# 2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile hemihydrate

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The asymmetric unit of the title compound, $C_{18}H_{17}ClN_2O_2 \cdot 0.5H_2O$, contains two organic molecules and one solvent water molecule. In each organic molecule, the cyclohexene ring adopts an envelope conformation with the C atom connecting the two methyl groups on the flap; the 4*H*-pyran ring is nearly planar [maximum deviation = 0.113 (3) Å in one molecule and 0.089 (3) Å in the other molecule] and is approximately perpendicular to the chlorophenyl ring [dihedral angle = 86.43 (15)° in one molecule and 89.73 (15)° in the other molecule]. Intermolecular N—H···N, N—H···O, O—H···O and O—H···Cl hydrogen bonding is present in the crystal.

## Related literature

For background to 2-amino-4*H*-benzopyran-3-carbonitriles, see: Gao *et al.* (2001); Xu *et al.* (2011); Luan *et al.* (2011). For the synthesis of 2-amino-4*H*-benzopyran-3-carbonitriles, see: Shi *et al.* (2003); Bao *et al.* (2007).
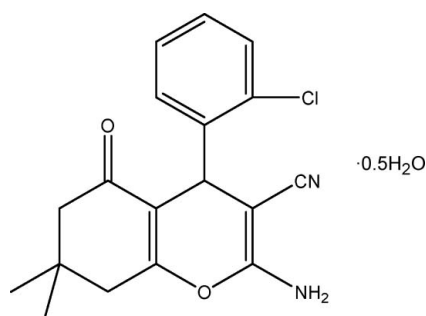


## Experimental

### Crystal data

| | |
|---|---|
| $C_{18}H_{17}ClN_2O_2 \cdot 0.5H_2O$ | $V$ = 6850 (2) Å³ |
| $M_r$ = 337.80 | $Z$ = 16 |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| $a$ = 31.431 (6) Å | $\mu$ = 0.24 mm$^{-1}$ |
| $b$ = 9.3230 (19) Å | $T$ = 291 K |
| $c$ = 25.079 (5) Å | $0.20 \times 0.20 \times 0.20$ mm |
| $\beta$ = 111.24 (3)° | |

### Data collection

| | |
|---|---|
| Bruker SMART APEX CCD diffractometer | 15314 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2001) | 6243 independent reflections |
| | 3806 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.945, $T_{max}$ = 0.959 | $R_{int}$ = 0.054 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.057 | 428 parameters |
| $wR(F^2)$ = 0.168 | H-atom parameters constrained |
| $S$ = 1.00 | $\Delta\rho_{max}$ = 0.36 e Å$^{-3}$ |
| 6243 reflections | $\Delta\rho_{min}$ = −0.50 e Å$^{-3}$ |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2A···N3$^i$ | 0.86 | 2.11 | 2.957 (4) | 167 |
| N2—H2B···O1$W^{ii}$ | 0.86 | 2.01 | 2.793 (4) | 152 |
| N4—H4A···N1$^{iii}$ | 0.86 | 2.20 | 3.048 (4) | 169 |
| N4—H4B···O2$^{iv}$ | 0.86 | 2.13 | 2.957 (3) | 161 |
| O1$W$—H1$X$···O4 | 0.96 | 1.95 | 2.754 (4) | 139 |
| O1$W$—H1$Y$···Cl2 | 0.96 | 2.29 | 3.168 (4) | 151 |

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

## References

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# 2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile hemihydrate

## Xiao-Lei Hu, Zhong-Xia Wang, Fang-Ming Wang and Guang-Fan Han

## S1. Comment

2-Amino-4*H*-benzopyran-3-carbonitriles have attracted strong interest because of their wide biological activities, such as anti-anaphylaxis, anti-achondroplasty and anti-cancer activity (Gao *et al.*, 2001). They also have potential application in the treatment of psoriatic arthritis and rheumatoid (Xu *et al.*, 2011). Furthermore, existence of amino group and cyano group make it a useful building block for organic transformations (Luan *et al.*, 2011). Many methods have been reported for synthesis of 2-amino-4*H*-benzopyran-3-carbonitriles (Shi *et al.*, 2003; Bao *et al.*, 2007). Herein we report the synthesis and crystal structure of 2-amino-5,6,7,8-tetrahydro-5-oxo-4-(2-chloro-phenyl)-7,7-dimethyl-4*H*-benzo[*b*]pyran-3-carbonitrile.

The molecular structure of the title compound is shown in Fig. 1. A nd it packing diagram is shown in Fig. 2. As shown in Fig. 1,there include two isomer molecules and one dissociated water molecule in an asymmetric unit of the title compound. And all their cyclohexyl rings show in half-boat conformations. The dihedral angles between the benzene plane and the cyclohexanone plane in each molecular structures are 75.07 (12)° and 78.25 (11)°. The four kinds of intermolecular hydrogen bonds in the crystal, such as N—H···N, N—H···O, O—H···O and O—H···Cl, link all molecules into a three-dimensional supramolecular structure.

## S2. Experimental

A mixture of 2-chlorobenzaldehyde (5 mmol) and malononitrile (5 mmol) in ethanol (10 ml) were stirred at 353 K for 2 h, using $K_2CO_3$ as catalyst. Then the reaction crude were cooled to room temperature and slowly added cold water (30 ml) with continuously stirring. The solid was filtrated, and recrystallized from ethanol. Then it was reacted with 5,5-di-methyl-1,3-cyclohexanedione (5 mmol) in glycol (10 ml) at 353 K for 4 h. The mixture was cooled and added cold water again. The solid was filtrated, and recrystallized from ethanol, yield 78%. Single crystal of the title compound suitable for X-ray analysis were obtained by evaporating from methanol/water solution at room temperature for 3 weeks.

## S3. Refinement

All H atoms were fixed geometrically and treated as riding with C—H = 0.93–0.98 Å, N–H = 0.86 and O–H = 0.96 Å, and refined in riding mode with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C,N,O)$ for the others.
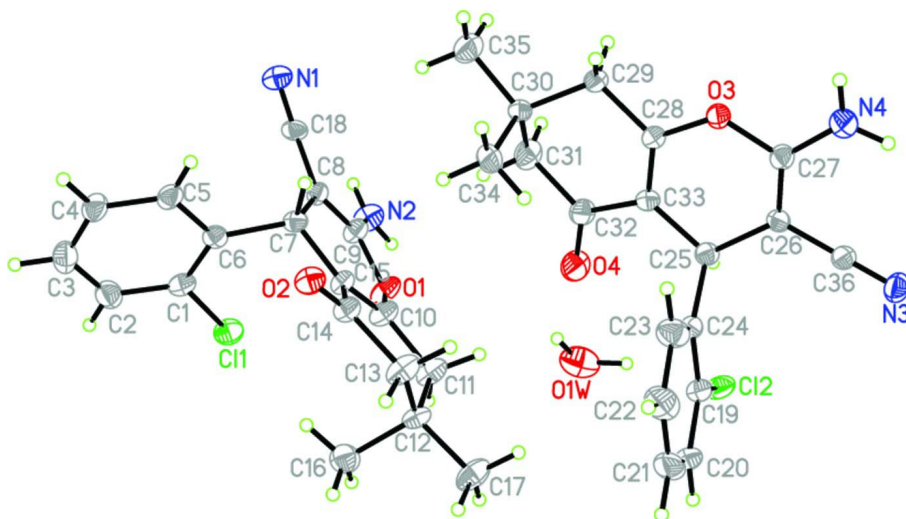
**Figure 1**

The molecular structure of the title compound, showing 30% probability displacement and the atom numbering scheme.
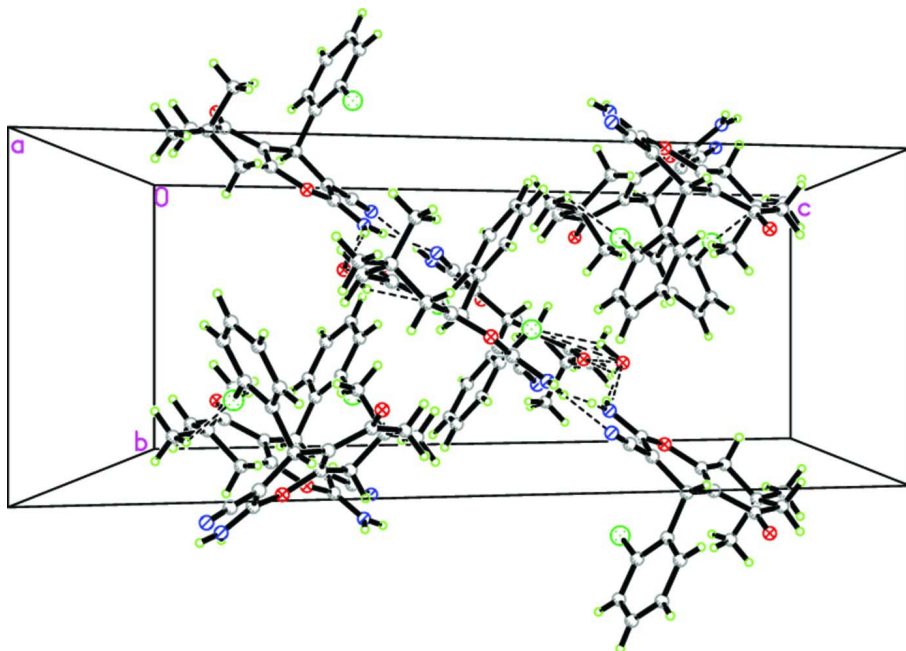


**Figure 2**

Packing diagram of the title compound viewed along the *a* axis. H-bonding interactions are shown as dashed lines.

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*Crystal data*

| | |
|---|---|
| $C_{18}H_{17}ClN_2O_2 \cdot 0.5H_2O$ | $\beta = 111.24\ (3)°$ |
| $M_r = 337.80$ | $V = 6850\ (2)$ Å³ |
| Monoclinic, $C2/c$ | $Z = 16$ |
| Hall symbol: -C 2yc | $F(000) = 2832$ |
| $a = 31.431\ (6)$ Å | $D_x = 1.310$ Mg m⁻³ |
| $b = 9.3230\ (19)$ Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $c = 25.079\ (5)$ Å | Cell parameters from 3715 reflections |

| | |
|---|---|
| $\theta$ = 2.1–23.9° | Prism, colorless |
| $\mu$ = 0.24 mm$^{-1}$ | 0.20 × 0.20 × 0.20 mm |
| $T$ = 291 K | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEX CCD diffractometer | 15314 measured reflections |
| Radiation source: sealed tube | 6243 independent reflections |
| Graphite monochromator | 3806 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int}$ = 0.054 |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2001) | $\theta_{max}$ = 25.4°, $\theta_{min}$ = 3.1° |
| | $h = -37 \rightarrow 31$ |
| | $k = -9 \rightarrow 11$ |
| $T_{min}$ = 0.945, $T_{max}$ = 0.959 | $l = -25 \rightarrow 30$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)]$ = 0.057 | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2)$ = 0.168 | |
| $S$ = 1.00 | H-atom parameters constrained |
| 6243 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0954P)^2]$ |
| 428 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} < 0.001$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{max}$ = 0.36 e Å$^{-3}$ |
| | $\Delta\rho_{min}$ = −0.50 e Å$^{-3}$ |

*Special details*

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

- 12.7873 (0.0387) *x* - 4.5876 (0.0107) *y* + 21.6869 (0.0196) *z* = 2.4952 (0.0356)

\* -0.0054 (0.0022) C1 \* 0.0083 (0.0024) C2 \* -0.0071 (0.0025) C3 \* 0.0030 (0.0023) C4 \* -0.0001 (0.0020) C5 \* 0.0014 (0.0020) C6

Rms deviation of fitted atoms = 0.0052

11.1322 (0.0507) *x* + 7.9044 (0.0087) *y* + 6.0068 (0.0449) *z* = 18.4619 (0.0327)

Angle to previous plane (with approximate e.s.d.) = 75.07 (12)

\* -0.0232 (0.0025) C10 \* 0.0250 (0.0019) C11 \* -0.0262 (0.0019) C13 \* 0.0290 (0.0024) C14 \* -0.0045 (0.0022) C15

Rms deviation of fitted atoms = 0.0233

- 6.9377 (0.0455) *x* + 5.2108 (0.0111) *y* + 20.6895 (0.0225) *z* = 5.0012 (0.0397)

Angle to previous plane (with approximate e.s.d.) = 44.67 (16)

\* -0.0049 (0.0022) C19 \* 0.0034 (0.0025) C20 \* 0.0014 (0.0027) C21 \* -0.0045 (0.0027) C22 \* 0.0029 (0.0025) C23 \* 0.0018 (0.0022) C24

Rms deviation of fitted atoms = 0.0034

1.7021 (0.0460) *x* - 8.5297 (0.0071) *y* + 8.8582 (0.0381) *z* = 6.0421 (0.0321)

Angle to previous plane (with approximate e.s.d.) = 78.25 (11)

\* 0.0432 (0.0021) C28 \* -0.0437 (0.0016) C29 \* 0.0442 (0.0017) C31 \* -0.0470 (0.0023) C32 \* 0.0032 (0.0020) C33

Rms deviation of fitted atoms = 0.0399

**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   | 0.87769 (10) | 0.7977 (4)  | 0.80107 (13) | 0.0404 (7)          |
| C2   | 0.87215 (12) | 0.9275 (4)  | 0.82590 (15) | 0.0495 (8)          |
| H2   | 0.8973       | 0.9748      | 0.8516       | 0.059*              |
| C3   | 0.82914 (13) | 0.9840 (4)  | 0.81178 (15) | 0.0531 (9)          |
| H3   | 0.8251       | 1.0715      | 0.8271       | 0.064*              |
| C4   | 0.79199 (11) | 0.9116 (3)  | 0.77502 (14) | 0.0453 (8)          |
| H4   | 0.7629       | 0.9499      | 0.7664       | 0.054*              |
| C5   | 0.79701 (11) | 0.7834 (3)  | 0.75071 (13) | 0.0395 (7)          |
| H5   | 0.7714       | 0.7367      | 0.7256       | 0.047*              |
| C6   | 0.84100 (10) | 0.7219 (3)  | 0.76370 (12) | 0.0335 (6)          |
| C7   | 0.84471 (9)  | 0.5760 (3)  | 0.73737 (12) | 0.0319 (6)          |
| H7   | 0.8135       | 0.5475      | 0.7140       | 0.038*              |
| C8   | 0.86352 (9)  | 0.4584 (3)  | 0.78183 (12) | 0.0322 (6)          |
| C9   | 0.90599 (10) | 0.3998 (3)  | 0.79355 (12) | 0.0379 (7)          |
| C10  | 0.91149 (10) | 0.5090 (4)  | 0.71063 (12) | 0.0405 (7)          |
| C11  | 0.93956 (11) | 0.5026 (4)  | 0.67499 (15) | 0.0499 (9)          |
| H11A | 0.9348       | 0.4110      | 0.6554       | 0.060*              |
| H11B | 0.9715       | 0.5087      | 0.6994       | 0.060*              |
| C12  | 0.92855 (10) | 0.6222 (4)  | 0.63111 (13) | 0.0395 (7)          |
| C13  | 0.87805 (11) | 0.6376 (5)  | 0.60281 (15) | 0.0527 (9)          |
| H13A | 0.8664       | 0.5554      | 0.5782       | 0.063*              |
| H13B | 0.8717       | 0.7223      | 0.5787       | 0.063*              |
| C14  | 0.85235 (10) | 0.6499 (3)  | 0.64347 (13) | 0.0381 (7)          |
| C15  | 0.87098 (9)  | 0.5780 (3)  | 0.69802 (12) | 0.0335 (6)          |
| C16  | 0.94814 (13) | 0.7637 (4)  | 0.66638 (15) | 0.0546 (9)          |
| H16A | 0.9448       | 0.8423      | 0.6405       | 0.082*              |
| H16B | 0.9799       | 0.7504      | 0.6890       | 0.082*              |
| H16C | 0.9316       | 0.7840      | 0.6910       | 0.082*              |
| C17  | 0.95296 (13) | 0.6054 (5)  | 0.59000 (14) | 0.0586 (10)         |
| H17A | 0.9409       | 0.5238      | 0.5659       | 0.088*              |
| H17B | 0.9850       | 0.5916      | 0.6109       | 0.088*              |
| H17C | 0.9486       | 0.6900      | 0.5668       | 0.088*              |
| C18  | 0.83765 (10) | 0.4130 (3)  | 0.81353 (13) | 0.0365 (7)          |
| C19  | 0.94532 (11) | 0.1569 (4)  | 0.51895 (14) | 0.0454 (8)          |
| C20  | 0.96005 (16) | 0.2732 (4)  | 0.49501 (17) | 0.0634 (11)         |
| H20  | 0.9910       | 0.2864      | 0.5024       | 0.076*              |
| C21  | 0.92824 (18) | 0.3689 (4)  | 0.46015 (17) | 0.0686 (12)         |
| H21  | 0.9379       | 0.4462      | 0.4440       | 0.082*              |
| C22  | 0.88321 (17) | 0.3500 (5)  | 0.44952 (17) | 0.0701 (12)         |
| H22  | 0.8619       | 0.4138      | 0.4259       | 0.084*              |
| C23  | 0.86889 (13) | 0.2357 (4)  | 0.47387 (15) | 0.0539 (9)          |
| H23  | 0.8379       | 0.2247      | 0.4665       | 0.065*              |
| C24  | 0.89882 (10) | 0.1381 (3)  | 0.50843 (12) | 0.0349 (6)          |
| C25  | 0.88120 (9)  | 0.0083 (3)  | 0.53129 (11) | 0.0324 (6)          |
| H25  | 0.9078       | −0.0417     | 0.5581       | 0.039*              |

| | | | |
|---|---|---|---|
| C26 | 0.85659 (9) | −0.0962 (3) | 0.48349 (11) | 0.0319 (6) |
| C27 | 0.81138 (9) | −0.1227 (3) | 0.46640 (12) | 0.0349 (6) |
| C28 | 0.80578 (9) | 0.0119 (3) | 0.54358 (12) | 0.0333 (6) |
| C29 | 0.77329 (10) | 0.0455 (3) | 0.57239 (14) | 0.0376 (7) |
| H29A | 0.7681 | −0.0404 | 0.5910 | 0.045* |
| H29B | 0.7443 | 0.0739 | 0.5438 | 0.045* |
| C30 | 0.79024 (10) | 0.1653 (3) | 0.61691 (12) | 0.0359 (7) |
| C31 | 0.83979 (12) | 0.1330 (4) | 0.65379 (13) | 0.0514 (9) |
| H31A | 0.8517 | 0.2110 | 0.6807 | 0.062* |
| H31B | 0.8409 | 0.0464 | 0.6757 | 0.062* |
| C32 | 0.86993 (11) | 0.1136 (4) | 0.61901 (13) | 0.0422 (7) |
| C33 | 0.85047 (10) | 0.0454 (3) | 0.56274 (12) | 0.0347 (6) |
| C34 | 0.78655 (12) | 0.3096 (3) | 0.58672 (15) | 0.0493 (8) |
| H34A | 0.8034 | 0.3059 | 0.5616 | 0.074* |
| H34B | 0.7989 | 0.3837 | 0.6147 | 0.074* |
| H34C | 0.7551 | 0.3299 | 0.5649 | 0.074* |
| C35 | 0.76102 (14) | 0.1704 (4) | 0.65389 (17) | 0.0600 (10) |
| H35A | 0.7717 | 0.2460 | 0.6816 | 0.090* |
| H35B | 0.7632 | 0.0804 | 0.6733 | 0.090* |
| H35C | 0.7298 | 0.1881 | 0.6301 | 0.090* |
| C36 | 0.88196 (9) | −0.1639 (3) | 0.45490 (12) | 0.0341 (6) |
| Cl1 | 0.93301 (3) | 0.73422 (10) | 0.82028 (4) | 0.0497 (2) |
| Cl2 | 0.98615 (3) | 0.04182 (10) | 0.56223 (4) | 0.0535 (3) |
| N1 | 0.81581 (8) | 0.3730 (3) | 0.83876 (11) | 0.0437 (7) |
| N2 | 0.92876 (9) | 0.3135 (3) | 0.83506 (11) | 0.0517 (7) |
| H2A | 0.9171 | 0.2864 | 0.8596 | 0.062* |
| H2B | 0.9553 | 0.2836 | 0.8378 | 0.062* |
| N3 | 0.90360 (9) | −0.2218 (3) | 0.43262 (11) | 0.0510 (7) |
| N4 | 0.78563 (9) | −0.2024 (3) | 0.42255 (12) | 0.0490 (7) |
| H4A | 0.7979 | −0.2469 | 0.4018 | 0.059* |
| H4B | 0.7569 | −0.2109 | 0.4154 | 0.059* |
| O1 | 0.93091 (7) | 0.4299 (3) | 0.75980 (9) | 0.0469 (6) |
| O2 | 0.81516 (6) | 0.7103 (2) | 0.62866 (8) | 0.0404 (5) |
| O3 | 0.78475 (6) | −0.0620 (2) | 0.49361 (9) | 0.0394 (5) |
| O4 | 0.91002 (8) | 0.1490 (3) | 0.63733 (10) | 0.0601 (7) |
| O1W | 1.00378 (11) | 0.1570 (4) | 0.68730 (14) | 0.0858 (9) |
| H1X | 0.9740 | 0.1980 | 0.6788 | 0.103* |
| H1Y | 1.0031 | 0.0925 | 0.6572 | 0.103* |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0300 (14) | 0.0491 (19) | 0.0441 (16) | 0.0001 (14) | 0.0158 (13) | 0.0035 (15) |
| C2 | 0.058 (2) | 0.0449 (18) | 0.0470 (19) | −0.0052 (16) | 0.0202 (16) | −0.0037 (15) |
| C3 | 0.065 (2) | 0.0428 (18) | 0.056 (2) | 0.0084 (17) | 0.0263 (18) | −0.0032 (16) |
| C4 | 0.0401 (17) | 0.0422 (18) | 0.057 (2) | 0.0121 (14) | 0.0216 (16) | 0.0047 (16) |
| C5 | 0.0461 (17) | 0.0383 (16) | 0.0427 (16) | 0.0056 (14) | 0.0264 (14) | 0.0090 (14) |
| C6 | 0.0379 (15) | 0.0331 (15) | 0.0311 (14) | 0.0011 (13) | 0.0144 (12) | 0.0079 (12) |

| | | | | | |
|---|---|---|---|---|---|
| C7 | 0.0257 (13) | 0.0305 (14) | 0.0398 (16) | 0.0047 (11) | 0.0122 (12) | 0.0083 (12) |
| C8 | 0.0358 (15) | 0.0309 (15) | 0.0332 (15) | 0.0051 (12) | 0.0165 (12) | 0.0032 (12) |
| C9 | 0.0427 (16) | 0.0400 (17) | 0.0365 (16) | 0.0123 (13) | 0.0212 (13) | 0.0135 (13) |
| C10 | 0.0361 (15) | 0.0556 (19) | 0.0319 (15) | 0.0101 (14) | 0.0147 (12) | 0.0134 (14) |
| C11 | 0.0471 (18) | 0.062 (2) | 0.0499 (19) | 0.0162 (16) | 0.0293 (16) | 0.0167 (17) |
| C12 | 0.0362 (15) | 0.0515 (19) | 0.0375 (16) | −0.0008 (14) | 0.0213 (13) | 0.0072 (14) |
| C13 | 0.0431 (18) | 0.077 (3) | 0.0424 (18) | 0.0100 (17) | 0.0210 (15) | 0.0091 (18) |
| C14 | 0.0357 (16) | 0.0418 (17) | 0.0389 (16) | 0.0047 (13) | 0.0160 (13) | 0.0054 (14) |
| C15 | 0.0321 (14) | 0.0389 (15) | 0.0325 (15) | 0.0048 (12) | 0.0155 (12) | 0.0022 (12) |
| C16 | 0.056 (2) | 0.058 (2) | 0.050 (2) | −0.0085 (17) | 0.0193 (17) | −0.0055 (17) |
| C17 | 0.058 (2) | 0.092 (3) | 0.0316 (17) | 0.007 (2) | 0.0230 (16) | 0.0071 (18) |
| C18 | 0.0351 (15) | 0.0315 (15) | 0.0446 (17) | −0.0005 (12) | 0.0166 (13) | 0.0109 (13) |
| C19 | 0.0461 (18) | 0.0511 (19) | 0.0476 (18) | −0.0146 (15) | 0.0274 (15) | −0.0103 (15) |
| C20 | 0.089 (3) | 0.060 (2) | 0.067 (2) | −0.030 (2) | 0.059 (2) | −0.014 (2) |
| C21 | 0.114 (4) | 0.050 (2) | 0.058 (2) | −0.032 (2) | 0.051 (2) | −0.0052 (19) |
| C22 | 0.101 (3) | 0.063 (3) | 0.048 (2) | −0.023 (2) | 0.028 (2) | −0.0009 (19) |
| C23 | 0.059 (2) | 0.055 (2) | 0.0469 (19) | −0.0096 (17) | 0.0180 (17) | 0.0055 (17) |
| C24 | 0.0441 (16) | 0.0340 (15) | 0.0318 (15) | −0.0084 (13) | 0.0199 (13) | −0.0054 (13) |
| C25 | 0.0294 (14) | 0.0376 (15) | 0.0284 (14) | −0.0032 (12) | 0.0084 (11) | −0.0006 (12) |
| C26 | 0.0340 (14) | 0.0311 (15) | 0.0313 (14) | −0.0050 (12) | 0.0126 (12) | −0.0013 (12) |
| C27 | 0.0330 (15) | 0.0351 (15) | 0.0376 (16) | 0.0028 (12) | 0.0138 (13) | −0.0013 (13) |
| C28 | 0.0307 (14) | 0.0344 (15) | 0.0374 (15) | −0.0007 (12) | 0.0153 (12) | −0.0027 (13) |
| C29 | 0.0359 (15) | 0.0325 (16) | 0.0514 (18) | −0.0008 (12) | 0.0242 (14) | −0.0031 (13) |
| C30 | 0.0470 (17) | 0.0296 (15) | 0.0389 (16) | −0.0066 (13) | 0.0252 (14) | 0.0006 (12) |
| C31 | 0.059 (2) | 0.064 (2) | 0.0319 (17) | 0.0008 (17) | 0.0175 (16) | −0.0021 (15) |
| C32 | 0.0450 (18) | 0.0496 (19) | 0.0319 (15) | −0.0044 (15) | 0.0138 (14) | −0.0021 (14) |
| C33 | 0.0375 (15) | 0.0338 (15) | 0.0373 (15) | −0.0058 (12) | 0.0191 (13) | 0.0002 (12) |
| C34 | 0.065 (2) | 0.0283 (16) | 0.064 (2) | −0.0015 (14) | 0.0340 (18) | −0.0024 (15) |
| C35 | 0.071 (2) | 0.059 (2) | 0.066 (2) | −0.0012 (19) | 0.045 (2) | −0.0007 (19) |
| C36 | 0.0286 (14) | 0.0431 (17) | 0.0284 (14) | −0.0043 (12) | 0.0076 (12) | −0.0027 (12) |
| Cl1 | 0.0312 (4) | 0.0594 (5) | 0.0549 (5) | 0.0005 (3) | 0.0112 (3) | 0.0006 (4) |
| Cl2 | 0.0403 (4) | 0.0652 (6) | 0.0657 (6) | −0.0023 (4) | 0.0321 (4) | 0.0019 (4) |
| N1 | 0.0330 (13) | 0.0491 (16) | 0.0484 (16) | 0.0086 (12) | 0.0141 (12) | 0.0181 (13) |
| N2 | 0.0412 (14) | 0.068 (2) | 0.0434 (15) | 0.0124 (14) | 0.0122 (12) | 0.0155 (14) |
| N3 | 0.0418 (15) | 0.070 (2) | 0.0426 (15) | −0.0052 (14) | 0.0167 (13) | −0.0163 (14) |
| N4 | 0.0450 (15) | 0.0532 (17) | 0.0496 (16) | −0.0059 (13) | 0.0181 (13) | −0.0095 (14) |
| O1 | 0.0421 (12) | 0.0658 (15) | 0.0399 (12) | 0.0231 (11) | 0.0234 (10) | 0.0228 (11) |
| O2 | 0.0289 (10) | 0.0487 (12) | 0.0405 (11) | 0.0057 (9) | 0.0086 (9) | 0.0075 (10) |
| O3 | 0.0291 (10) | 0.0435 (12) | 0.0474 (12) | −0.0045 (9) | 0.0159 (9) | −0.0140 (10) |
| O4 | 0.0471 (14) | 0.0865 (19) | 0.0428 (13) | −0.0122 (13) | 0.0117 (11) | −0.0204 (13) |
| O1W | 0.0741 (19) | 0.089 (2) | 0.085 (2) | −0.0176 (17) | 0.0176 (17) | 0.0101 (18) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C6 | 1.387 (4) | C20—C21 | 1.388 (6) |
| C1—C2 | 1.401 (5) | C20—H20 | 0.9300 |
| C1—Cl1 | 1.732 (3) | C21—C22 | 1.354 (6) |
| C2—C3 | 1.372 (5) | C21—H21 | 0.9300 |

| | | | |
|---|---|---|---|
| C2—H2 | 0.9300 | C22—C23 | 1.382 (5) |
| C3—C4 | 1.375 (5) | C22—H22 | 0.9300 |
| C3—H3 | 0.9300 | C23—C24 | 1.369 (5) |
| C4—C5 | 1.377 (4) | C23—H23 | 0.9300 |
| C4—H4 | 0.9300 | C24—C25 | 1.526 (4) |
| C5—C6 | 1.421 (4) | C25—C33 | 1.492 (4) |
| C5—H5 | 0.9300 | C25—C26 | 1.521 (4) |
| C6—C7 | 1.535 (4) | C25—H25 | 0.9800 |
| C7—C15 | 1.499 (4) | C26—C27 | 1.350 (4) |
| C7—C8 | 1.523 (4) | C26—C36 | 1.401 (4) |
| C7—H7 | 0.9800 | C27—N4 | 1.331 (4) |
| C8—C9 | 1.372 (4) | C27—O3 | 1.379 (3) |
| C8—C18 | 1.393 (4) | C28—C33 | 1.346 (4) |
| C9—N2 | 1.305 (4) | C28—O3 | 1.372 (3) |
| C9—O1 | 1.374 (3) | C28—C29 | 1.482 (4) |
| C10—C15 | 1.358 (4) | C29—C30 | 1.532 (4) |
| C10—O1 | 1.376 (3) | C29—H29A | 0.9700 |
| C10—C11 | 1.467 (4) | C29—H29B | 0.9700 |
| C11—C12 | 1.516 (4) | C30—C35 | 1.524 (4) |
| C11—H11A | 0.9700 | C30—C31 | 1.526 (5) |
| C11—H11B | 0.9700 | C30—C34 | 1.527 (4) |
| C12—C13 | 1.493 (4) | C31—C32 | 1.513 (4) |
| C12—C17 | 1.500 (4) | C31—H31A | 0.9700 |
| C12—C16 | 1.583 (5) | C31—H31B | 0.9700 |
| C13—C14 | 1.517 (4) | C32—O4 | 1.220 (4) |
| C13—H13A | 0.9700 | C32—C33 | 1.464 (4) |
| C13—H13B | 0.9700 | C34—H34A | 0.9600 |
| C14—O2 | 1.227 (3) | C34—H34B | 0.9600 |
| C14—C15 | 1.443 (4) | C34—H34C | 0.9600 |
| C16—H16A | 0.9600 | C35—H35A | 0.9600 |
| C16—H16B | 0.9600 | C35—H35B | 0.9600 |
| C16—H16C | 0.9600 | C35—H35C | 0.9600 |
| C17—H17A | 0.9600 | C36—N3 | 1.158 (4) |
| C17—H17B | 0.9600 | N2—H2A | 0.8599 |
| C17—H17C | 0.9600 | N2—H2B | 0.8600 |
| C18—N1 | 1.151 (4) | N4—H4A | 0.8600 |
| C19—C20 | 1.397 (5) | N4—H4B | 0.8599 |
| C19—C24 | 1.399 (4) | O1W—H1X | 0.9600 |
| C19—Cl2 | 1.723 (4) | O1W—H1Y | 0.9599 |
| | | | |
| C6—C1—C2 | 122.3 (3) | C19—C20—H20 | 120.2 |
| C6—C1—Cl1 | 121.3 (2) | C22—C21—C20 | 120.3 (4) |
| C2—C1—Cl1 | 116.5 (2) | C22—C21—H21 | 119.9 |
| C3—C2—C1 | 119.1 (3) | C20—C21—H21 | 119.9 |
| C3—C2—H2 | 120.4 | C21—C22—C23 | 119.9 (4) |
| C1—C2—H2 | 120.4 | C21—C22—H22 | 120.1 |
| C2—C3—C4 | 120.2 (3) | C23—C22—H22 | 120.1 |
| C2—C3—H3 | 119.9 | C24—C23—C22 | 122.2 (4) |

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|---|---|---|---|
| C4—C3—H3 | 119.9 | C24—C23—H23 | 118.9 |
| C3—C4—C5 | 121.2 (3) | C22—C23—H23 | 118.9 |
| C3—C4—H4 | 119.4 | C23—C24—C19 | 117.9 (3) |
| C5—C4—H4 | 119.4 | C23—C24—C25 | 120.3 (3) |
| C4—C5—C6 | 120.5 (3) | C19—C24—C25 | 121.7 (3) |
| C4—C5—H5 | 119.8 | C33—C25—C26 | 108.9 (2) |
| C6—C5—H5 | 119.8 | C33—C25—C24 | 114.0 (2) |
| C1—C6—C5 | 116.8 (3) | C26—C25—C24 | 111.2 (2) |
| C1—C6—C7 | 124.6 (3) | C33—C25—H25 | 107.5 |
| C5—C6—C7 | 118.6 (3) | C26—C25—H25 | 107.5 |
| C15—C7—C8 | 109.3 (2) | C24—C25—H25 | 107.5 |
| C15—C7—C6 | 114.7 (2) | C27—C26—C36 | 118.9 (3) |
| C8—C7—C6 | 113.1 (2) | C27—C26—C25 | 122.9 (3) |
| C15—C7—H7 | 106.3 | C36—C26—C25 | 118.1 (2) |
| C8—C7—H7 | 106.3 | N4—C27—C26 | 128.3 (3) |
| C6—C7—H7 | 106.3 | N4—C27—O3 | 110.0 (2) |
| C9—C8—C18 | 118.7 (3) | C26—C27—O3 | 121.7 (3) |
| C9—C8—C7 | 122.2 (2) | C33—C28—O3 | 122.5 (3) |
| C18—C8—C7 | 119.0 (2) | C33—C28—C29 | 126.2 (3) |
| N2—C9—C8 | 128.7 (3) | O3—C28—C29 | 111.3 (2) |
| N2—C9—O1 | 110.3 (2) | C28—C29—C30 | 113.0 (2) |
| C8—C9—O1 | 121.0 (2) | C28—C29—H29A | 109.0 |
| C15—C10—O1 | 122.5 (3) | C30—C29—H29A | 109.0 |
| C15—C10—C11 | 126.7 (3) | C28—C29—H29B | 109.0 |
| O1—C10—C11 | 110.8 (2) | C30—C29—H29B | 109.0 |
| C10—C11—C12 | 112.5 (3) | H29A—C29—H29B | 107.8 |
| C10—C11—H11A | 109.1 | C35—C30—C31 | 110.2 (3) |
| C12—C11—H11A | 109.1 | C35—C30—C34 | 108.6 (3) |
| C10—C11—H11B | 109.1 | C31—C30—C34 | 110.6 (3) |
| C12—C11—H11B | 109.1 | C35—C30—C29 | 109.8 (3) |
| H11A—C11—H11B | 107.8 | C31—C30—C29 | 107.9 (3) |
| C13—C12—C17 | 113.8 (3) | C34—C30—C29 | 109.7 (2) |
| C13—C12—C11 | 109.9 (3) | C32—C31—C30 | 112.9 (2) |
| C17—C12—C11 | 112.5 (3) | C32—C31—H31A | 109.0 |
| C13—C12—C16 | 108.5 (3) | C30—C31—H31A | 109.0 |
| C17—C12—C16 | 106.2 (3) | C32—C31—H31B | 109.0 |
| C11—C12—C16 | 105.5 (3) | C30—C31—H31B | 109.0 |
| C12—C13—C14 | 114.9 (3) | H31A—C31—H31B | 107.8 |
| C12—C13—H13A | 108.5 | O4—C32—C33 | 119.6 (3) |
| C14—C13—H13A | 108.5 | O4—C32—C31 | 121.8 (3) |
| C12—C13—H13B | 108.5 | C33—C32—C31 | 118.5 (3) |
| C14—C13—H13B | 108.5 | C28—C33—C32 | 117.5 (3) |
| H13A—C13—H13B | 107.5 | C28—C33—C25 | 123.3 (3) |
| O2—C14—C15 | 121.0 (3) | C32—C33—C25 | 119.1 (2) |
| O2—C14—C13 | 120.8 (3) | C30—C34—H34A | 109.5 |
| C15—C14—C13 | 118.0 (3) | C30—C34—H34B | 109.5 |
| C10—C15—C14 | 117.7 (3) | H34A—C34—H34B | 109.5 |
| C10—C15—C7 | 122.3 (3) | C30—C34—H34C | 109.5 |

| | | | |
|---|---|---|---|
| C14—C15—C7 | 119.9 (2) | H34A—C34—H34C | 109.5 |
| C12—C16—H16A | 109.5 | H34B—C34—H34C | 109.5 |
| C12—C16—H16B | 109.5 | C30—C35—H35A | 109.5 |
| H16A—C16—H16B | 109.5 | C30—C35—H35B | 109.5 |
| C12—C16—H16C | 109.5 | H35A—C35—H35B | 109.5 |
| H16A—C16—H16C | 109.5 | C30—C35—H35C | 109.5 |
| H16B—C16—H16C | 109.5 | H35A—C35—H35C | 109.5 |
| C12—C17—H17A | 109.5 | H35B—C35—H35C | 109.5 |
| C12—C17—H17B | 109.5 | N3—C36—C26 | 178.1 (3) |
| H17A—C17—H17B | 109.5 | C9—N2—H2A | 120.0 |
| C12—C17—H17C | 109.5 | C9—N2—H2B | 120.0 |
| H17A—C17—H17C | 109.5 | H2A—N2—H2B | 120.0 |
| H17B—C17—H17C | 109.5 | C27—N4—H4A | 119.9 |
| N1—C18—C8 | 178.4 (3) | C27—N4—H4B | 120.1 |
| C20—C19—C24 | 120.2 (4) | H4A—N4—H4B | 120.0 |
| C20—C19—Cl2 | 117.9 (3) | C9—O1—C10 | 119.6 (2) |
| C24—C19—Cl2 | 122.0 (2) | C28—O3—C27 | 118.7 (2) |
| C21—C20—C19 | 119.6 (4) | H1X—O1W—H1Y | 109.5 |
| C21—C20—H20 | 120.2 | | |
| | | | |
| C6—C1—C2—C3 | −1.7 (5) | C21—C22—C23—C24 | −0.7 (6) |
| Cl1—C1—C2—C3 | 179.2 (3) | C22—C23—C24—C19 | 0.1 (5) |
| C1—C2—C3—C4 | 1.9 (5) | C22—C23—C24—C25 | −176.1 (3) |
| C2—C3—C4—C5 | −1.4 (5) | C20—C19—C24—C23 | 0.6 (4) |
| C3—C4—C5—C6 | 0.7 (5) | Cl2—C19—C24—C23 | 179.4 (2) |
| C2—C1—C6—C5 | 1.0 (4) | C20—C19—C24—C25 | 176.8 (3) |
| Cl1—C1—C6—C5 | −180.0 (2) | Cl2—C19—C24—C25 | −4.4 (4) |
| C2—C1—C6—C7 | −177.1 (3) | C23—C24—C25—C33 | −54.9 (4) |
| Cl1—C1—C6—C7 | 1.9 (4) | C19—C24—C25—C33 | 129.0 (3) |
| C4—C5—C6—C1 | −0.5 (4) | C23—C24—C25—C26 | 68.7 (4) |
| C4—C5—C6—C7 | 177.7 (3) | C19—C24—C25—C26 | −107.4 (3) |
| C1—C6—C7—C15 | −64.6 (4) | C33—C25—C26—C27 | 12.9 (4) |
| C5—C6—C7—C15 | 117.3 (3) | C24—C25—C26—C27 | −113.5 (3) |
| C1—C6—C7—C8 | 61.8 (4) | C33—C25—C26—C36 | −169.2 (3) |
| C5—C6—C7—C8 | −116.3 (3) | C24—C25—C26—C36 | 64.3 (3) |
| C15—C7—C8—C9 | 18.8 (4) | C36—C26—C27—N4 | −3.6 (5) |
| C6—C7—C8—C9 | −110.4 (3) | C25—C26—C27—N4 | 174.2 (3) |
| C15—C7—C8—C18 | −164.1 (3) | C36—C26—C27—O3 | 178.5 (3) |
| C6—C7—C8—C18 | 66.7 (3) | C25—C26—C27—O3 | −3.7 (4) |
| C18—C8—C9—N2 | −7.1 (5) | C33—C28—C29—C30 | 19.0 (4) |
| C7—C8—C9—N2 | 170.0 (3) | O3—C28—C29—C30 | −161.9 (2) |
| C18—C8—C9—O1 | 173.3 (3) | C28—C29—C30—C35 | −167.1 (3) |
| C7—C8—C9—O1 | −9.6 (5) | C28—C29—C30—C31 | −47.0 (3) |
| C15—C10—C11—C12 | 20.3 (5) | C28—C29—C30—C34 | 73.6 (3) |
| O1—C10—C11—C12 | −161.7 (3) | C35—C30—C31—C32 | 175.0 (3) |
| C10—C11—C12—C13 | −44.9 (4) | C34—C30—C31—C32 | −64.9 (4) |
| C10—C11—C12—C17 | −172.9 (3) | C29—C30—C31—C32 | 55.1 (4) |
| C10—C11—C12—C16 | 71.8 (4) | C30—C31—C32—O4 | 147.2 (3) |

| | | | |
|---|---|---|---|
| C17—C12—C13—C14 | 178.1 (3) | C30—C31—C32—C33 | −35.1 (4) |
| C11—C12—C13—C14 | 50.9 (4) | O3—C28—C33—C32 | −174.9 (3) |
| C16—C12—C13—C14 | −63.9 (4) | C29—C28—C33—C32 | 4.1 (5) |
| C12—C13—C14—O2 | 154.8 (3) | O3—C28—C33—C25 | 1.2 (4) |
| C12—C13—C14—C15 | −30.5 (5) | C29—C28—C33—C25 | −179.8 (3) |
| O1—C10—C15—C14 | −176.0 (3) | O4—C32—C33—C28 | −178.1 (3) |
| C11—C10—C15—C14 | 1.8 (5) | C31—C32—C33—C28 | 4.1 (4) |
| O1—C10—C15—C7 | 1.4 (5) | O4—C32—C33—C25 | 5.6 (5) |
| C11—C10—C15—C7 | 179.2 (3) | C31—C32—C33—C25 | −172.1 (3) |
| O2—C14—C15—C10 | 177.6 (3) | C26—C25—C33—C28 | −11.7 (4) |
| C13—C14—C15—C10 | 2.9 (5) | C24—C25—C33—C28 | 113.1 (3) |
| O2—C14—C15—C7 | 0.2 (5) | C26—C25—C33—C32 | 164.3 (3) |
| C13—C14—C15—C7 | −174.5 (3) | C24—C25—C33—C32 | −70.9 (3) |
| C8—C7—C15—C10 | −14.7 (4) | C27—C26—C36—N3 | −117 (10) |
| C6—C7—C15—C10 | 113.6 (3) | C25—C26—C36—N3 | 65 (10) |
| C8—C7—C15—C14 | 162.6 (3) | N2—C9—O1—C10 | 174.3 (3) |
| C6—C7—C15—C14 | −69.1 (4) | C8—C9—O1—C10 | −6.0 (5) |
| C9—C8—C18—N1 | −92 (12) | C15—C10—O1—C9 | 10.3 (5) |
| C7—C8—C18—N1 | 91 (12) | C11—C10—O1—C9 | −167.8 (3) |
| C24—C19—C20—C21 | −0.8 (5) | C33—C28—O3—C27 | 9.9 (4) |
| Cl2—C19—C20—C21 | −179.6 (3) | C29—C28—O3—C27 | −169.2 (2) |
| C19—C20—C21—C22 | 0.2 (6) | N4—C27—O3—C28 | 173.2 (3) |
| C20—C21—C22—C23 | 0.5 (6) | C26—C27—O3—C28 | −8.6 (4) |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N2—H2A···N3ⁱ | 0.86 | 2.11 | 2.957 (4) | 167 |
| N2—H2B···O1Wⁱⁱ | 0.86 | 2.01 | 2.793 (4) | 152 |
| N4—H4A···N1ⁱⁱⁱ | 0.86 | 2.20 | 3.048 (4) | 169 |
| N4—H4B···O2ⁱᵛ | 0.86 | 2.13 | 2.957 (3) | 161 |
| O1W—H1X···O4 | 0.96 | 1.95 | 2.754 (4) | 139 |
| O1W—H1Y···Cl2 | 0.96 | 2.29 | 3.168 (4) | 151 |

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