Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

# Crystal structure of 1-(1-chloroethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium chloride

Ziroat E. Urunbaeva,[a] Kambarali K. Turgunov,[b,c]* Abdusalom Sh. Saidov[a] and Valentina I. Vinogradova[b]

[a]Samarkand State University named after Sh. Rashidov, University blv. 15, Samarkand 140104, Uzbekistan, [b]S. Yunusov Institute of the Chemistry of Plant Substances Academy of Sciences of Uzbekistan, Mirzo Ulugbek Str., 77, Tashkent 100170, Uzbekistan, and [c]Turin Polytechnic University in Tashkent 100095, 17 Little Ring Road, Tashkent, Uzbekistan. *Correspondence e-mail: kk_turgunov@rambler.ru

Received 10 July 2024
Accepted 19 November 2024

Edited by N. Alvarez Failache, Universidad de la Repüblica, Uruguay

**Keywords:** crystal structure; enantiomer; homoveratrylamine; lactic acid; tetrahydroisoquinoline.

**CCDC reference:** 2403944

**Supporting information:** this article has supporting information at journals.iucr.org/e

1-(1-Chloroethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline was synthesized through the reaction of homoveratrylamine with racemic lactic acid. The formation of two enantiomers, *RR* and *SS*, was detected by performing X-ray diffraction analysis on their chloride salts. The asymmetric unit of the crystal consists of a $C_{13}H_{19}ClNO_2^+$ molecular cation and a $Cl^-$ anion. Two protonated enantiomers of the title compound, with *RR* and *SS* configurations of the chiral atoms, are connected into hydrogen-bonded dimers bridged by $Cl^-$ anions. Weak C—H···Cl interactions lead to the formation of a chain running along the *a*-axis direction of the unit cell, which corresponds to the longest dimension (the preferential growth direction) of the needle-shaped monocrystal. The crystal studied was refined as a two-component twin.

## 1. Chemical context

Isoquinoline alkaloids, widely distributed in the plant and animal kingdoms, have received much attention because of their important biological activities (Lundstorom, 1983). For example, 1.2.3.4-tetrahydroisoquinoline and 2-methyl-1.2.3.4-tetrahydroisoquinoline, present in mammalian brains, are known to induce Parkinson's disease (Ohta *et al.*, 1987; Niwa *et al.* 1987). Effective synthetic methods for preparing of 1.2.3.4-tetrahydroisoquinoline derivatives have been found (Shinohara *et al.* 1997). 1-Substituted-1,2,3,4-tetrahydroisoquinolines are especially intriguing among the synthetic derivatives of the isoquinoline alkaloid. They feature biologically active compounds, for example, an antiepileptic agent (Gitto *et al.*, 2003) and a derivative with inhibitory activity against bladder contraction (Naito *et al.*, 2005). A lot of work has been done on the synthesis and structural studies of 1-substituted-1,2,3,4-tetrahydroisoquinolines in search of active compounds (Olszak *et al.*, 1996; Pashev *et al., 2020;* Turgunov *et al.* 2016).

In this context, we treated homoveratrylamine with lactic acid and obtained the corresponding amide intermediate. Cyclization of the amide with $POCl_3$ and $NaBH_4$ afforded the

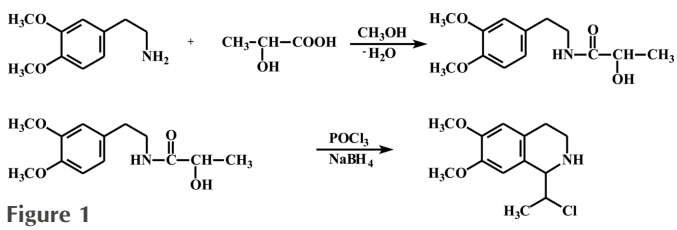
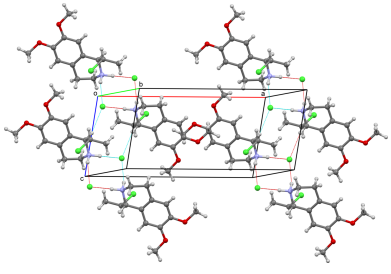
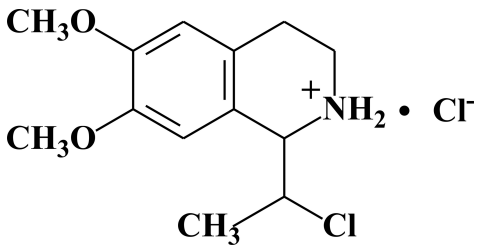



**Figure 1**
Synthesis scheme of the title compound.



OPEN ACCESS
Published under a CC BY 4.0 licence

title compound (Fig. 1). Racemic lactic acid was used in the synthesis, so four stereoisomers (*R,R; R,S; S,S; S,R*) of 1-(1-chloroethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline were expected. Currently, we have detected the formation of two enantiomers, *RR* and *SS*, packed in a single crystal by X-ray diffraction (XRD) analysis. A detailed analysis of the reaction products is ongoing and will be published in our future work. To obtain good crystals suitable for XRD analysis, hydrochlorides of the isoquinolines were used.




## 2. Structural commentary

The title compound crystallizes in the monoclinic $P2_1/c$ (No. 14) space group. The asymmetric unit of the crystal contains one independent molecule with an *1S*, *11S* configuration of chiral carbon atoms, so the crystal consists of *RR* and *SS* enantiomers. The C4*A*/C4–C8/C8*A* aromatic ring is twisted slightly with a slightly high value for the r.m.s. deviation (0.0245 Å) of the fitted atoms from the mean plane of the ring. The methoxy groups at C6 and C7 atoms are slightly rotated around the C6—O1 and C7—O2 bonds (Fig. 2), the dihedral angles between the plane of the aromatic ring and the planes defined by atoms C6/O1/C9 and C7/O2/C10 being 13.0 (3) and 6.5 (3)°, respectively. The C4*A*—C4 and C8*A*—C1 bonds are slightly out of the plane, the deviations of C1 and C4 from the mean plane of aromatic ring being 0.206 (2) and −0.147 (2) Å, respectively. The heterocyclic ring of tetrahydroisoquinoline adopts a half chair conformation.

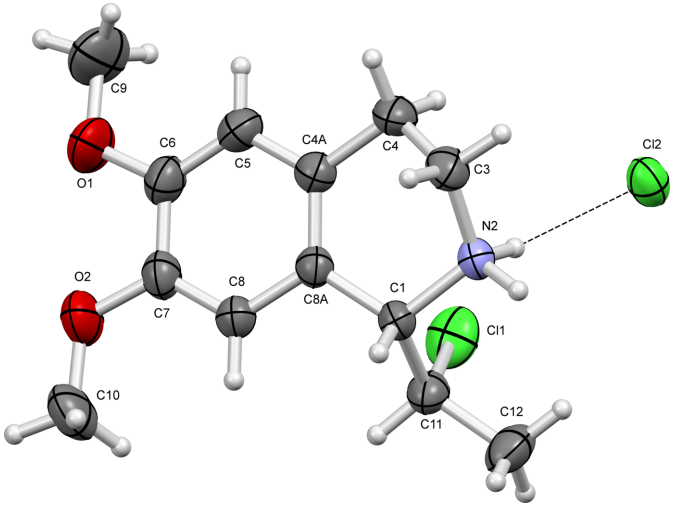



**Figure 2**
Displacement ellipsoid plot of the title compound with atom labels. Ellipsoids are drawn at the 50% probability level. The hydrogen bond formed between the molecular cation and the chlorine anion is showed as a dashed line.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H1*A*···Cl2$^{i}$ | 0.98 | 2.62 | 3.450 (2) | 143 |
| N2—H2*A*···Cl2$^{ii}$ | 0.95 (2) | 2.14 (2) | 3.0895 (19) | 177 (2) |
| N2—H2*B*···Cl1 | 0.92 (2) | 2.75 (3) | 3.1828 (19) | 110 (2) |
| N2—H2*B*···Cl2 | 0.92 (2) | 2.27 (2) | 3.0751 (19) | 146 (2) |
| C11—H11*A*···Cl1$^{iii}$ | 0.98 | 2.93 | 3.767 (2) | 144 |
| C12—H12*A*···Cl2$^{iii}$ | 0.96 | 2.75 | 3.710 (3) | 174 |

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

## 3. Supramolecular features

The presence of both enantiomers of the title compound in the crystal allows the molecules to link into inversion dimers through N2—H2*A*···Cl2 and N2—H2*B*···Cl2$^{i}$ [symmetry code: (i) $2-x, 1-y, 2-z$] intermolecular interactions, forming rings with the graph-set motif $R_2^2(8)$ (Fig. 3, Table 1) where the Cl2 anions act as double hydrogen-bond acceptors. In addition, pairs of C1—H1*A*···Cl2 weak interactions lead to chain formation along the *a*-axis direction, which is the longest cell dimension (preferential growth direction) of the monocrystal. A C12—H12*A*···Cl2 weak interaction leads to the formation of hydrogen-bonded layers parallel to the *bc* plane.

## 4. Database survey

A search in the Cambridge Structural Database (CSD, version 5.43, update of November 2022; Groom *et al.*, 2016) revealed 123 structures of 1-substituted and 2-substituted 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolines. Among these, 15 structures correspond to 1-substituted 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolines. Enantiopure crystal structures were determined for (*R*)-1-hydroxymethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (refcode: BIMCEG) and (*S*)-1-hy-

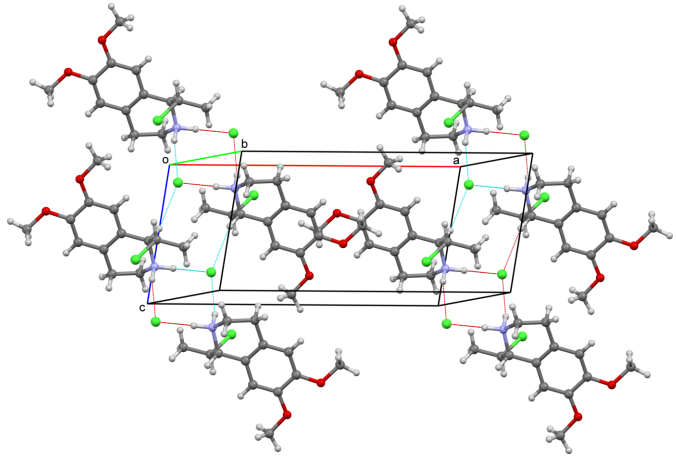



**Figure 3**
Hydrogen bonding in the crystal of the title compound.

droxymethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline chloride (refcode: BIMCIK), alkaloids isolated from seeds of *Calycotome Villosa* (Antri *et al.*, 2004). A search in the Cambridge Structural Database for the cationic form of 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline resulted in 13 hits. Ten of these, where the molecule contains a chiral atom, are enantiopure crystals containing only proper symmetry elements. Therefore, in these crystal structures, the interlinking of molecules by hydrogen bonds differs from our case.

## 5. Synthesis and crystallization

*N-(3,4-Dimethoxyphenylethyl)-2-hydroxypropanamide*. A mixture of 1.81 g (0.01 mol) of homoveratrilamine and 0.9 g (0.01 mol) of lactic acid was dissolved in 5 ml of methanol. Self-heating occurred. Then the mixture was heated in an oil bath for 2 h at a temperature of 451–453 K. The progress of the reaction was monitored by TLC. The reaction mixture was dissolved in 100 mL of chloroform. The chloroform layer was first washed three times with 3% hydrochloric acid. The chloroform solution was then washed with water until neutral, followed by washing with 2% sodium hydroxide solution and water until neutral. The resulting chloroform solution was dried over $Na_2SO_4$ and then evaporated. The residue was crystallized from a mixture (acetone-hexane). White crystals with m.p. 343–344 K. Yield 70% (1.77 g). $R_f$ = 0.40 chloroform-methanol (8:2).

$^1$H NMR: (400 MHz, $CDCl_3$, $\delta$, ppm., $J$/Hz): 1.34 (3H, *d*, $J$ = 6.7, H-3′), 2.73 (2H, *t*, $J$ = 7.1, H-$\alpha$), 3.46 (2H, *q*, $J$ = 6.7, H-$\beta$), 3.81 (3H, *s*, $OCH_3$), 3.82 (3H, *s*, $OCH_3$), 4.10 (1H, *wide s*, OH), 4.17 (1H, *q*, $J$ = 6.8 H −2′), 6.69 (2H, *top – top*, H-2,6), 6.77 (1H, *d*, $J$ = 8.6, H-5), 6.90 (1H, *wide s*, NH).

$^{13}$C NMR: 21.26 C-3, 35.19 C-$\alpha$; 40.60 C-$\beta$, 55.96 C-$OCH_3$, 55.96 C-$OCH_3$, 68.10 C-2I, 111.44 C-2, 111.97 C-5, 131 C-1, 120.73 C-6, 147.73 C-3, 149.01 C-4, 175.59 C-1-CO.

MS $m/z$ ($M^+$) 253, 224, 165, 123.9 (124), 59.8 (60).

*1-(1-Chloroethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline.* 1.550 mg (0.0061 mol) of *N*-(3,4-dimethoxyphenylethyl)-2-hydroxypropanamide were dissolved in 30 ml of absolute benzene, then 0.9404 mg (0.0061 mol) or 0.6–1 ml of $POCl_3$ were added. The reaction mixture was refluxed with a calcium chloride tube for 2 h. The progress of the reaction was monitored by TLC. After the reaction was complete after 2.5 h, benzene and residual $POCl_3$ were removed and the residue was dried. The residue was then dissolved in 50 mL of methanol. 0.6 g of $NaBH_4$ was added in small portions at 273–323 K for 3 h with constant stirring. This mixture was left overnight. The solvent was then removed and the residue was dissolved in distilled water. The aqueous layer was extracted several times with chloroform. The chloroform layer was combined and washed with water. After that, the chloroform layer was dried with $Na_2SO_4$. The residue was dissolved in methanol and precipitated as the hydrochloride using concentrated HCl solution. The precipitate was filtered, washed in acetone and dried. Yield 0.843 g (59%) (0.843 g), m.p. 476–477 K, $R_f$ = 0.57 (chloroform–methanol 8:1.5).

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{13}H_{19}ClNO_2^+\cdot Cl^-$ |
| $M_r$ | 292.19 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 293 |
| $a$, $b$, $c$ (Å) | 16.1298 (3), 12.3736 (3), 7.46745 (16) |
| $\beta$ (°) | 100.190 (2) |
| $V$ (Å$^3$) | 1466.87 (6) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 3.94 |
| Crystal size (mm) | 0.25 × 0.10 × 0.05 |
| Data collection | |
| Diffractometer | XtaLAB Synergy, Single source at home/near, HyPix3000 |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018) |
| $T_{min}$, $T_{max}$ | 0.784, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12790, 4641, 4142 |
| $R_{int}$ | 0.061 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.602 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.050, 0.155, 1.09 |
| No. of reflections | 4641 |
| No. of parameters | 170 |
| No. of restraints | 2 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.32, −0.26 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020), *SHELXL2014/7* (Sheldrick, 2015*b*).

$^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm, $J$ / Hz): 1.87 (3H, *d*, $J$ = 7, H-3′), 2.91 (2H, *m*, H-3a), 3.23 (2H, *m*, H-4), 3.84 (1H, *m*, H-3e), 3.85 (3H, *s*, $OCH_3$), 3.86 (3H, *s*, $OCH_3$), 4.59 (1H, *q*, $J$ = 3.5, H-2′), 4.74 (1H, *d*, $J$ = 3.3, H-1), 6.61 (1H, *s*, H-8), 6.69 (1H, *s*, H-5).

### 5.1. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal under investigation exhibited twinning, which was identified during the initial analysis of the diffraction data. The twin law was determined based on the symmetry of the crystal and the diffraction analysis. In this case, a twofold rotation axis (along the $c$ axis) related the two twin domains, with each domain contributing to the overall diffraction pattern. The twin fraction was estimated to be approximately 0.60 for component 1 and 0.40 for component 2, based on the refinement of the intensity data. Reflections in the HKLF 5 format were used for structure determination and refinement. The H atoms bonded to C atoms were placed geometrically (with C—H distances of 0.98 Å for CH, 0.97 Å for $CH_2$, 0.96 Å for $CH_3$ and 0.93 Å for $C_{ar}$) and included in the refinement in a riding-motion approximation with $U_{iso}$(H) = 1.2$U_{eq}$(C) [$U_{iso}$ = 1.5$U_{eq}$(C) for methyl H atoms]. The hydrogen atoms on the N1 were located in difference-Fourier maps and refined freely.

## Acknowledgements

X-ray diffraction studies were performed at the Centre of Collective Usage of Equipment of the Institute of Bioorganic Chemistry of the Uzbekistan Academy of Sciences. Professor Bakhtiyar Ibragimov is acknowledged for support of the diffraction measurements.

## References

El Antri, A., Messouri, I., Bouktaib, M., El Alami, R., Bolte, M., El Bali, B. & Lachkar, M. (2004). *Molecules*, **9**, 650–657.
Gitto, R., Barreca, M. L., De Luca, L., De Sarro, G., Ferreri, G., Quartarone, S., Russo, E., Constanti, A. & Chimirri, A. (2003). *J. Med. Chem.* **46**, 197–200.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Lundstorom, J. (1983). *The Alkaloids*, Vol. 21 edited by A. Brossi, pp. 255–327. New York: Academic Press.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Naito, R., Yonetoku, Y., Okamoto, Y., Toyoshima, A., Ikeda, K. & Takeuchi, M. (2005). *J. Med. Chem.* **48**, 6597–6606.
Niwa, T., Takeda, N., Kaneda, N., Hashizume, Y. & Nagatsu, T. (1987). *Biochem. Biophys. Res. Commun.* **144**, 1084–1089.
Ohta, S., Kohno, M., Makino, Y., Tachikawa, O. & Hirobe, M. (1987). *Biomed. Res.* **8**, 453–456.
Olszak, T. A., Stepień, A., Grabowski, M. J. & Brzezińska, E. (1996). *Acta Cryst.* C**52**, 1038–1040.
Pashev, A., Burdzhiev, N. & Stanoeva, E. (2020). *Beilstein J. Org. Chem.* **16**, 1456–1464.
Rigaku OD (2018). *CrysAlis PRO*. Rigaku OD, Yarnton, England.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Shinohara, T., Toda, J. & Sano, T. (1997). *Chem. Pharm. Bull.* **45**, 813–819.
Turgunov, K. K., Zhurakulov, Sh. N., Englert, U., Vinogradova, V. I. & Tashkhodjaev, B. (2016). *Acta Cryst.* C**72**, 607–611.

# supporting information

*Acta Cryst.* (2024). E**80**, 1322-1325 [https://doi.org/10.1107/S2056989024011277]

## Crystal structure of 1-(1-chloroethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium chloride

**Ziroat E. Urunbaeva, Kambarali K. Turgunov, Abdusalom Sh. Saidov and Valentina I. Vinogradova**

### Computing details

#### 1-(1-Chloroethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium chloride

*Crystal data*

$C_{13}H_{19}ClNO_2^+ \cdot Cl^-$
$M_r$ = 292.19
Monoclinic, $P2_1/c$
$a$ = 16.1298 (3) Å
$b$ = 12.3736 (3) Å
$c$ = 7.46745 (16) Å
$\beta$ = 100.190 (2)°
$V$ = 1466.87 (6) Å$^3$
$Z$ = 4
$F(000)$ = 616
$D_x$ = 1.323 Mg m$^{-3}$
Melting point: 476(2) K
Cu $K\alpha$ radiation, $\lambda$ = 1.54184 Å
Cell parameters from 5593 reflections
$\theta$ = 2.8–68.0°
$\mu$ = 3.94 mm$^{-1}$
$T$ = 293 K
Prism, colourless
0.25 × 0.10 × 0.05 mm

*Data collection*

XtaLAB Synergy, Single source at home/near, HyPix3000 diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm$^{-1}$
wσcans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2018)
$T_{min}$ = 0.784, $T_{max}$ = 1.000
12790 measured reflections
4641 independent reflections
4142 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.061
$\theta_{max}$ = 68.2°, $\theta_{min}$ = 7.0°
$h$ = −17→19
$k$ = −14→14
$l$ = −8→7

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.155
$S$ = 1.09
4641 reflections
170 parameters
2 restraints
Primary atom site location: iterative
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1122P)^2 + 0.0537P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 e Å$^{-3}$

*Special details*

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

**Refinement**. Refined as a 2-component twin

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl1 | 0.77537 (4) | 0.66403 (6) | 0.75105 (11) | 0.0673 (3) |
| Cl2 | 0.91248 (3) | 0.52447 (5) | 1.18130 (7) | 0.0506 (2) |
| O1 | 0.51533 (12) | 0.3579 (2) | 0.3763 (3) | 0.0747 (6) |
| O2 | 0.58615 (12) | 0.47214 (18) | 0.1566 (3) | 0.0644 (6) |
| C1 | 0.85038 (13) | 0.49829 (17) | 0.5981 (3) | 0.0358 (5) |
| H1A | 0.884823 | 0.477867 | 0.507792 | 0.043* |
| N2 | 0.89415 (11) | 0.45706 (15) | 0.7799 (2) | 0.0374 (4) |
| H2A | 0.9536 (13) | 0.465 (2) | 0.791 (4) | 0.045* |
| H2B | 0.8830 (17) | 0.498 (2) | 0.876 (3) | 0.045* |
| C3 | 0.87520 (15) | 0.34188 (19) | 0.8137 (3) | 0.0465 (5) |
| H3A | 0.908683 | 0.318072 | 0.927730 | 0.056* |
| H3B | 0.889133 | 0.296935 | 0.716790 | 0.056* |
| C4 | 0.78257 (15) | 0.3314 (2) | 0.8215 (3) | 0.0496 (6) |
| H4A | 0.770169 | 0.370253 | 0.926464 | 0.060* |
| H4B | 0.768603 | 0.255903 | 0.834578 | 0.060* |
| C4A | 0.72980 (14) | 0.37668 (19) | 0.6497 (3) | 0.0416 (5) |
| C5 | 0.64592 (15) | 0.3445 (2) | 0.5957 (3) | 0.0503 (6) |
| H5A | 0.621781 | 0.297843 | 0.669519 | 0.060* |
| C6 | 0.59837 (15) | 0.3808 (2) | 0.4351 (4) | 0.0512 (6) |
| C7 | 0.63650 (15) | 0.4458 (2) | 0.3182 (3) | 0.0473 (6) |
| C8 | 0.71844 (14) | 0.47887 (19) | 0.3714 (3) | 0.0414 (5) |
| H8A | 0.743570 | 0.522290 | 0.294466 | 0.050* |
| C8A | 0.76461 (13) | 0.44768 (17) | 0.5409 (3) | 0.0369 (5) |
| C9 | 0.4704 (2) | 0.3114 (4) | 0.5026 (6) | 0.1007 (14) |
| H9A | 0.413028 | 0.299237 | 0.445017 | 0.151* |
| H9B | 0.495855 | 0.243834 | 0.544775 | 0.151* |
| H9C | 0.471544 | 0.359488 | 0.603867 | 0.151* |
| C10 | 0.6234 (2) | 0.5306 (3) | 0.0284 (4) | 0.0711 (9) |
| H10A | 0.581969 | 0.544019 | −0.078361 | 0.107* |
| H10B | 0.644673 | 0.598139 | 0.080729 | 0.107* |
| H10C | 0.668884 | 0.489221 | −0.004100 | 0.107* |
| C11 | 0.84659 (14) | 0.62126 (19) | 0.6022 (3) | 0.0455 (5) |
| H11A | 0.822722 | 0.645643 | 0.478997 | 0.055* |
| C12 | 0.93059 (18) | 0.6771 (2) | 0.6574 (4) | 0.0650 (7) |
| H12A | 0.922258 | 0.753986 | 0.656226 | 0.097* |
| H12B | 0.955872 | 0.654494 | 0.777642 | 0.097* |
| H12C | 0.966957 | 0.658458 | 0.573374 | 0.097* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0646 (4) | 0.0535 (4) | 0.0826 (5) | 0.0072 (3) | 0.0094 (4) | −0.0177 (3) |
| Cl2 | 0.0439 (3) | 0.0715 (5) | 0.0365 (3) | 0.0006 (2) | 0.0075 (2) | −0.0008 (2) |
| O1 | 0.0424 (9) | 0.0996 (16) | 0.0760 (12) | −0.0225 (10) | −0.0063 (9) | 0.0100 (12) |
| O2 | 0.0483 (10) | 0.0862 (15) | 0.0512 (11) | −0.0048 (9) | −0.0120 (9) | 0.0104 (9) |
| C1 | 0.0369 (10) | 0.0382 (11) | 0.0306 (10) | −0.0027 (8) | 0.0019 (8) | 0.0023 (8) |
| N2 | 0.0359 (9) | 0.0418 (10) | 0.0326 (9) | −0.0012 (7) | 0.0008 (7) | 0.0016 (7) |
| C3 | 0.0476 (12) | 0.0411 (13) | 0.0471 (12) | 0.0041 (9) | −0.0015 (10) | 0.0066 (9) |
| C4 | 0.0517 (13) | 0.0465 (14) | 0.0478 (12) | −0.0070 (10) | 0.0009 (10) | 0.0129 (10) |
| C4A | 0.0426 (11) | 0.0403 (12) | 0.0405 (11) | −0.0027 (9) | 0.0040 (9) | 0.0012 (9) |
| C5 | 0.0455 (12) | 0.0496 (14) | 0.0552 (13) | −0.0112 (10) | 0.0073 (10) | 0.0035 (11) |
| C6 | 0.0390 (11) | 0.0559 (15) | 0.0555 (13) | −0.0083 (10) | 0.0000 (10) | −0.0027 (11) |
| C7 | 0.0428 (11) | 0.0532 (14) | 0.0418 (12) | −0.0003 (10) | −0.0036 (9) | −0.0009 (10) |
| C8 | 0.0396 (11) | 0.0455 (13) | 0.0377 (11) | −0.0032 (9) | 0.0032 (9) | 0.0009 (9) |
| C8A | 0.0371 (10) | 0.0367 (11) | 0.0353 (10) | −0.0010 (8) | 0.0022 (8) | −0.0024 (8) |
| C9 | 0.0469 (16) | 0.137 (4) | 0.114 (3) | −0.030 (2) | 0.0021 (18) | 0.028 (3) |
| C10 | 0.0628 (17) | 0.096 (2) | 0.0488 (15) | 0.0066 (16) | −0.0060 (13) | 0.0178 (14) |
| C11 | 0.0465 (11) | 0.0380 (12) | 0.0482 (12) | −0.0029 (9) | −0.0019 (9) | 0.0039 (9) |
| C12 | 0.0558 (15) | 0.0462 (15) | 0.0872 (19) | −0.0150 (12) | −0.0029 (14) | 0.0039 (13) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C11 | 1.813 (3) | C4A—C5 | 1.399 (3) |
| O1—C6 | 1.364 (3) | C5—C6 | 1.379 (4) |
| O1—C9 | 1.410 (4) | C5—H5A | 0.9300 |
| O2—C7 | 1.369 (3) | C6—C7 | 1.407 (4) |
| O2—C10 | 1.416 (4) | C7—C8 | 1.374 (3) |
| C1—N2 | 1.504 (3) | C8—C8A | 1.405 (3) |
| C1—C8A | 1.510 (3) | C8—H8A | 0.9300 |
| C1—C11 | 1.523 (3) | C9—H9A | 0.9600 |
| C1—H1A | 0.9800 | C9—H9B | 0.9600 |
| N2—C3 | 1.488 (3) | C9—H9C | 0.9600 |
| N2—H2A | 0.95 (2) | C10—H10A | 0.9600 |
| N2—H2B | 0.92 (2) | C10—H10B | 0.9600 |
| C3—C4 | 1.511 (3) | C10—H10C | 0.9600 |
| C3—H3A | 0.9700 | C11—C12 | 1.512 (3) |
| C3—H3B | 0.9700 | C11—H11A | 0.9800 |
| C4—C4A | 1.516 (3) | C12—H12A | 0.9600 |
| C4—H4A | 0.9700 | C12—H12B | 0.9600 |
| C4—H4B | 0.9700 | C12—H12C | 0.9600 |
| C4A—C8A | 1.382 (3) | | |
| | | | |
| C6—O1—C9 | 117.5 (2) | C5—C6—C7 | 119.3 (2) |
| C7—O2—C10 | 117.4 (2) | O2—C7—C8 | 125.1 (2) |
| N2—C1—C8A | 112.04 (17) | O2—C7—C6 | 115.3 (2) |
| N2—C1—C11 | 109.57 (17) | C8—C7—C6 | 119.7 (2) |

| | | | |
|---|---|---|---|
| C8A—C1—C11 | 112.46 (18) | C7—C8—C8A | 120.6 (2) |
| N2—C1—H1A | 107.5 | C7—C8—H8A | 119.7 |
| C8A—C1—H1A | 107.5 | C8A—C8—H8A | 119.7 |
| C11—C1—H1A | 107.5 | C4A—C8A—C8 | 119.9 (2) |
| C3—N2—C1 | 113.60 (16) | C4A—C8A—C1 | 123.00 (18) |
| C3—N2—H2A | 108.8 (15) | C8—C8A—C1 | 117.02 (19) |
| C1—N2—H2A | 110.2 (16) | O1—C9—H9A | 109.5 |
| C3—N2—H2B | 108.3 (17) | O1—C9—H9B | 109.5 |
| C1—N2—H2B | 113.2 (17) | H9A—C9—H9B | 109.5 |
| H2A—N2—H2B | 102 (2) | O1—C9—H9C | 109.5 |
| N2—C3—C4 | 108.83 (18) | H9A—C9—H9C | 109.5 |
| N2—C3—H3A | 109.9 | H9B—C9—H9C | 109.5 |
| C4—C3—H3A | 109.9 | O2—C10—H10A | 109.5 |
| N2—C3—H3B | 109.9 | O2—C10—H10B | 109.5 |
| C4—C3—H3B | 109.9 | H10A—C10—H10B | 109.5 |
| H3A—C3—H3B | 108.3 | O2—C10—H10C | 109.5 |
| C3—C4—C4A | 110.28 (19) | H10A—C10—H10C | 109.5 |
| C3—C4—H4A | 109.6 | H10B—C10—H10C | 109.5 |
| C4A—C4—H4A | 109.6 | C12—C11—C1 | 115.2 (2) |
| C3—C4—H4B | 109.6 | C12—C11—Cl1 | 109.50 (19) |
| C4A—C4—H4B | 109.6 | C1—C11—Cl1 | 109.62 (16) |
| H4A—C4—H4B | 108.1 | C12—C11—H11A | 107.4 |
| C8A—C4A—C5 | 119.0 (2) | C1—C11—H11A | 107.4 |
| C8A—C4A—C4 | 120.46 (19) | Cl1—C11—H11A | 107.4 |
| C5—C4A—C4 | 120.6 (2) | C11—C12—H12A | 109.5 |
| C6—C5—C4A | 121.2 (2) | C11—C12—H12B | 109.5 |
| C6—C5—H5A | 119.4 | H12A—C12—H12B | 109.5 |
| C4A—C5—H5A | 119.4 | C11—C12—H12C | 109.5 |
| O1—C6—C5 | 125.2 (2) | H12A—C12—H12C | 109.5 |
| O1—C6—C7 | 115.6 (2) | H12B—C12—H12C | 109.5 |

| | | | |
|---|---|---|---|
| C8A—C1—N2—C3 | 34.0 (2) | C5—C6—C7—C8 | −4.8 (4) |
| C11—C1—N2—C3 | 159.49 (19) | O2—C7—C8—C8A | 179.7 (2) |
| C1—N2—C3—C4 | −64.4 (2) | C6—C7—C8—C8A | 0.5 (4) |
| N2—C3—C4—C4A | 55.1 (3) | C5—C4A—C8A—C8 | −5.6 (3) |
| C3—C4—C4A—C8A | −19.8 (3) | C4—C4A—C8A—C8 | 172.3 (2) |
| C3—C4—C4A—C5 | 158.0 (2) | C5—C4A—C8A—C1 | 171.9 (2) |
| C8A—C4A—C5—C6 | 1.2 (4) | C4—C4A—C8A—C1 | −10.1 (3) |
| C4—C4A—C5—C6 | −176.7 (2) | C7—C8—C8A—C4A | 4.8 (4) |
| C9—O1—C6—C5 | 12.7 (5) | C7—C8—C8A—C1 | −172.9 (2) |
| C9—O1—C6—C7 | −167.9 (3) | N2—C1—C8A—C4A | 3.4 (3) |
| C4A—C5—C6—O1 | −176.7 (3) | C11—C1—C8A—C4A | −120.5 (2) |
| C4A—C5—C6—C7 | 4.0 (4) | N2—C1—C8A—C8 | −178.93 (18) |
| C10—O2—C7—C8 | 5.4 (4) | C11—C1—C8A—C8 | 57.1 (3) |
| C10—O2—C7—C6 | −175.3 (3) | N2—C1—C11—C12 | 55.1 (3) |
| O1—C6—C7—O2 | −3.5 (4) | C8A—C1—C11—C12 | −179.6 (2) |
| C5—C6—C7—O2 | 175.9 (2) | N2—C1—C11—Cl1 | −68.91 (19) |
| O1—C6—C7—C8 | 175.8 (2) | C8A—C1—C11—Cl1 | 56.4 (2) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H1*A*···Cl2$^{i}$ | 0.98 | 2.62 | 3.450 (2) | 143 |
| N2—H2*A*···Cl2$^{ii}$ | 0.95 (2) | 2.14 (2) | 3.0895 (19) | 177 (2) |
| N2—H2*B*···Cl1 | 0.92 (2) | 2.75 (3) | 3.1828 (19) | 110 (2) |
| N2—H2*B*···Cl2 | 0.92 (2) | 2.27 (2) | 3.0751 (19) | 146 (2) |
| C11—H11*A*···Cl1$^{iii}$ | 0.98 | 2.93 | 3.767 (2) | 144 |
| C12—H12*A*···Cl2$^{iii}$ | 0.96 | 2.75 | 3.710 (3) | 174 |

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