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# 1-[Bis(4-fluorophenyl)methyl]-4-[(2*Z*)-3-phenylprop-2-en-1-yl]piperazine-1,4-diium dichloride hemihydrate

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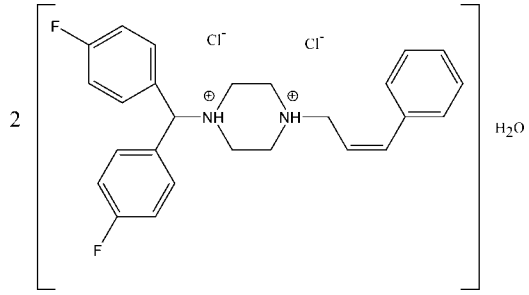
Key indicators: single-crystal X-ray study; $T$ = 173 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.057; $wR$ factor = 0.153; data-to-parameter ratio = 28.1.

The asymmetric unit of the title monohydrated salt, $2C_{26}H_{28}F_2N_2^{2+}\cdot 4Cl^-\cdot H_2O$, consists of a 1-[bis(4-fluorophenyl)-methyl]-4-[(2*Z*)-3-phenylprop-2-en-1-yl]piperazine-1,4-diium cation with a diprotonated piperizine ring in close proximity to two chloride anions and a single water molecule that lies on a twofold rotation axis. In the cation, the piperazine ring adopts a slightly distorted chair conformation. The dihedral angles between the phenyl ring and the 4-fluorophenyl rings are 89.3 (9) and 35.0 (5)°. The two fluorophenyl rings are inclined at 65.0 (5)° to one another. In the crystal, N—H···Cl hydrogen bonds and weak C—H···Cl intermolecular interactions link the molecules into chains along [010]. In addition, weak C—H···O interactions between the piperizine and prop-2-en-1-yl groups with the water molecule, along with weak C—H···Cl interactions between the prop-2en-1-yl and methyl groups with the chloride ions, weak C—H···F interactions between the two fluorophenyl groups and weak O—H···Cl interactions between the water molecule and chloride ions form a three-dimensional supramolecular network.

## Related literature

For the use of flunarizine {systematic name: (*E*)-1-[bis(4-fluorophenyl)methyl]-4-(3-phenyl-2-propenyl)piperazine} as an antihistamine and vasodilator, see: Agnoli *et al.* (1988); Prasanna & Row (2001). For the synthesis of (*E*)-isomers of 1-benzhydryl-4-cinnamyl piperazines, see: Cignarella & Testa (1968) and that of the Z-isomer of cinnerizine, [systematic name: (*E*)-1-(diphenylmethyl)-4-(3-phenylprop-2-enyl)piperazine], see; Shivaprakash & Chandrasekara Reddy (2014). For puckering parameters, see Cremer & Pople (1975). For standard bond lengths, see: Allen *et al.* (1987).




## Experimental

### Crystal data

$2C_{26}H_{28}F_2N_2^{2+}\cdot 4Cl^-\cdot H_2O$
$M_r$ = 972.82
Monoclinic, $P2/c$
$a$ = 18.2973 (6) Å
$b$ = 7.02041 (14) Å
$c$ = 20.1554 (6) Å
$\beta$ = 104.601 (3)°
$V$ = 2505.44 (13) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.29 mm$^{-1}$
$T$ = 173 K
0.44 × 0.38 × 0.16 mm

### Data collection

Agilent Eos Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis PRO* and *CrysAlis RED*; Agilent, 2012)
$T_{min}$ = 0.914, $T_{max}$ = 1.000
32975 measured reflections
8607 independent reflections
6582 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.034

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.153
$S$ = 1.09
8607 reflections
306 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.65 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.41 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···Cl1$^{i}$ | 0.84 (2) | 2.14 (2) | 2.9782 (13) | 176 (2) |
| N2—H2···Cl2$^{ii}$ | 0.86 (3) | 2.17 (3) | 3.0248 (13) | 174 (2) |
| C1—H1*A*···O1*W*$^{i}$ | 0.99 | 2.68 | 3.512 (2) | 142 |
| C5—H5*A*···O1*W*$^{i}$ | 0.99 | 2.67 | 3.470 (2) | 138 |
| C5—H5*B*···Cl1$^{ii}$ | 0.99 | 2.51 | 3.4934 (16) | 176 |
| C14—H14···Cl2$^{i}$ | 1.00 | 2.49 | 3.4735 (15) | 168 |
| C19—H19···F2$^{iii}$ | 0.95 | 2.46 | 3.244 (2) | 140 |
| O1*W*—H1*W*···Cl1 | 0.80 (3) | 2.48 (3) | 3.2603 (12) | 163 (3) |

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

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Agilent, 2012); program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007; Palatinus & van der Lee, 2008; Palatinus *et al.*, 2012); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

We express our sincere thanks to Dr Anil Kush, Director, VMSRF for his keen interest and support throughout this work. JPJ acknowledges the NSF–MRI program (grant No. CHE-1039027) for funds to purchase the X-ray diffractometer.

Supporting information for this paper is available from the IUCr electronic archives (Reference: SJ5400).

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# supplementary materials

*Acta Cryst.* (2014). E**70**, o694–o695 [doi:10.1107/S1600536814011064]

## 1-[Bis(4-fluorophenyl)methyl]-4-[(2*Z*)-3-phenylprop-2-en-1-yl]piperazine-1,4-diium dichloride hemihydrate

**S. Shivaprakash, G. Chandrasekara Reddy and Jerry P. Jasinski**

### 1. Comment

Flunarizine, (E)-1-[bis(4-fluorophenyl)methyl]-4-(3-phenyl-2- propenyl)piperazine, is a clinically useful drug used as an antihistamine and vasodilator (Agnoli *et al.* (1988), Prasanna & Row (2001). Because the greater biological importance of (E)-isomers of 1-benzhydryl-4-cinnamyl piperazines has been recognised, several synthetic methods for these isomers have been described (Cignarella & Testa, 1968). However, the synthesis of (Z)-1-[bis(4-fluorophenyl)methyl]-4-(3-phenyl-2-propenyl)piperazine has only recently been reported (Shivaprakash & Chandrasekara Reddy, 2014).

The title compound, $2(C_{26}H_{28}F_2N_2)$, 4(Cl), $H_2O$, (I), is a close analogue of the existing drug, flunarizine, which has an (E) configuration. The crystal structure of flunarizine has been reported (Prasanna & Row, 2001). We have prepared the (Z) isomer (I) for the first time as the crystalline hydrochloride salt to study structure activity relationships and we report its structure here.

The asymmetric unit of the title monohydrated salt, $2(C_{26}H_{28}F_2N_2^{2+})$, $4(Cl^-)$, $H_2O$, (I), consists of a [(Z)-1-[bis(4-fluorophenyl)methyl]-4-(3-phenyl-2-propenyl)piperazine] cation with a diprotonated piperizine ring in close proximity to two chloride anions and a single water molecule that lies on a two-fold rotation axis (Fig. 1). The piperazine group adopts a slightly distorted chair conformation (puckering parameters Q, $\theta$, and $\varphi$ = 0.5911 (15)Å, 0.95 (15)° and 154 (8)°, respectively (Cremer & Pople, 1975). Bond lengths are within normal ranges (Allen *et al.*, 1987). In the cation, the dihedral angles between the mean planes of the two 4-fluorophenyl rings with that of the phenyl ring are 89.3 (9)° and 35.0 (5)°, respectively. The two fluorophenyl groups are inclined at 65.0 (5)° to one another. In the crystal, N—H···Cl hydrogen bonds and weak C—H···Cl intermolecular interactions link the molecules into chains along [010] (Fig. 2). In addition, weak C—H···O interactions between the piperizine and prop-2-en-1-yl groups with the water molecule along with weak C—H···Cl interactions between the prop-2en-1-yl and methyl groups with the chloride ions and weak C—H···F interactions between the two fluorophenyl groups and weak O—H···Cl interactions between the water molecule and chloride ions (Table 1) form a 3-D supramolecular network.

### 2. Experimental

To a solution of 1-(4, 4′-difluoro phenylmethyl)-4-(2-acetaldehyde) piperazine (5.6 g, 17.0 mmol) in dichloromethane (50 ml) under a nitrogen atmosphere was added benzyltriphenyl phosphonium chloride, (6.9 g, 17.9 mmol). The mixture was cooled to 278 °K and t-BuOK (4.6 g, 41.3 mmol) was added with stirring. After completion, the reaction mass was quenched into water (100 ml). The organic layer was separated, dried over anhydrous sodium sulfate and concentrated under vacuum. The solution was then subjected to column chromatography over silica gel with an EtOAc/Hexane (1:9) elutant mixture to afford (Z)-1-[bis-(4-fluorophenyl)-methyl]-4-(cinnamyl) piperazine as a viscous liquid. This was then converted into the hydrochloride salt using ethanolic HCl and crystallized from acetone/ethanol (2:8) mp 473-475°K.

### 3. Refinement

The H1, H2 and H1W atoms were located from a difference map and refined isotropically. All of the remaining H atoms were placed in their calculated positions and then refined using a riding model with Atom—H lengths of 0.95Å (CH) or 0.99Å ($CH_2$). Isotropic displacement parameters for these atoms were set to 1.2 (CH, $CH_2$) times $U_{eq}$ of the parent atom.

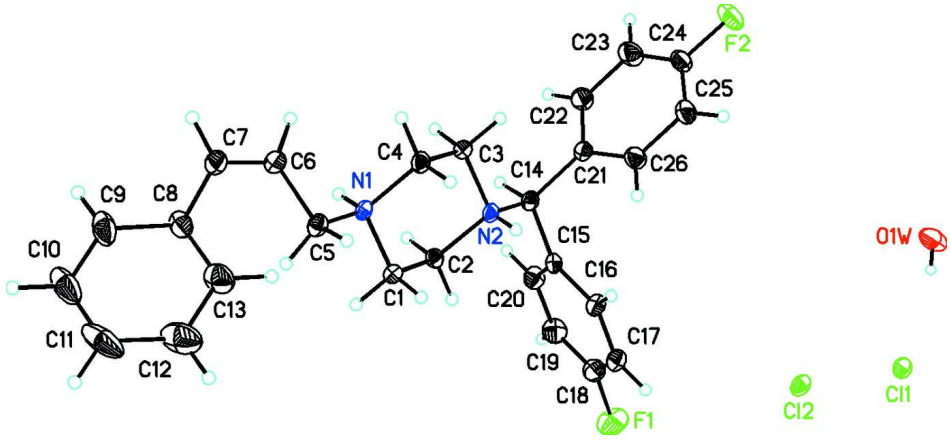


**Figure 1**

ORTEP drawing of the asymmetric unit of (I), showing the labeling scheme and with 30% probability displacement ellipsoids.

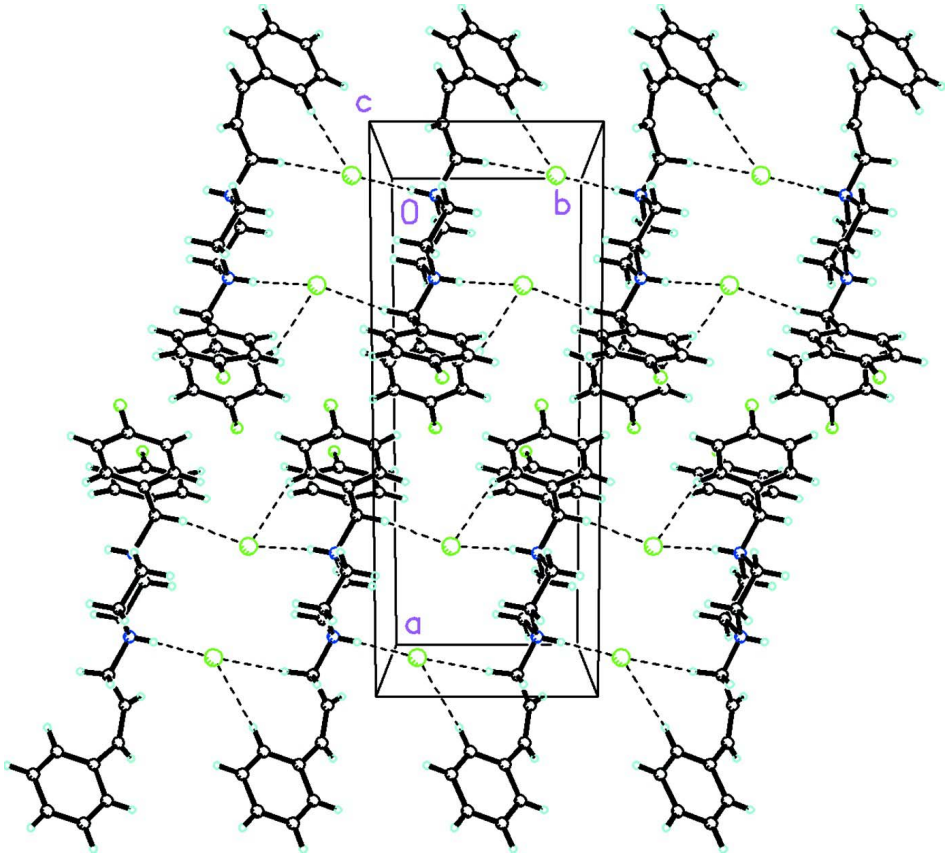


**Figure 2**

Crystal packing of (I) viewed along the *c* axis. Dashed lines indicate N—H···Cl hydrogen bonds and weak C—H···Cl intermolecular interactions which link the molecules into chains along [010].

**1-[Bis(4-fluorophenyl)methyl]-4-[(2*Z*)-3-phenylprop-2-en-1-yl]piperazine-1,4-diium dichloride hemihydrate**

*Crystal data*

$2C_{26}H_{28}F_2N_2^{2+}\cdot 4Cl^-\cdot H_2O$
$M_r = 972.82$
Monoclinic, $P2/c$
$a = 18.2973\ (6)$ Å
$b = 7.02041\ (14)$ Å
$c = 20.1554\ (6)$ Å
$\beta = 104.601\ (3)°$
$V = 2505.44\ (13)$ Å$^3$
$Z = 2$
$F(000) = 1020$
$D_x = 1.290$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7981 reflections
$\theta = 3.5–32.4°$
$\mu = 0.29$ mm$^{-1}$
$T = 173$ K
Irregular, colourless
0.44 × 0.38 × 0.16 mm

*Data collection*

Agilent Eos Gemini diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 16.0416 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*CrysAlis PRO* and *CrysAlis RED*; Agilent, 2012)
$T_{min} = 0.914$, $T_{max} = 1.000$
32975 measured reflections
8607 independent reflections
6582 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.034
$\theta_{max}$ = 32.8°, $\theta_{min}$ = 3.1°
$h$ = −27→26
$k$ = −10→10
$l$ = −29→29

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.153
$S$ = 1.09
8607 reflections
306 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 1.0043P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.65 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.41 e Å$^{-3}$

*Special details*

**Experimental**. $^1$H NMR: $\delta$ 7.20 - 7.35(m, 9 H, Ar-H), 6.87-6.98 (m, 4 H, Ar-H), 6.50 (d, J = 12 Hz, 1 H), 5.76 (ddd, J = 12.0, 6.6 Hz, 1 H), 4.20(s, 1 H), 3.27 (dd, J = 6.6, 1.8 Hz, 2 H), 2.40 (bd, 8 H). $^{13}$C NMR: $\delta$ 163.1, 160.6, 138.3, 137.1, 132.6, 132.5, 131.5, 129.3, 129.2, 128.9, 128.2, 126.9, 115.5, 115.3, 74.5, 56.1, 53.4, 51.7. HRMS calculated for $C_{26}H_{26}F_2N_2$ [M+H] + 405.2142; found 405.2145.

**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.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| F1 | 0.47811 (8) | 0.7591 (2) | 0.63602 (8) | 0.0647 (4) |
| F2 | 0.57160 (8) | 0.7045 (2) | 0.20291 (6) | 0.0572 (3) |
| N1 | 0.92882 (7) | 0.74830 (17) | 0.58339 (6) | 0.0225 (2) |
| H1 | 0.9389 (11) | 0.865 (3) | 0.5856 (10) | 0.032 (5)* |
| N2 | 0.76733 (7) | 0.75240 (17) | 0.51554 (6) | 0.0219 (2) |
| H2 | 0.7600 (14) | 0.632 (4) | 0.5145 (13) | 0.054 (7)* |
| C1 | 0.87041 (8) | 0.7138 (2) | 0.62188 (8) | 0.0263 (3) |
| H1A | 0.8893 | 0.7589 | 0.6697 | 0.032* |
| H1B | 0.8603 | 0.5754 | 0.6231 | 0.032* |
| C2 | 0.79796 (8) | 0.8174 (2) | 0.58809 (7) | 0.0253 (3) |
| H2A | 0.7599 | 0.7938 | 0.6144 | 0.030* |
| H2B | 0.8078 | 0.9562 | 0.5886 | 0.030* |
| C3 | 0.82618 (8) | 0.7885 (2) | 0.47723 (8) | 0.0274 (3) |
| H3A | 0.8359 | 0.9271 | 0.4762 | 0.033* |
| H3B | 0.8075 | 0.7440 | 0.4293 | 0.033* |
| C4 | 0.89918 (9) | 0.6860 (2) | 0.51080 (8) | 0.0279 (3) |
| H4A | 0.8901 | 0.5468 | 0.5095 | 0.033* |
| H4B | 0.9373 | 0.7127 | 0.4848 | 0.033* |
| C5 | 1.00129 (8) | 0.6496 (2) | 0.61791 (8) | 0.0280 (3) |
| H5A | 1.0139 | 0.6773 | 0.6677 | 0.034* |
| H5B | 0.9946 | 0.5102 | 0.6118 | 0.034* |
| C6 | 1.06496 (9) | 0.7136 (2) | 0.58886 (9) | 0.0308 (3) |
| H6 | 1.0524 | 0.7780 | 0.5460 | 0.037* |

| | | | | |
|---|---|---|---|---|
| C7 | 1.13753 (10) | 0.6868 (3) | 0.61864 (9) | 0.0366 (4) |
| H7 | 1.1721 | 0.7381 | 0.5952 | 0.044* |
| C8 | 1.17121 (9) | 0.5878 (3) | 0.68320 (9) | 0.0388 (4) |
| C9 | 1.23672 (11) | 0.6637 (5) | 0.72635 (12) | 0.0609 (7) |
| H9 | 1.2568 | 0.7796 | 0.7142 | 0.073* |
| C10 | 1.27239 (13) | 0.5731 (6) | 0.78600 (13) | 0.0792 (11) |
| H10 | 1.3171 | 0.6264 | 0.8145 | 0.095* |
| C11 | 1.24474 (16) | 0.4094 (6) | 0.80465 (12) | 0.0829 (12) |
| H11 | 1.2700 | 0.3480 | 0.8461 | 0.100* |
| C12 | 1.17920 (16) | 0.3301 (5) | 0.76321 (14) | 0.0731 (8) |
| H12 | 1.1592 | 0.2155 | 0.7765 | 0.088* |
| C13 | 1.14318 (12) | 0.4205 (4) | 0.70195 (11) | 0.0517 (5) |
| H13 | 1.0990 | 0.3659 | 0.6731 | 0.062* |
| C14 | 0.69337 (8) | 0.8548 (2) | 0.48296 (8) | 0.0251 (3) |
| H14 | 0.7049 | 0.9942 | 0.4854 | 0.030* |
| C15 | 0.63586 (8) | 0.8223 (2) | 0.52455 (8) | 0.0257 (3) |
| C16 | 0.60876 (9) | 0.6424 (2) | 0.53524 (9) | 0.0308 (3) |
| H16 | 0.6271 | 0.5335 | 0.5165 | 0.037* |
| C17 | 0.55524 (9) | 0.6199 (3) | 0.57288 (9) | 0.0357 (4) |
| H17 | 0.5370 | 0.4972 | 0.5805 | 0.043* |
| C18 | 0.52962 (10) | 0.7797 (3) | 0.59865 (10) | 0.0396 (4) |
| C19 | 0.55408 (11) | 0.9604 (3) | 0.58915 (11) | 0.0439 (4) |
| H19 | 0.5348 | 1.0684 | 0.6075 | 0.053* |
| C20 | 0.60802 (10) | 0.9802 (3) | 0.55179 (9) | 0.0355 (4) |
| H20 | 0.6261 | 1.1035 | 0.5448 | 0.043* |
| C21 | 0.66394 (8) | 0.8064 (2) | 0.40760 (8) | 0.0263 (3) |
| C22 | 0.65150 (11) | 0.9551 (3) | 0.36112 (9) | 0.0367 (4) |
| H22 | 0.6645 | 1.0812 | 0.3768 | 0.044* |
| C23 | 0.62021 (12) | 0.9224 (3) | 0.29177 (10) | 0.0463 (5) |
| H23 | 0.6114 | 1.0246 | 0.2599 | 0.056* |
| C24 | 0.60250 (10) | 0.7394 (3) | 0.27056 (9) | 0.0378 (4) |
| C25 | 0.61411 (11) | 0.5880 (3) | 0.31451 (9) | 0.0401 (4) |
| H25 | 0.6013 | 0.4624 | 0.2982 | 0.048* |
| C26 | 0.64509 (11) | 0.6225 (3) | 0.38353 (9) | 0.0374 (4) |
| H26 | 0.6536 | 0.5191 | 0.4149 | 0.045* |
| Cl2 | 0.24638 (3) | 0.67703 (5) | 0.48578 (2) | 0.03563 (11) |
| Cl1 | 0.03137 (3) | 0.83990 (6) | 0.40147 (2) | 0.04480 (13) |
| O1W | 0.0000 | 1.0343 (4) | 0.2500 | 0.0721 (9) |
| H1W | 0.009 (2) | 0.965 (5) | 0.2828 (16) | 0.095 (12)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| F1 | 0.0528 (8) | 0.0800 (10) | 0.0764 (10) | 0.0008 (7) | 0.0443 (7) | −0.0034 (8) |
| F2 | 0.0648 (8) | 0.0718 (9) | 0.0270 (5) | −0.0031 (7) | −0.0032 (5) | −0.0023 (6) |
| N1 | 0.0233 (6) | 0.0167 (5) | 0.0277 (6) | −0.0048 (4) | 0.0065 (4) | −0.0019 (4) |
| N2 | 0.0232 (6) | 0.0172 (5) | 0.0252 (6) | −0.0048 (4) | 0.0057 (4) | −0.0032 (4) |
| C1 | 0.0257 (7) | 0.0268 (7) | 0.0268 (7) | −0.0042 (5) | 0.0074 (5) | 0.0011 (5) |
| C2 | 0.0268 (7) | 0.0246 (7) | 0.0242 (7) | −0.0031 (5) | 0.0059 (5) | −0.0049 (5) |
| C3 | 0.0259 (7) | 0.0326 (7) | 0.0246 (7) | −0.0066 (6) | 0.0079 (5) | −0.0016 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C4 | 0.0269 (7) | 0.0286 (7) | 0.0291 (7) | −0.0058 (6) | 0.0087 (5) | −0.0083 (6) |
| C5 | 0.0255 (7) | 0.0218 (6) | 0.0354 (8) | −0.0002 (5) | 0.0055 (6) | 0.0035 (6) |
| C6 | 0.0285 (7) | 0.0307 (7) | 0.0337 (8) | −0.0028 (6) | 0.0084 (6) | 0.0004 (6) |
| C7 | 0.0276 (8) | 0.0473 (10) | 0.0362 (9) | −0.0054 (7) | 0.0105 (6) | −0.0044 (7) |
| C8 | 0.0229 (7) | 0.0622 (12) | 0.0310 (8) | 0.0065 (7) | 0.0065 (6) | −0.0085 (8) |
| C9 | 0.0273 (9) | 0.109 (2) | 0.0442 (11) | −0.0009 (11) | 0.0045 (8) | −0.0229 (12) |
| C10 | 0.0341 (11) | 0.163 (3) | 0.0369 (12) | 0.0208 (16) | 0.0014 (9) | −0.0149 (16) |
| C11 | 0.0559 (15) | 0.161 (3) | 0.0311 (11) | 0.0581 (19) | 0.0092 (10) | 0.0130 (15) |
| C12 | 0.0650 (16) | 0.096 (2) | 0.0596 (15) | 0.0335 (15) | 0.0176 (12) | 0.0297 (15) |
| C13 | 0.0427 (11) | 0.0628 (14) | 0.0455 (11) | 0.0125 (10) | 0.0034 (8) | 0.0102 (10) |
| C14 | 0.0268 (7) | 0.0187 (6) | 0.0291 (7) | −0.0030 (5) | 0.0058 (5) | −0.0020 (5) |
| C15 | 0.0232 (6) | 0.0260 (7) | 0.0261 (7) | −0.0029 (5) | 0.0027 (5) | −0.0045 (5) |
| C16 | 0.0276 (7) | 0.0285 (7) | 0.0372 (8) | −0.0037 (6) | 0.0098 (6) | −0.0039 (6) |
| C17 | 0.0278 (8) | 0.0412 (9) | 0.0381 (9) | −0.0067 (7) | 0.0085 (6) | −0.0017 (7) |
| C18 | 0.0268 (8) | 0.0566 (11) | 0.0378 (9) | −0.0006 (8) | 0.0126 (7) | −0.0026 (8) |
| C19 | 0.0438 (10) | 0.0455 (11) | 0.0462 (11) | 0.0061 (8) | 0.0185 (8) | −0.0103 (8) |
| C20 | 0.0388 (9) | 0.0285 (8) | 0.0397 (9) | −0.0006 (7) | 0.0110 (7) | −0.0071 (7) |
| C21 | 0.0253 (7) | 0.0257 (7) | 0.0277 (7) | −0.0024 (5) | 0.0060 (5) | −0.0008 (5) |
| C22 | 0.0427 (9) | 0.0303 (8) | 0.0351 (9) | −0.0008 (7) | 0.0059 (7) | 0.0031 (7) |
| C23 | 0.0562 (12) | 0.0420 (10) | 0.0351 (9) | 0.0020 (9) | 0.0011 (8) | 0.0093 (8) |
| C24 | 0.0342 (8) | 0.0521 (11) | 0.0245 (7) | −0.0011 (8) | 0.0023 (6) | −0.0019 (7) |
| C25 | 0.0479 (10) | 0.0377 (9) | 0.0326 (9) | −0.0091 (8) | 0.0064 (7) | −0.0079 (7) |
| C26 | 0.0532 (11) | 0.0284 (8) | 0.0285 (8) | −0.0073 (7) | 0.0063 (7) | −0.0013 (6) |
| Cl2 | 0.0432 (2) | 0.01969 (17) | 0.0464 (2) | −0.00479 (15) | 0.01574 (17) | −0.00344 (15) |
| Cl1 | 0.0689 (3) | 0.02108 (18) | 0.0417 (2) | −0.01358 (19) | 0.0089 (2) | −0.00149 (15) |
| O1W | 0.137 (3) | 0.0383 (12) | 0.0386 (13) | 0.000 | 0.0176 (15) | 0.000 |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| F1—C18 | 1.354 (2) | C10—H10 | 0.9500 |
| F2—C24 | 1.360 (2) | C10—C11 | 1.346 (5) |
| N1—H1 | 0.84 (2) | C11—H11 | 0.9500 |
| N1—C1 | 1.4903 (19) | C11—C12 | 1.393 (5) |
| N1—C4 | 1.4920 (19) | C12—H12 | 0.9500 |
| N1—C5 | 1.5023 (19) | C12—C13 | 1.397 (3) |
| N2—H2 | 0.86 (3) | C13—H13 | 0.9500 |
| N2—C2 | 1.4992 (18) | C14—H14 | 1.0000 |
| N2—C3 | 1.4962 (19) | C14—C15 | 1.519 (2) |
| N2—C14 | 1.5268 (19) | C14—C21 | 1.517 (2) |
| C1—H1A | 0.9900 | C15—C16 | 1.394 (2) |
| C1—H1B | 0.9900 | C15—C20 | 1.389 (2) |
| C1—C2 | 1.515 (2) | C16—H16 | 0.9500 |
| C2—H2A | 0.9900 | C16—C17 | 1.391 (2) |
| C2—H2B | 0.9900 | C17—H17 | 0.9500 |
| C3—H3A | 0.9900 | C17—C18 | 1.368 (3) |
| C3—H3B | 0.9900 | C18—C19 | 1.374 (3) |
| C3—C4 | 1.518 (2) | C19—H19 | 0.9500 |
| C4—H4A | 0.9900 | C19—C20 | 1.391 (3) |
| C4—H4B | 0.9900 | C20—H20 | 0.9500 |
| C5—H5A | 0.9900 | C21—C22 | 1.383 (2) |

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|---|---|---|---|
| C5—H5B | 0.9900 | C21—C26 | 1.391 (2) |
| C5—C6 | 1.499 (2) | C22—H22 | 0.9500 |
| C6—H6 | 0.9500 | C22—C23 | 1.390 (3) |
| C6—C7 | 1.326 (2) | C23—H23 | 0.9500 |
| C7—H7 | 0.9500 | C23—C24 | 1.366 (3) |
| C7—C8 | 1.467 (3) | C24—C25 | 1.366 (3) |
| C8—C9 | 1.397 (3) | C25—H25 | 0.9500 |
| C8—C13 | 1.372 (3) | C25—C26 | 1.385 (2) |
| C9—H9 | 0.9500 | C26—H26 | 0.9500 |
| C9—C10 | 1.371 (4) | O1W—H1W | 0.80 (3) |

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| C1—N1—H1 | 108.0 (14) | C9—C10—H10 | 119.6 |
| C1—N1—C4 | 109.37 (11) | C11—C10—C9 | 120.7 (3) |
| C1—N1—C5 | 110.43 (12) | C11—C10—H10 | 119.6 |
| C4—N1—H1 | 111.1 (14) | C10—C11—H11 | 120.0 |
| C4—N1—C5 | 112.28 (12) | C10—C11—C12 | 120.1 (2) |
| C5—N1—H1 | 105.5 (14) | C12—C11—H11 | 120.0 |
| C2—N2—H2 | 110.0 (17) | C11—C12—H12 | 120.3 |
| C2—N2—C14 | 110.42 (11) | C11—C12—C13 | 119.4 (3) |
| C3—N2—H2 | 106.5 (17) | C13—C12—H12 | 120.3 |
| C3—N2—C2 | 108.12 (11) | C8—C13—C12 | 120.4 (2) |
| C3—N2—C14 | 111.93 (11) | C8—C13—H13 | 119.8 |
| C14—N2—H2 | 109.8 (16) | C12—C13—H13 | 119.8 |
| N1—C1—H1A | 109.6 | N2—C14—H14 | 106.6 |
| N1—C1—H1B | 109.6 | C15—C14—N2 | 110.76 (12) |
| N1—C1—C2 | 110.42 (12) | C15—C14—H14 | 106.6 |
| H1A—C1—H1B | 108.1 | C21—C14—N2 | 112.19 (12) |
| C2—C1—H1A | 109.6 | C21—C14—H14 | 106.6 |
| C2—C1—H1B | 109.6 | C21—C14—C15 | 113.49 (12) |
| N2—C2—C1 | 111.21 (12) | C16—C15—C14 | 122.98 (14) |
| N2—C2—H2A | 109.4 | C20—C15—C14 | 118.21 (14) |
| N2—C2—H2B | 109.4 | C20—C15—C16 | 118.80 (15) |
| C1—C2—H2A | 109.4 | C15—C16—H16 | 119.5 |
| C1—C2—H2B | 109.4 | C17—C16—C15 | 120.94 (16) |
| H2A—C2—H2B | 108.0 | C17—C16—H16 | 119.5 |
| N2—C3—H3A | 109.5 | C16—C17—H17 | 121.0 |
| N2—C3—H3B | 109.5 | C18—C17—C16 | 118.02 (17) |
| N2—C3—C4 | 110.88 (13) | C18—C17—H17 | 121.0 |
| H3A—C3—H3B | 108.1 | F1—C18—C17 | 118.46 (19) |
| C4—C3—H3A | 109.5 | F1—C18—C19 | 118.21 (18) |
| C4—C3—H3B | 109.5 | C17—C18—C19 | 123.32 (17) |
| N1—C4—C3 | 111.06 (12) | C18—C19—H19 | 121.1 |
| N1—C4—H4A | 109.4 | C18—C19—C20 | 117.90 (17) |
| N1—C4—H4B | 109.4 | C20—C19—H19 | 121.1 |
| C3—C4—H4A | 109.4 | C15—C20—C19 | 121.03 (17) |
| C3—C4—H4B | 109.4 | C15—C20—H20 | 119.5 |
| H4A—C4—H4B | 108.0 | C19—C20—H20 | 119.5 |
| N1—C5—H5A | 109.4 | C22—C21—C14 | 117.74 (14) |
| N1—C5—H5B | 109.4 | C22—C21—C26 | 118.70 (15) |

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| H5A—C5—H5B | 108.0 | C26—C21—C14 | 123.46 (14) |
| C6—C5—N1 | 111.30 (13) | C21—C22—H22 | 119.6 |
| C6—C5—H5A | 109.4 | C21—C22—C23 | 120.81 (17) |
| C6—C5—H5B | 109.4 | C23—C22—H22 | 119.6 |
| C5—C6—H6 | 117.7 | C22—C23—H23 | 120.8 |
| C7—C6—C5 | 124.69 (16) | C24—C23—C22 | 118.38 (17) |
| C7—C6—H6 | 117.7 | C24—C23—H23 | 120.8 |
| C6—C7—H7 | 115.9 | F2—C24—C23 | 119.28 (17) |
| C6—C7—C8 | 128.16 (17) | F2—C24—C25 | 117.85 (17) |
| C8—C7—H7 | 115.9 | C25—C24—C23 | 122.87 (17) |
| C9—C8—C7 | 118.3 (2) | C24—C25—H25 | 120.9 |
| C13—C8—C7 | 123.18 (17) | C24—C25—C26 | 118.21 (17) |
| C13—C8—C9 | 118.4 (2) | C26—C25—H25 | 120.9 |
| C8—C9—H9 | 119.6 | C21—C26—H26 | 119.5 |
| C10—C9—C8 | 120.9 (3) | C25—C26—C21 | 121.02 (17) |
| C10—C9—H9 | 119.6 | C25—C26—H26 | 119.5 |

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|---|---|---|---|
| F1—C18—C19—C20 | 178.84 (18) | C9—C10—C11—C12 | 0.0 (4) |
| F2—C24—C25—C26 | −179.58 (17) | C10—C11—C12—C13 | 0.8 (4) |
| N1—C1—C2—N2 | 59.47 (16) | C11—C12—C13—C8 | −1.1 (4) |
| N1—C5—C6—C7 | 163.61 (17) | C13—C8—C9—C10 | 0.2 (3) |
| N2—C3—C4—N1 | −58.67 (16) | C14—N2—C2—C1 | 178.60 (12) |
| N2—C14—C15—C16 | −61.46 (18) | C14—N2—C3—C4 | 179.76 (11) |
| N2—C14—C15—C20 | 119.97 (15) | C14—C15—C16—C17 | −179.06 (15) |
| N2—C14—C21—C22 | −123.12 (15) | C14—C15—C20—C19 | 178.65 (16) |
| N2—C14—C21—C26 | 60.5 (2) | C14—C21—C22—C23 | −176.00 (17) |
| C1—N1—C4—C3 | 57.27 (16) | C14—C21—C26—C25 | 176.01 (17) |
| C1—N1—C5—C6 | −168.49 (13) | C15—C14—C21—C22 | 110.39 (16) |
| C2—N2—C3—C4 | 57.92 (15) | C15—C14—C21—C26 | −65.9 (2) |
| C2—N2—C14—C15 | −57.12 (15) | C15—C16—C17—C18 | 0.5 (3) |
| C2—N2—C14—C21 | 174.93 (12) | C16—C15—C20—C19 | 0.0 (3) |
| C3—N2—C2—C1 | −58.64 (15) | C16—C17—C18—F1 | −179.29 (16) |
| C3—N2—C14—C15 | −177.63 (12) | C16—C17—C18—C19 | 0.0 (3) |
| C3—N2—C14—C21 | 54.42 (15) | C17—C18—C19—C20 | −0.5 (3) |
| C4—N1—C1—C2 | −57.40 (16) | C18—C19—C20—C15 | 0.4 (3) |
| C4—N1—C5—C6 | 69.16 (16) | C20—C15—C16—C17 | −0.5 (2) |
| C5—N1—C1—C2 | 178.55 (12) | C21—C14—C15—C16 | 65.78 (19) |
| C5—N1—C4—C3 | −179.78 (12) | C21—C14—C15—C20 | −112.80 (16) |
| C5—C6—C7—C8 | 1.9 (3) | C21—C22—C23—C24 | −0.4 (3) |
| C6—C7—C8—C9 | −141.2 (2) | C22—C21—C26—C25 | −0.3 (3) |
| C6—C7—C8—C13 | 41.5 (3) | C22—C23—C24—F2 | 179.79 (18) |
| C7—C8—C9—C10 | −177.3 (2) | C22—C23—C24—C25 | 0.1 (3) |
| C7—C8—C13—C12 | 178.0 (2) | C23—C24—C25—C26 | 0.1 (3) |
| C8—C9—C10—C11 | −0.5 (4) | C24—C25—C26—C21 | 0.0 (3) |
| C9—C8—C13—C12 | 0.7 (3) | C26—C21—C22—C23 | 0.5 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···Cl1$^{i}$ | 0.84 (2) | 2.14 (2) | 2.9782 (13) | 176 (2) |
| N2—H2···Cl2$^{ii}$ | 0.86 (3) | 2.17 (3) | 3.0248 (13) | 174 (2) |
| C1—H1*A*···O1*W*$^{i}$ | 0.99 | 2.68 | 3.512 (2) | 142 |
| C5—H5*A*···O1*W*$^{i}$ | 0.99 | 2.67 | 3.470 (2) | 138 |
| C5—H5*B*···Cl1$^{ii}$ | 0.99 | 2.51 | 3.4934 (16) | 176 |
| C14—H14···Cl2$^{i}$ | 1.00 | 2.49 | 3.4735 (15) | 168 |
| C19—H19···F2$^{iii}$ | 0.95 | 2.46 | 3.244 (2) | 140 |
| O1*W*—H1*W*···Cl1 | 0.80 (3) | 2.48 (3) | 3.2603 (12) | 163 (3) |

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