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# Redetermination of {5-[(7-chloroquinolinium-4-yl)amino]-2-hydroxybenzyl}diethylammonium dichloride dihydrate

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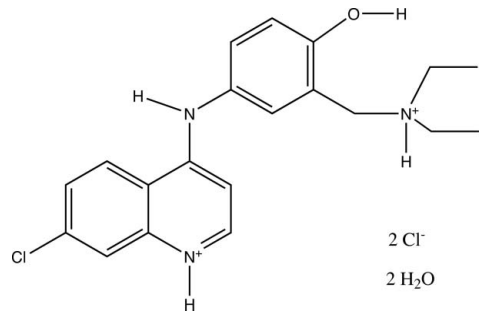
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.038; $wR$ factor = 0.100; data-to-parameter ratio = 13.6.

The structure of the title compound (common name: amodiaquinium dichloride dihydrate), $C_{20}H_{24}ClN_3O_2^{+}\cdot 2Cl^{-}\cdot 2H_2O$, was previously determined from powder diffraction data [Llinàs *et al.* (2006). *Acta Cryst.* E**62**, o4196-o4199]. It has now been refined from diffractometer data to a significantly higher precision. The dihedral angle between the quinoline and benzene rings is 54.57 (6)°. The central amino N atom interacts more strongly with the quinoline ring than with the benzene ring, as indicated by the shorter C—N bond length [1.341 (2) Å compared to 1.431 (2) Å]. In the crystal, molecules are packed into a three-dimensional network/supramolecular structure through hydrogen bonds between the amodiaquinium cations, chloride anions and water molecules.

## Related literature

Amodiaquine, as a dihydrochloride salt, is often used as a synthetic antimalarial drug against chloroquine-sensitive and chloroquine-resistant strains of *Plasmodium falciparum*, see: Olliaro & Taylor (2003). For related structures, see: Llinàs *et al.* (2006); Yennawar & Viswamitra (1991); Semeniuk *et al.* (2008).




## Experimental

### Crystal data

$C_{20}H_{24}ClN_3O^{2+}\cdot 2Cl^{-}\cdot 2H_2O$
$M_r$ = 464.80
Monoclinic, $P2_1/c$
$a$ = 7.7622 (1) Å
$b$ = 26.8709 (4) Å
$c$ = 10.7085 (2) Å
$\beta$ = 92.784 (1)°
$V$ = 2230.91 (6) Å$^3$
$Z$ = 4
Cu $K\alpha$ radiation
$\mu$ = 3.94 mm$^{-1}$
$T$ = 100 K
0.56 × 0.14 × 0.12 mm

### Data collection

Bruker SMART 6000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min}$ = 0.312, $T_{max}$ = 0.623
31612 measured reflections
3917 independent reflections
3699 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.088

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.100
$S$ = 1.10
3917 reflections
287 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.40 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···$A$ |
|---|---|---|---|---|
| N1—H1*N*···Cl2 | 0.89 (2) | 2.32 (2) | 3.1913 (16) | 166.8 (19) |
| N2—H2*N*···O2*W*$^{i}$ | 0.83 (2) | 2.07 (2) | 2.880 (2) | 167 (2) |
| N3—H3*N*···Cl3 | 0.85 (2) | 2.26 (2) | 3.0771 (14) | 161 (2) |
| O1—H1*O*···Cl2$^{ii}$ | 0.84 | 2.22 | 3.0640 (12) | 177 |
| O1*W*—H1*WA*···Cl3$^{iii}$ | 0.88 (3) | 2.30 (3) | 3.1778 (16) | 175 (3) |
| O1*W*—H1*WB*···Cl3$^{i}$ | 0.80 (3) | 2.42 (3) | 3.2100 (16) | 171 (3) |
| O2*W*—H2*WA*···O1*W* | 0.83 (3) | 1.95 (3) | 2.775 (2) | 174 (2) |
| O2*W*—H2*WB*···Cl2$^{ii}$ | 0.83 (3) | 2.33 (3) | 3.1585 (15) | 173 (3) |

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

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: *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *PLATON*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2163).

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# supplementary materials

*Acta Cryst.* (2010). E**66**, o2353-o2354 [ **doi:10.1107/S1600536810031806** ]

# Redetermination of {5-[(7-chloroquinolinium-4-yl)amino]-2-hydroxybenzyl}diethylammonium dichloride dihydrate

**P. Mangwala Kimpende and L. Van Meervelt**

## Comment

Amodiaquine, 4-[7-chloro-4-quinolinyl)amino]-2-[(diethylamino)methyl]phenol, is as dihydrochloride salt, often used as synthetic antimalarial drug against chloroquine-sensitive and chloroquine-resistant strains of *Plasmodium falciparum* (Olliaro & Taylor, 2003). The single-crystal structure of the monohydrate form has been reported by Yennawar & Viswamitra (1991) and by Semeniuk *et al.* (2008). The room temperature structure of the dihydrate form based on powder diffraction at 1.79 Å resolution has been reported by Llinàs *et al.* (2006). Here we report the crystal structure of the title compound (I) at 100 K and a resolution of 0.84 Å (Fig. 1).

Two N atoms (N1 and N3) are protonated indicating that the dihydrochloride salt of amodiaquine is present. The shape of the molecule is mainly dominated by three torsion angles: C8–C9–N2–C19 ($\tau_1$ = -7.7 (3)°), C9–N2–C10–C11 ($\tau_2$ = -52.8 (2)°) and C11–C12–C16–N3 ($\tau_3$ = -85.85 (18)°). It was suggested by Yennawar & Viswamitra (1991) that the C–N bonds linking both aromatic rings have double-bond character. However, we observe a large difference between both bonds C9–N2 (1.341 (2) Å) and N2–C10 (1.431 (2) Å), indicating that N2 interacts more with the quinoline than with the benzene unit. It is also clear from inspection of $\tau_1$ and $\tau_2$ that the overlap of the lone pair of the $sp^2$-hybridized N2 with the quinoline unit is favoured, and this despite the short H2N···H2 contact distance (2.08 Å). The dihedral angle between the quinoline and benzene units is 54.57 (6)°. An intramolecular close contact between H16A and O1 (2.396 Å) is observed by Llinàs *et al.* (2006). The r.m.s. deviation when fitting the amodiaquinium units obtained by single-crystal and powder diffraction (Llinàs *et al.*, 2006) is 0.0739 Å. The hydrogen bonds in the crystal packing (Table 1, Fig. 2) are similar to those described by Llinàs *et al.* (2006).

## Experimental

Amodiaquinium dichloride dihydrate was purchased from Sigma-Aldrich (Belgium). Colourless crystals were obtained at room temperature by slow evaporation from a DMSO solution of (I).

## Refinement

H atoms of the NH groups and of both waters were located in a difference map. The other H atoms were positioned with idealized geometry using a riding model with C–H = 0.95-0.99 Å. All H atoms were refined with isotropic displacement parameters (set to 1.2 or 1.5 times the $U_{eq}$ of the parent atom).

## Figures

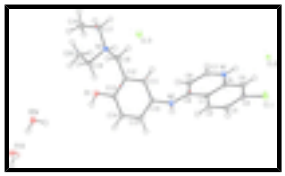


Fig. 1. The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

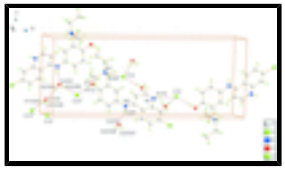


Fig. 2. N–H···Cl, N–H···O, O–H···Cl, and O–H···O hydrogen bonds (dotted lines) in the crystal structure of the title compound. [Symmetry codes : (i) *x* , - *y* + 1/2, *z* - 1/2; (ii) -*x* - 1, *y* - 1/2, - *z* + 1/2; (iii) - *x* , *y* -1/2, - *z* + 1/2.]

## {5-[(7-chloroquinolinium-4-yl)amino]-2-hydroxybenzyl}diethylammonium dichloride dihydrate

*Crystal data*

| | |
|---|---|
| $C_{20}H_{24}ClN_3O^{2+}\cdot 2Cl^{-}\cdot 2H_2O$ | $F(000) = 976$ |
| $M_r = 464.80$ | $D_x = 1.384$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 6662 reflections |
| $a = 7.7622$ (1) Å | $\theta = 3.3$–$70.5°$ |
| $b = 26.8709$ (4) Å | $\mu = 3.94$ mm$^{-1}$ |
| $c = 10.7085$ (2) Å | $T = 100$ K |
| $\beta = 92.784$ (1)° | Prism, colourless |
| $V = 2230.91$ (6) Å$^3$ | 0.56 × 0.14 × 0.12 mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART 6000 CCD diffractometer | 3917 independent reflections |
| Radiation source: fine-focus sealed tube | 3699 reflections with $I > 2\sigma(I)$ |
| crossed Göbel mirrors | $R_{int} = 0.088$ |
| Detector resolution: 0.92 pixels mm$^{-1}$ | $\theta_{max} = 66.6°$, $\theta_{min} = 3.3°$ |
| ω and φ scans | $h = -8\rightarrow 9$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 1997) | $k = -31\rightarrow 31$ |
| $T_{min} = 0.312$, $T_{max} = 0.623$ | $l = -12\rightarrow 12$ |
| 31612 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | Hydrogen site location: difference Fourier map |

| | |
|---|---|
| $wR(F^2) = 0.100$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.10$ | $w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 1.0601P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 3917 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 287 parameters | $\Delta\rho_{max} = 0.40$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.32$ 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | −0.2951 (2) | 0.51757 (6) | 0.06525 (16) | 0.0118 (3) |
| C2 | −0.2063 (2) | 0.52058 (6) | −0.04673 (16) | 0.0131 (4) |
| H2 | −0.1539 | 0.4915 | −0.0782 | 0.016* |
| C3 | −0.1939 (2) | 0.56445 (7) | −0.11087 (16) | 0.0140 (4) |
| H3 | −0.1362 | 0.5658 | −0.1870 | 0.017* |
| C4 | −0.2681 (2) | 0.60736 (7) | −0.06187 (17) | 0.0147 (4) |
| C5 | −0.3573 (2) | 0.60667 (6) | 0.04469 (17) | 0.0141 (4) |
| H5 | −0.4080 | 0.6362 | 0.0753 | 0.017* |
| C6 | −0.3724 (2) | 0.56123 (6) | 0.10810 (16) | 0.0118 (3) |
| C7 | −0.4831 (2) | 0.51792 (7) | 0.27924 (16) | 0.0141 (4) |
| H7 | −0.5498 | 0.5183 | 0.3513 | 0.017* |
| C8 | −0.4081 (2) | 0.47445 (6) | 0.24440 (16) | 0.0138 (4) |
| H8 | −0.4226 | 0.4453 | 0.2928 | 0.017* |
| C9 | −0.3097 (2) | 0.47234 (6) | 0.13779 (16) | 0.0118 (3) |
| C10 | −0.2219 (2) | 0.38571 (6) | 0.17370 (16) | 0.0127 (4) |
| C11 | −0.1590 (2) | 0.38657 (6) | 0.29763 (16) | 0.0125 (4) |
| H11 | −0.1216 | 0.4171 | 0.3343 | 0.015* |
| C12 | −0.1502 (2) | 0.34316 (6) | 0.36829 (16) | 0.0115 (3) |
| C13 | −0.2084 (2) | 0.29835 (6) | 0.31382 (17) | 0.0121 (3) |
| C14 | −0.2641 (2) | 0.29733 (6) | 0.18823 (17) | 0.0139 (4) |
| H14 | −0.2977 | 0.2667 | 0.1501 | 0.017* |
| C15 | −0.2709 (2) | 0.34090 (7) | 0.11850 (17) | 0.0140 (4) |
| H15 | −0.3091 | 0.3400 | 0.0329 | 0.017* |
| C16 | −0.0831 (2) | 0.34431 (6) | 0.50266 (16) | 0.0133 (4) |
| H16A | −0.1354 | 0.3166 | 0.5485 | 0.016* |

| | | | | |
|---|---|---|---|---|
| H16B | −0.1191 | 0.3759 | 0.5414 | 0.016* |
| C17 | 0.1735 (2) | 0.34491 (6) | 0.65140 (16) | 0.0136 (4) |
| H17A | 0.1177 | 0.3744 | 0.6876 | 0.016* |
| H17B | 0.2995 | 0.3509 | 0.6553 | 0.016* |
| C18 | 0.1364 (3) | 0.29984 (7) | 0.73055 (17) | 0.0206 (4) |
| H18A | 0.0146 | 0.2906 | 0.7179 | 0.031* |
| H18B | 0.1614 | 0.3077 | 0.8189 | 0.031* |
| H18C | 0.2090 | 0.2720 | 0.7061 | 0.031* |
| C19 | 0.1800 (2) | 0.29476 (7) | 0.45331 (16) | 0.0145 (4) |
| H19A | 0.1337 | 0.2938 | 0.3655 | 0.017* |
| H19B | 0.1390 | 0.2646 | 0.4960 | 0.017* |
| C20 | 0.3754 (3) | 0.29404 (8) | 0.45504 (19) | 0.0242 (4) |
| H20A | 0.4172 | 0.3254 | 0.4210 | 0.036* |
| H20B | 0.4137 | 0.2662 | 0.4040 | 0.036* |
| H20C | 0.4217 | 0.2900 | 0.5412 | 0.036* |
| N1 | −0.4650 (2) | 0.56009 (6) | 0.21445 (14) | 0.0137 (3) |
| H1N | −0.514 (3) | 0.5883 (9) | 0.237 (2) | 0.016* |
| N2 | −0.2317 (2) | 0.43058 (5) | 0.10177 (14) | 0.0126 (3) |
| H2N | −0.190 (3) | 0.4290 (8) | 0.032 (2) | 0.015* |
| N3 | 0.1117 (2) | 0.33997 (5) | 0.51605 (14) | 0.0114 (3) |
| H3N | 0.152 (3) | 0.3658 (9) | 0.482 (2) | 0.015 (5)* |
| O1 | −0.20278 (17) | 0.25706 (4) | 0.38692 (12) | 0.0160 (3) |
| H1O | −0.2483 | 0.2331 | 0.3472 | 0.024* |
| O1W | −0.0091 (2) | 0.02817 (6) | 0.17421 (15) | 0.0321 (4) |
| H1WA | −0.080 (4) | 0.0063 (12) | 0.139 (3) | 0.038* |
| H1WB | 0.063 (4) | 0.0345 (11) | 0.126 (3) | 0.038* |
| O2W | −0.08987 (19) | 0.09265 (5) | 0.36517 (13) | 0.0201 (3) |
| H2WA | −0.073 (3) | 0.0731 (10) | 0.307 (3) | 0.024* |
| H2WB | −0.157 (4) | 0.1146 (10) | 0.337 (2) | 0.024* |
| Cl1 | −0.24427 (7) | 0.663720 (16) | −0.13878 (5) | 0.02505 (15) |
| Cl2 | −0.63123 (6) | 0.667531 (14) | 0.24913 (4) | 0.01525 (13) |
| Cl3 | 0.24523 (6) | 0.444735 (15) | 0.45660 (4) | 0.02012 (14) |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0116 (8) | 0.0129 (8) | 0.0105 (8) | −0.0019 (7) | −0.0021 (7) | 0.0008 (6) |
| C2 | 0.0133 (8) | 0.0126 (8) | 0.0134 (8) | −0.0003 (7) | 0.0005 (7) | −0.0025 (6) |
| C3 | 0.0148 (9) | 0.0163 (8) | 0.0110 (8) | −0.0015 (7) | 0.0004 (7) | 0.0011 (7) |
| C4 | 0.0153 (9) | 0.0129 (8) | 0.0156 (8) | −0.0009 (7) | −0.0013 (7) | 0.0041 (7) |
| C5 | 0.0144 (9) | 0.0110 (8) | 0.0168 (8) | 0.0017 (7) | 0.0000 (7) | −0.0009 (7) |
| C6 | 0.0100 (8) | 0.0141 (8) | 0.0110 (8) | −0.0001 (6) | −0.0012 (7) | −0.0003 (6) |
| C7 | 0.0133 (8) | 0.0174 (9) | 0.0117 (8) | −0.0014 (7) | 0.0017 (7) | 0.0012 (7) |
| C8 | 0.0144 (8) | 0.0135 (8) | 0.0135 (8) | −0.0013 (7) | 0.0002 (7) | 0.0023 (6) |
| C9 | 0.0109 (8) | 0.0127 (8) | 0.0115 (8) | −0.0005 (6) | −0.0038 (7) | 0.0002 (6) |
| C10 | 0.0128 (8) | 0.0119 (8) | 0.0134 (8) | 0.0025 (7) | 0.0013 (7) | 0.0018 (6) |
| C11 | 0.0128 (8) | 0.0093 (8) | 0.0153 (8) | 0.0010 (6) | 0.0014 (7) | −0.0012 (6) |
| C12 | 0.0104 (8) | 0.0134 (8) | 0.0108 (8) | 0.0020 (6) | 0.0024 (7) | 0.0006 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C13 | 0.0098 (8) | 0.0106 (8) | 0.0159 (9) | 0.0018 (6) | 0.0015 (7) | 0.0030 (6) |
| C14 | 0.0154 (9) | 0.0106 (8) | 0.0154 (9) | −0.0005 (6) | −0.0014 (7) | −0.0011 (6) |
| C15 | 0.0145 (9) | 0.0152 (9) | 0.0120 (8) | 0.0023 (7) | −0.0018 (7) | 0.0001 (6) |
| C16 | 0.0127 (9) | 0.0154 (8) | 0.0119 (8) | 0.0008 (7) | 0.0014 (7) | −0.0010 (6) |
| C17 | 0.0160 (9) | 0.0158 (8) | 0.0087 (8) | −0.0004 (7) | −0.0016 (7) | −0.0013 (6) |
| C18 | 0.0265 (10) | 0.0228 (10) | 0.0123 (8) | −0.0023 (8) | −0.0021 (8) | 0.0032 (7) |
| C19 | 0.0168 (9) | 0.0153 (8) | 0.0113 (8) | 0.0019 (7) | −0.0004 (7) | −0.0029 (6) |
| C20 | 0.0173 (10) | 0.0341 (11) | 0.0210 (10) | 0.0059 (8) | −0.0007 (8) | −0.0101 (8) |
| N1 | 0.0149 (8) | 0.0124 (7) | 0.0140 (7) | 0.0027 (6) | 0.0025 (6) | −0.0007 (6) |
| N2 | 0.0169 (8) | 0.0113 (7) | 0.0098 (7) | 0.0003 (6) | 0.0021 (6) | 0.0013 (5) |
| N3 | 0.0137 (8) | 0.0113 (7) | 0.0093 (7) | −0.0015 (6) | 0.0004 (6) | 0.0019 (6) |
| O1 | 0.0223 (7) | 0.0093 (6) | 0.0163 (6) | −0.0028 (5) | −0.0011 (5) | 0.0030 (5) |
| O1W | 0.0378 (9) | 0.0334 (9) | 0.0259 (8) | −0.0084 (7) | 0.0113 (7) | −0.0119 (7) |
| O2W | 0.0264 (8) | 0.0181 (7) | 0.0161 (6) | 0.0032 (6) | 0.0033 (6) | 0.0022 (5) |
| Cl1 | 0.0353 (3) | 0.0141 (2) | 0.0266 (3) | 0.00221 (18) | 0.0109 (2) | 0.00951 (17) |
| Cl2 | 0.0173 (2) | 0.0126 (2) | 0.0157 (2) | 0.00398 (15) | −0.00045 (17) | −0.00229 (14) |
| Cl3 | 0.0266 (3) | 0.0168 (2) | 0.0171 (2) | −0.00626 (17) | 0.00212 (19) | 0.00298 (15) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—C6 | 1.405 (2) | C14—H14 | 0.9500 |
| C1—C2 | 1.414 (3) | C15—H15 | 0.9500 |
| C1—C9 | 1.450 (2) | C16—N3 | 1.516 (2) |
| C2—C3 | 1.370 (3) | C16—H16A | 0.9900 |
| C2—H2 | 0.9500 | C16—H16B | 0.9900 |
| C3—C4 | 1.402 (3) | C17—N3 | 1.510 (2) |
| C3—H3 | 0.9500 | C17—C18 | 1.514 (2) |
| C4—C5 | 1.364 (3) | C17—H17A | 0.9900 |
| C4—Cl1 | 1.7381 (17) | C17—H17B | 0.9900 |
| C5—C6 | 1.405 (2) | C18—H18A | 0.9800 |
| C5—H5 | 0.9500 | C18—H18B | 0.9800 |
| C6—N1 | 1.376 (2) | C18—H18C | 0.9800 |
| C7—N1 | 1.340 (2) | C19—N3 | 1.497 (2) |
| C7—C8 | 1.365 (3) | C19—C20 | 1.516 (3) |
| C7—H7 | 0.9500 | C19—H19A | 0.9900 |
| C8—C9 | 1.405 (3) | C19—H19B | 0.9900 |
| C8—H8 | 0.9500 | C20—H20A | 0.9800 |
| C9—N2 | 1.340 (2) | C20—H20B | 0.9800 |
| C10—C15 | 1.386 (3) | C20—H20C | 0.9800 |
| C10—C11 | 1.392 (3) | N1—H1N | 0.89 (2) |
| C10—N2 | 1.431 (2) | N2—H2N | 0.83 (3) |
| C11—C12 | 1.390 (2) | N3—H3N | 0.85 (3) |
| C11—H11 | 0.9500 | O1—H1O | 0.8400 |
| C12—C13 | 1.403 (2) | O1W—H1WA | 0.88 (3) |
| C12—C16 | 1.507 (2) | O1W—H1WB | 0.80 (3) |
| C13—O1 | 1.357 (2) | O2W—H2WA | 0.83 (3) |
| C13—C14 | 1.393 (3) | O2W—H2WB | 0.84 (3) |
| C14—C15 | 1.388 (3) | | |
| C6—C1—C2 | 117.57 (16) | C12—C16—N3 | 112.69 (14) |

| | | | |
|---|---|---|---|
| C6—C1—C9 | 118.64 (16) | C12—C16—H16A | 109.1 |
| C2—C1—C9 | 123.79 (16) | N3—C16—H16A | 109.1 |
| C3—C2—C1 | 121.54 (16) | C12—C16—H16B | 109.1 |
| C3—C2—H2 | 119.2 | N3—C16—H16B | 109.1 |
| C1—C2—H2 | 119.2 | H16A—C16—H16B | 107.8 |
| C2—C3—C4 | 118.68 (16) | N3—C17—C18 | 114.01 (14) |
| C2—C3—H3 | 120.7 | N3—C17—H17A | 108.8 |
| C4—C3—H3 | 120.7 | C18—C17—H17A | 108.8 |
| C5—C4—C3 | 122.46 (16) | N3—C17—H17B | 108.8 |
| C5—C4—Cl1 | 118.58 (14) | C18—C17—H17B | 108.8 |
| C3—C4—Cl1 | 118.96 (14) | H17A—C17—H17B | 107.6 |
| C4—C5—C6 | 118.29 (16) | C17—C18—H18A | 109.5 |
| C4—C5—H5 | 120.9 | C17—C18—H18B | 109.5 |
| C6—C5—H5 | 120.9 | H18A—C18—H18B | 109.5 |
| N1—C6—C1 | 120.02 (16) | C17—C18—H18C | 109.5 |
| N1—C6—C5 | 118.59 (16) | H18A—C18—H18C | 109.5 |
| C1—C6—C5 | 121.40 (16) | H18B—C18—H18C | 109.5 |
| N1—C7—C8 | 121.68 (16) | N3—C19—C20 | 112.36 (15) |
| N1—C7—H7 | 119.2 | N3—C19—H19A | 109.1 |
| C8—C7—H7 | 119.2 | C20—C19—H19A | 109.1 |
| C7—C8—C9 | 120.83 (16) | N3—C19—H19B | 109.1 |
| C7—C8—H8 | 119.6 | C20—C19—H19B | 109.1 |
| C9—C8—H8 | 119.6 | H19A—C19—H19B | 107.9 |
| N2—C9—C8 | 122.57 (16) | C19—C20—H20A | 109.5 |
| N2—C9—C1 | 119.97 (16) | C19—C20—H20B | 109.5 |
| C8—C9—C1 | 117.46 (16) | H20A—C20—H20B | 109.5 |
| C15—C10—C11 | 119.80 (16) | C19—C20—H20C | 109.5 |
| C15—C10—N2 | 119.74 (15) | H20A—C20—H20C | 109.5 |
| C11—C10—N2 | 120.43 (15) | H20B—C20—H20C | 109.5 |
| C12—C11—C10 | 120.72 (16) | C7—N1—C6 | 121.31 (15) |
| C12—C11—H11 | 119.6 | C7—N1—H1N | 121.8 (14) |
| C10—C11—H11 | 119.6 | C6—N1—H1N | 116.8 (14) |
| C11—C12—C13 | 119.18 (16) | C9—N2—C10 | 124.30 (16) |
| C11—C12—C16 | 120.54 (16) | C9—N2—H2N | 120.2 (15) |
| C13—C12—C16 | 120.26 (15) | C10—N2—H2N | 115.4 (15) |
| O1—C13—C14 | 122.72 (15) | C19—N3—C17 | 113.52 (13) |
| O1—C13—C12 | 117.46 (16) | C19—N3—C16 | 113.13 (14) |
| C14—C13—C12 | 119.79 (16) | C17—N3—C16 | 110.65 (14) |
| C15—C14—C13 | 120.30 (16) | C19—N3—H3N | 108.9 (15) |
| C15—C14—H14 | 119.8 | C17—N3—H3N | 103.8 (15) |
| C13—C14—H14 | 119.8 | C16—N3—H3N | 106.1 (15) |
| C10—C15—C14 | 120.05 (16) | C13—O1—H1O | 109.5 |
| C10—C15—H15 | 120.0 | H1WA—O1W—H1WB | 108 (3) |
| C14—C15—H15 | 120.0 | H2WA—O2W—H2WB | 107 (2) |
| C6—C1—C2—C3 | 0.7 (3) | C11—C12—C13—O1 | −177.99 (16) |
| C9—C1—C2—C3 | −178.97 (16) | C16—C12—C13—O1 | 0.6 (2) |
| C1—C2—C3—C4 | 1.5 (3) | C11—C12—C13—C14 | 3.8 (3) |
| C2—C3—C4—C5 | −2.5 (3) | C16—C12—C13—C14 | −177.60 (16) |
| C2—C3—C4—Cl1 | 177.02 (14) | O1—C13—C14—C15 | 178.55 (16) |

| | | | |
|---|---|---|---|
| C3—C4—C5—C6 | 1.1 (3) | C12—C13—C14—C15 | −3.4 (3) |
| Cl1—C4—C5—C6 | −178.43 (13) | C11—C10—C15—C14 | 2.8 (3) |
| C2—C1—C6—N1 | 178.00 (16) | N2—C10—C15—C14 | −179.04 (17) |
| C9—C1—C6—N1 | −2.3 (2) | C13—C14—C15—C10 | 0.1 (3) |
| C2—C1—C6—C5 | −2.1 (3) | C11—C12—C16—N3 | −85.8 (2) |
| C9—C1—C6—C5 | 177.54 (16) | C13—C12—C16—N3 | 95.62 (19) |
| C4—C5—C6—N1 | −178.85 (16) | C8—C7—N1—C6 | 1.3 (3) |
| C4—C5—C6—C1 | 1.3 (3) | C1—C6—N1—C7 | 0.2 (3) |
| N1—C7—C8—C9 | −0.6 (3) | C5—C6—N1—C7 | −179.66 (16) |
| C7—C8—C9—N2 | 178.87 (17) | C8—C9—N2—C10 | −7.7 (3) |
| C7—C8—C9—C1 | −1.6 (3) | C1—C9—N2—C10 | 172.72 (15) |
| C6—C1—C9—N2 | −177.47 (16) | C15—C10—N2—C9 | 129.05 (19) |
| C2—C1—C9—N2 | 2.2 (3) | C11—C10—N2—C9 | −52.8 (3) |
| C6—C1—C9—C8 | 2.9 (2) | C20—C19—N3—C17 | −59.3 (2) |
| C2—C1—C9—C8 | −177.40 (17) | C20—C19—N3—C16 | 173.55 (15) |
| C15—C10—C11—C12 | −2.3 (3) | C18—C17—N3—C19 | −55.1 (2) |
| N2—C10—C11—C12 | 179.55 (16) | C18—C17—N3—C16 | 73.33 (19) |
| C10—C11—C12—C13 | −1.0 (3) | C12—C16—N3—C19 | −55.29 (19) |
| C10—C11—C12—C16 | −179.61 (16) | C12—C16—N3—C17 | 176.05 (14) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1N···Cl2 | 0.89 (2) | 2.32 (2) | 3.1913 (16) | 166.8 (19) |
| N2—H2N···O2W$^{i}$ | 0.83 (2) | 2.07 (2) | 2.880 (2) | 167 (2) |
| N3—H3N···Cl3 | 0.85 (2) | 2.26 (2) | 3.0771 (14) | 161 (2) |
| O1—H1O···Cl2$^{ii}$ | 0.84 | 2.22 | 3.0640 (12) | 177 |
| O1W—H1WA···Cl3$^{iii}$ | 0.88 (3) | 2.30 (3) | 3.1778 (16) | 175 (3) |
| O1W—H1WB···Cl3$^{i}$ | 0.80 (3) | 2.42 (3) | 3.2100 (16) | 171 (3) |
| O2W—H2WA···O1W | 0.83 (3) | 1.95 (3) | 2.775 (2) | 174 (2) |
| O2W—H2WB···Cl2$^{ii}$ | 0.83 (3) | 2.33 (3) | 3.1585 (15) | 173 (3) |

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

**Fig. 1**

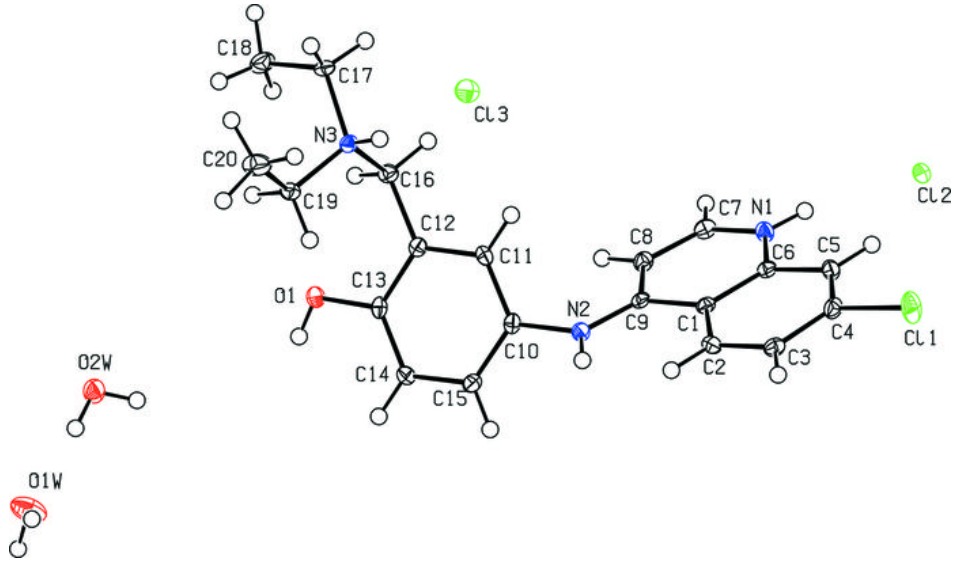
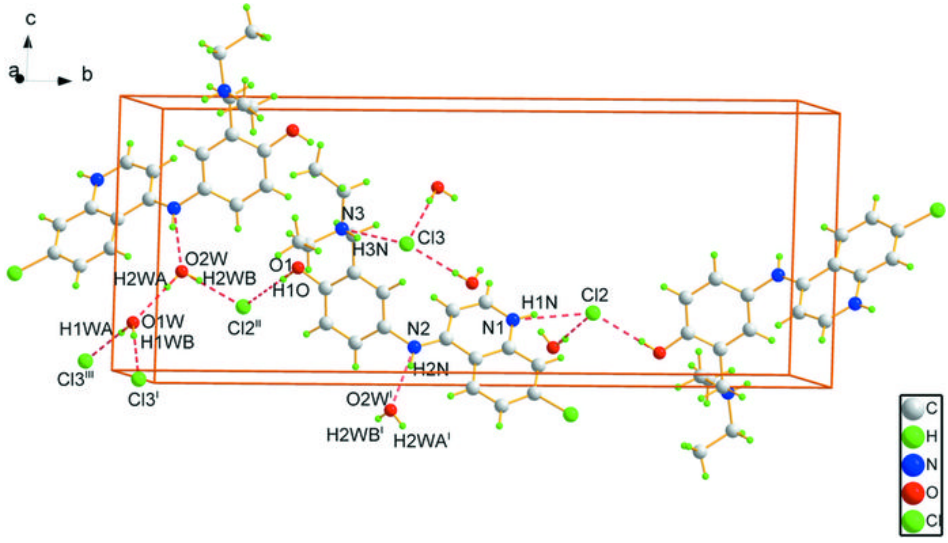

C18
C17
Cl3
N3
C20
C16
C19
C12
C11
C7
N1
Cl2
C8
C6
C5
C13
O1
N2
C9
C1
C4
Cl1
C10
C2
C3
O2W
C14
C15
O1W

**Fig. 2**


c
a
b
N3
H3N
Cl3
O2W
H2WA
H2WB
O1
H1O
Cl2ii
H1WA
O1W
H1WB
Cl3iii
Cl3i
N2
H2N
O2Wi
H2WBi
H2WAi
H1N
N1
Cl2
C
H
N
O
Cl