 105.5 (14) |
| O3—N2—C2 | 117.76 (9) | C7—O5—C10 | 109.34 (9) |
| O5—C7—C8 | 110.53 (10) | C9—O6—C8 | 109.74 (9) |
| | | | |
| C6—C1—C2—C3 | −1.45 (17) | C2—C1—N1—O1 | 137.79 (11) |
| N1—C1—C2—C3 | 173.08 (10) | C6—C1—N1—O2 | 130.77 (11) |
| C6—C1—C2—N2 | 173.60 (10) | C2—C1—N1—O2 | −43.91 (15) |
| N1—C1—C2—N2 | −11.86 (16) | C3—C2—N2—O4 | −37.51 (14) |
| C1—C2—C3—C4 | 0.51 (17) | C1—C2—N2—O4 | 147.24 (11) |
| N2—C2—C3—C4 | −174.73 (10) | C3—C2—N2—O3 | 140.47 (11) |
| C2—C3—C4—C5 | 0.50 (17) | C1—C2—N2—O3 | −34.78 (15) |
| C2—C3—C4—Cl1 | 179.11 (8) | O5—C7—C8—O6 | −58.54 (13) |
| C3—C4—C5—C6 | −0.58 (18) | O6—C9—C10—O5 | 57.95 (14) |
| Cl1—C4—C5—C6 | −179.16 (9) | C8—C7—O5—C10 | 58.67 (13) |
| C2—C1—C6—C5 | 1.35 (17) | C9—C10—O5—C7 | −58.31 (13) |
| N1—C1—C6—C5 | −173.37 (10) | C10—C9—O6—C8 | −56.48 (14) |
| C4—C5—C6—C1 | −0.36 (17) | C7—C8—O6—C9 | 56.69 (13) |
| C6—C1—N1—O1 | −47.53 (14) | | |

*Hydrogen-bond geometry (Å, º)*

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|---|---|---|---|---|
| C3—H3⋯O5 | 0.938 (15) | 2.331 (15) | 3.2553 (14) | 168.3 (13) |
| C5—H5⋯O4[i] | 0.969 (17) | 2.697 (18) | 3.6166 (16) | 158.7 (13) |
| C6—H6⋯O6[ii] | 0.949 (15) | 2.468 (15) | 3.4017 (14) | 168.1 (12) |
| C7—H7*B*⋯O4 | 0.990 (17) | 2.624 (17) | 3.4618 (16) | 142.5 (13) |
| C8—H8*B*⋯O1[iii] | 0.996 (19) | 2.446 (18) | 3.2604 (16) | 138.6 (13) |
| C9—H9*B*⋯O3[iv] | 0.951 (18) | 2.649 (18) | 3.5930 (16) | 172.3 (14) |

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