Crystal structure of (E)-3-({6-[2-(4-chlorophenyl)-ethenyl]-3-oxo-2,3-dihydropyridazin-4-yl}methyl)-pyridin-1-ium chloride dihydrate

Said Daoui, a Emine Berrin Çınar,b* Necmi Dege, b Noureddine Benchat, a Eiad Saifc* and Khalid Karrouched

aLaboratory of Applied Chemistry and Environment (LCAE), Faculty of Sciences, Mohamed I University, 60000 Oujda, Morocco, bDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, Samsun, 55200, Turkey, cDepartment of Computer and Electronic Engineering, Sana’a Community College, Sana’a, Yemen, and dLaboratory of Analytical Chemistry and Bromatology, Faculty of Medicine and Pharmacy, Mohammed V University in Rabat, Morocco.

*Correspondence e-mail: emineberrin.cinar@omu.edu.tr, eiad.saif@scc.edu.ye

In the title compound, C₁₈H₁₅ClN₃O⁺·C₁₂Cl·2H₂O, three intramolecular hydrogen bonds are observed, N—H···O, O—H···Cl and O—H···O. In the crystal, molecules are connected by C—H···Cl and N—H···O hydrogen bonds. Strong C—H···Cl, N—H···O, O—H···Cl and O—H···O hydrogen-bonding interactions are implied by the Hirshfeld surface analysis, which indicate that H···H contacts make the largest contribution to the overall crystal packing at 33.0%.

1. Chemical context

Pyridazine derivatives are an important class of heterocyclic chemicals that exhibit a wide range of biological actions. For example, their biological activity and antimicrobial properties have been researched extensively (Neumann et al., 2018). As a result, the pyridazine ring can be found in a range of commercial medicinal compounds, including Cadralazine and Hydralazine, Minaprine, Pipofezine and others (Abu-Hashem et al., 2020). Pyridazine derivatives can be found also in the backbones of several organic light-emitting diodes (OLEDs) (Liu et al., 2017), organic solar cells (OSCs) (Knall et al., 2021), chemosensors (Peng et al., 2020), trifluoroacetic acid (TFA) sensors (Li et al., 2018), bioconjugates (Bahou et al., 2021), low carbon steel corrosion inhibitors (Khadiria et al., 2016), and several other materials. They have also been used as starting materials in organic synthesis (Llona-Minguez et al., 2017), acylating agents (Kung et al., 2002), precursors for N-heterocyclic carbenes (NHCs) (Liu et al., 2012) and metallocarbene precursors. An overview of aryglyoxal monohydrates-based one-pot multi-component synthesis of potentially biologically active pyridazines is given by Mousavi (2022).

2. Structural commentary

A perspective view of the title molecule is shown in Fig. 1. The pyridazine and pyridine rings subtend a dihedral angle of 57.27 (5)°. The other two rings, pyridazine and chlorobenzene,
are almost planar, making an angle of 8.54°. The lengths of the C—C [1.349 (3) Å], C—N [1.313 (2) Å], N—N [1.351 (2) Å] and C=O [1.237 (2) Å] bonds are comparable with values published for other pyridazinones (see the Database survey section). Three intramolecular hydrogen bonds are observed, N2—H2C=C1/C1/C1O2, O2—H2A—Cl2 and O2—H2B—O3 (Table 1).

3. Supramolecular features

The water molecules and chloride anions are located in channels between the organic cations and are connected by O—H···O and O—H···Cl hydrogen bonds (Table 1) into chains, which are further connected via N—H···O and C—H···Cl hydrogen bonds into a three-dimensional supramolecular architecture. Fig. 2a shows a view of the hydrogen bonds along the b-axis direction. π–π interactions are present (Fig. 2b) between the pyridazine rings [centroid–centroid distance = 3.4902 (12) Å], and also between the pyridine and benzene rings [3.7293 (13) and 3.8488 (13) Å], forming sheets.

4. Database survey

There are no direct precedents for the structure of the title compound in the crystallographic literature. A search of the Cambridge Structural Database (ConQuest version 2021.3.0; Groom et al., 2016) for the 2,3-dihydropyridazin-4-yl moiety gave various hits, four of them for similar pyridazine compounds but with different substituents on the pyridazine ring: 5-(2-chlorobenzyl)-6-methyl-3(2H)pyridazinone (ZA YJIS; Moreau et al., 1995), 2-{4-[5-chloro-1-benzofuran-2-yl)methyl]-3-methyl-6-oxo-1,6-dihydropyridazin-1-yl}acetate (XULSEE; Boukharsa et al., 2015), 4-{3-(trifluoromethyl)phenyl]-3-methyl-6-oxo-1,6-dihydropyridazin-1-yl}acetate (XULSEE; Boukharsa et al., 2015), 5-(2-Chlorobenzyl)-2-(2-hydroxyethyl)-6-methylpyridazin-3(2H)-one (IJEYJ; Abourichaa et al., 2003). In ZA YJIS, the lengths of the C—C [1.343 (3) Å], C—N [1.301 (4) Å], N—N [1.357 (3) Å] and C—O [1.255 (3) Å] bonds in the pyridazinone ring are very similar to those in the title compound. In XULSEE, te Cl—C1 bond length is 1.742 (2) Å while in the pyridazine ring, the N1—N2 bond length is 1.365 (2) Å and O2—C2 is 1.228 (2) Å. In GISZAK, the N1—N2 bond is 1.343 (5) Å whereas the C8—O1 bond is 1.246 (5) Å. In IJEYJ, the pyridazinone ring has a similar value for the N4—N5 bond of 1.367 (2) Å.

5. Hirshfeld surface analysis

To investigate the effect of the molecular interactions on the crystal packing, the Hirshfeld surface (Fig. 3) and fingerprint plots of the organic cation were analysed (Turner et al., 2017). In Fig. 4a, the circular depressions (deep red) on the Hirshfeld surface imply strong hydrogen-bonding interactions of types C—H···Cl, N—H···O, O—H···Cl and O—H···O.
shape-index map (Fig. 4b), the \( \pi \cdots \pi \) interactions are indicated by the red and blue triangles. Fig. 4c and Fig. 4d show \( d_e \) and \( d_i \) surfaces and Fig. 4e and 4f the curvedness and fragment path surfaces. Fig. 5a shows the overall two-dimensional fingerprint plot. The fingerprint plot delineated into H\( \cdots \)H contacts (33.0% contribution, Fig. 5b) has a point with the tip at \( d_e + d_i = 2.05 \) \( \AA \). The pair of wings in the fingerprint plot defined into H\( \cdots \)C/C\( \cdots \)H contacts (19.3 percent contribution to the HS), Fig. 5c, has a pair of thin edges at \( d_e + d_i = 2.99 \) \( \AA \) while the pair of wings for the H\( \cdots \)Cl/Cl\( \cdots \)H contacts (15.9% contribution, Fig. 5d) are seen as two spikes with the points at \( d_e + d_i = 2.97 \) \( \AA \) and \( d_e + d_i = 2.41 \) \( \AA \). The fingerprint plot for H\( \cdots \)O/O\( \cdots \)H contacts (11.5% contribution, Fig. 5e) has two spikes with the tips at \( d_e + d_i = 2.11 \) \( \AA \) and \( d_e + d_i = 1.83 \) \( \AA \). As seen in Fig. 5f the C\( \cdots \)C contacts (7.4%) have an arrow-shaped distribution of points with tips at \( d_e + d_i = 3.37 \) \( \AA \). The contributions of the N\( \cdots \)H/H\( \cdots \)N contacts to the Hirshfeld surface (5.8%) are less important (Fig. 5g). Fig. 6 shows a pie chart of all interactions with their percentage contributions.

6. Synthesis and crystallization

The title compound was synthesized according to a previously published procedure (Daoui \textit{et al.}, 2019, 2021). To a solution of \( (E)-6-(4\text{-chlorostyryl})-4,5\text{-dihydropyridazin-3(2H)} \)-one
(0.23 g, 1 mmol) and nicotinaldehyde (0.107 g, 1 mmol) in 30 ml of ethanol, sodium ethanoate (0.23 g, 2.8 mmol) was added. The mixture was refluxed for 3 h. The reaction mixture was cooled, diluted with cold water and acidified with concentrated hydrochloric acid. The precipitate was filtered, washed with water, dried and recrystallized from ethanol. White single crystals were obtained by slow evaporation at room temperature, yield 86%; m.p. 453 K; FT–IR (KBr): δ 3322 (NH), 1651 (C=O), 1584 cm⁻¹ (C≡N); ¹H NMR (300 MHz, DMSO-δ) δ 13.8 (s, 1H, H-pyridyl), 8.83 (d, J = 1.8 Hz, 1H, H-pyridyl), 8.49 (d, J = 5.6 Hz, 1H, H-pyridyl), 8.57 (dt, J = 8.1, 1.8 Hz, 1H, H-pyridyl), 8.05 (s, 1H, H-pyridazinone), 7.60 (dd, J = 8.4 Hz, 2H, H1, H-Ar), 7.36 (d, J = 16.7 Hz, 1H, CH≡CH), 7.08 (d, J = 16.7 Hz, 1H, CH=CH), 4.09 ppm (s, 2H, CH₂); ¹⁳C NMR (75 MHz, DMSO-δ) δ 213.20 (C₁₀), 165.11 (C₁₁), 134.90, 132.84, 130.85, 128.82, 128.62, 128.54, 126.80, 125.08, 124.23 (C₁₂), 133.20 (C₁₃), 26.4903 (16). ESI-MS: m/z 324.08 [M+H]+.

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. All C-bound H atoms were placed in calculated positions (C—H = 0.93–0.98 Å) and thereafter treated as riding. A torsional parameter was refined for the methyl group. The positions of N- and O-bound H atoms were refined freely (distances are in Table 1). For all H atoms, U_iso(H) = 1.2 U_eq(C,N,O).

Acknowledgements

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS 2 diffractometer. The authors’ contributions are as follows. Conceptualization, SD, EBÇ, ND, and ES; methodology, KK, EBÇ, and ND; investigation, NB and ND; writing (original draft), EBÇ and SD; writing (review and editing of the manuscript), SD, NB, ES, KK and EBÇ; visualization, EBÇ and KK; funding acquisition, ND; resources, ND and KK; supervision, SD and NB.

Funding information

Funding for this research was provided by: Ondokuz Mayıs University under Project No. PYO/FEN.1906.19.001.

Table 2

| Crystal data | Chemical formula | C₁₈H₁₅ClN₃O⁺·Cl⁻·2H₂O | Mᵣ  |
|--------------|------------------|------------------------|-----|
| Crystal system, space group | Monoclinic, P2₁/a |
| Temperature (K) | 296 |
| β (°) | 109.762 (5) |
| Z | 2 |
| Radiation type | Mo Ka |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 8493, 3083 |
| R[F²] | 0.050, 0.142, 0.98 |
| No. of restraints | 2 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| Δρ_max, Δρ_min (e Å⁻³) | 0.26, −0.43 |

References

Abourichaa, S., Benchat, N., Anaflous, A., Melhaoui, A., Ben-Hadda, T., Ouassaid, B., Mimouni, M., El Bali, B. & Bolte, M. (2003). Acta Cryst. E59, o1041–o1042.
Abu-Hashem, A. A., Fatby, U. & Gouda, M. A. (2020). J. Heterocycl. Chem. 57, 3461–3474.
Bahou, C., Szijj, P. A., Spears, R. J., Wall, A., Javid, F., Sattikar, A., Love, E. A., Baker, J. R. & Chudasama, V. (2021). Bioconjugate Chem. 32, 672–679.
Boukharsa, Y., El Ammari, L., Tiaufik, J., Saadi, M. & Ansar, M. (2015). Acta Cryst. E71, o291–o292.

Daoui, S., Baydere, C., El Kalai, F., Saddik, R., Dege, N., Karrouchi, K. & Benchat, N. (2019). Acta Cryst. E75, 1734–1737.
Daoui, S., Cinar, E. B., Dege, N., Chelfi, T., El Kalai, F., Abudunia, A., Karrouchi, K. & Benchat, N. (2021). Acta Cryst. E77, 23–27.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
Farrugia, L. J. (2012). J. Appl. Cryst. 45, 849–854.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Khadiria, A., Saddik, R., Bekkouchea, K., Aouniti, A., Hammouti, B., Benchat, N., Bouachrine, M. & Solmaz, R. (2016). J. Taiwan Inst. Chem. Eng. 58, 552–564.
Knall, A. C., Rabenstein, S., Hoeffer, S. F., Reinfels, M., Hobisch, M., Ehmann, H. M. A., Pastukhova, N., Pavlica, E., Bratina, G., Honzu, I., Wen, S., Yang, R., Trimmel, G. & Rath, T. (2021). New J. Chem. 45, 1001–1009.
Kung, Y. J., Chung, H. A., Kim, J. J. & Yoon, Y. J. (2002). Synthesis, 6, 733–738.
Li, M., Yuan, Y. & Chen, Y. (2018). ACS Appl. Mater. Interfaces, 10, 1237–1243.
Li, S., Zhang, X., Ou, C., Wang, S., Yang, X., Zhou, X., Mi, B., Cao, D. & Gao, Z. (2017). ACS Appl. Mater. Interfaces, 9, 26242–26251.
Li, X. & Chen, W. (2012). Organometallics, 31, 6614–6622.
Llona-Minguez, S., Högland, A., Ghassemian, A., Desrooses, M., Calderón, J. M., Valerie, N. C. K., Witta, E., Almlof, I., Kiimmel, T., Mateus, A., Cazes-Körner, C., Sanjiv, K., Homan, E., Loseva, O., Baranczewski, P., Darabi, M., Meh dizadeh, A., Fayazi, S., Jemth, A. S., Berglund, U. W., Sigmundsson, K., Lundbäck, T., Jensen, D. & Gao, Z. (2017). ACS Appl. Mater. Interfaces, 9, 12309–12319.

Acta Cryst. (2022). E78, 458–462

Daoui et al. • C₁₈H₁₅ClN₃O⁺·Cl⁻·2H₂O 461
A. J., Artursson, P., Scobie, M. & Helleday, T. J. (2017). *Med. Chem.* **60**, 4279–4292.
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.
Moreau, S., Metin, J., Coudert, P. & Couquelet, J. (1995). *Acta Cryst.* **C51**, 1834–1836.
Mousavi, H. (2022). *J. Mol. Struct.* **1251**, 131742–131771.
Neumann, K., Gambardella, A., Lilienkampf, A. & Bradley, M. (2018). *Chem. Sci.* **9**, 7198–7203.
Peng, S., Lv, J., Liu, G., Fan, C. & Pu, S. (2020). *Tetrahedron* **76**, 131618–131627.

Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
Stoe & Cie. (2002). *X-AREA* and *X-RED32*. Stoe & Cie GmbH, Darmstadt, Germany.
Turner, M. J., MacKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer 17.5*. University of Western Australia. http://hirshfeldsurface.net.
Wang, W., Zou, X. M., Zhu, Y. Q., Hu, X. H. & Yang, H. Z. (2008). *Acta Cryst.* **E64**, o464.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Crystal structure of (E)-3-([6-[(2-(4-chlorophenyl)ethenyl)-3-oxo-2,3-dihydropyridazin-4-yl]methyl]pyridin-1-ium chloride dihydrate

Said Daoui, Emine Berrin Çınar, Necmi Dege, Noureddine Benchat, Eiad Saif and Khalid Karrouchi

Computing details

Data collection: X-AREA (Stoe & Cie, 2002); cell refinement: X-AREA (Stoe & Cie, 2002); data reduction: X-RED32 (Stoe & Cie, 2002); program(s) used to solve structure: SHELXT2018/3 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009) and Mercury (Macrae et al., 2020); software used to prepare material for publication: WinGX (Farrugia, 2012), SHELXL2018/3 (Sheldrick, 2015b), PLATON (Spek, 2020) and publCIF (Westrip, 2010).

(C)-3-((6-[2-(4-Chlorophenyl)ethenyl]-3-oxo-2,3-dihydropyridazin-4-yl)methyl)pyridin-1-ium chloride dihydrate

Crystal data

C18H15ClN3O+·Cl−·2H2O  
Mr = 396.26
Monoclinic, I2/a
a = 19.6562 (14) Å
b = 7.5587 (3) Å
c = 26.4903 (16) Å
β = 109.762 (5)°
V = 3704.0 (4) Å³
Z = 8

F(000) = 1648
Dₐ = 1.421 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 18653 reflections
θ = 1.6–30.3°
μ = 0.37 mm⁻¹
T = 296 K
Prism, colorless
0.68 × 0.41 × 0.16 mm

Data collection

Stoe IPDS 2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Plane graphite monochromator
Detector resolution: 6.67 pixels mm⁻¹
rotation method scans
Absorption correction: numerical
(X-RED32; Stoe & Cie, 2002)

T min = 0.818, T max = 0.961
13762 measured reflections
5273 independent reflections
3083 reflections with I > 2σ(I)
R int = 0.064
θ min = 29.9°, θ max = 1.6°
h = −21→27
k = −8→10
l = −36→36

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.050
wR(F²) = 0.142
S = 0.98
5273 reflections

265 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

\[ w = \frac{1}{\sigma^2(F^2_o) + (0.0709P)^2} \]
where \( P = (F^2_o + 2F^2_c)/3 \)

\[ (\Delta/\sigma)_{\text{max}} < 0.001 \]
\[ \Delta \rho_{\text{max}} = 0.26 \text{ e Å}^{-3} \]
\[ \Delta \rho_{\text{min}} = -0.43 \text{ e Å}^{-3} \]

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.

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

|    | x     | y     | z     | Uiso/Ueq |
|----|-------|-------|-------|-----------|
| Cl2| 0.43892 (4) | 0.44826 (8) | 0.29544 (2) | 0.06204 (18) |
| Cl1| 0.16095 (4) | 0.93975 (11) | 0.67565 (3) | 0.0831 (2) |
| O2 | 0.51631 (9) | 0.7860 (3) | 0.36086 (6) | 0.0569 (4) |
| O1 | 0.63332 (8) | 0.6580 (2) | 0.47656 (6) | 0.0603 (4) |
| N2 | 0.52423 (9) | 0.7727 (2) | 0.46837 (7) | 0.0440 (4) |
| N1 | 0.46811 (9) | 0.8166 (2) | 0.48443 (6) | 0.0437 (4) |
| O3 | 0.47043 (12) | 1.0366 (3) | 0.28189 (9) | 0.0724 (5) |
| N3 | 0.83161 (10) | 0.6802 (3) | 0.61940 (8) | 0.0521 (4) |
| C11| 0.58620 (10) | 0.6148 (3) | 0.54755 (7) | 0.0414 (4) |
| C9 | 0.47235 (10) | 0.7645 (3) | 0.53269 (7) | 0.0427 (4) |
| C12| 0.58492 (10) | 0.6822 (3) | 0.49587 (7) | 0.0434 (4) |
| C15| 0.71539 (10) | 0.5767 (3) | 0.61025 (7) | 0.0420 (4) |
| C6 | 0.34431 (11) | 0.8182 (3) | 0.61458 (8) | 0.0470 (5) |
| C10| 0.53148 (11) | 0.6600 (3) | 0.56490 (7) | 0.0441 (4) |
| H10| 0.5323 | 0.6223 | 0.5985 | 0.053* |
| C8 | 0.41189 (11) | 0.8140 (3) | 0.54971 (8) | 0.0477 (5) |
| H8 | 0.3747 | 0.8785 | 0.5256 | 0.057* |
| C7 | 0.40518 (11) | 0.7752 (3) | 0.59642 (8) | 0.0481 (5) |
| H7 | 0.4434 | 0.7136 | 0.6206 | 0.058* |
| C14| 0.76951 (11) | 0.6075 (3) | 0.58944 (8) | 0.0479 (5) |
| H14| 0.7626 | 0.5772 | 0.5540 | 0.057* |
| C13| 0.64570 (11) | 0.4898 (3) | 0.57732 (8) | 0.0496 (5) |
| H13A| 0.6554 | 0.4116 | 0.5515 | 0.060* |
| H13B| 0.6288 | 0.4173 | 0.6009 | 0.060* |
| C5 | 0.34973 (12) | 0.7804 (3) | 0.66698 (9) | 0.0540 (5) |
| H5 | 0.3919 | 0.7288 | 0.6898 | 0.065* |
| C16| 0.72876 (12) | 0.6223 (3) | 0.66349 (8) | 0.0514 (5) |
| H16| 0.6936 | 0.6025 | 0.6792 | 0.062* |
| C18| 0.84516 (12) | 0.7257 (3) | 0.67006 (9) | 0.0577 (5) |
| H18| 0.8892 | 0.7768 | 0.6897 | 0.069* |
| C3 | 0.23208 (13) | 0.8927 (3) | 0.65221 (9) | 0.0566 (6) |
| C2 | 0.22442 (12) | 0.9330 (3) | 0.60014 (9) | 0.0583 (6) |
| H2 | 0.1820 | 0.9840 | 0.5776 | 0.070* |
| C1 | 0.28082 (12) | 0.8966 (3) | 0.58179 (9) | 0.0561 (5) |
| Atom   | x     | y     | z     | U11   | U22   | U33   | U12   | U13   | U23   |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| H1     | 0.276 | 0.925 | 0.546 | 0.067 |       |       |       |       |       |
| C17    | 0.793 | 0.696 | 0.693 | 0.059 |       |       |       |       |       |
| H17    | 0.802 | 0.727 | 0.729 | 0.071 |       |       |       |       |       |
| C4     | 0.294 | 0.817 | 0.686 | 0.060 |       |       |       |       |       |
| H4     | 0.298 | 0.792 | 0.721 | 0.072 |       |       |       |       |       |
| H3     | 0.861 | 0.701 | 0.606 | 0.070 |       |       |       |       |       |
| H2C    | 0.520 | 0.802 | 0.436 | 0.053 |       |       |       |       |       |
| H2A    | 0.494 | 0.700 | 0.344 | 0.094 |       |       |       |       |       |
| H2B    | 0.503 | 0.874 | 0.341 | 0.079 |       |       |       |       |       |
| H3A    | 0.495 | 1.018 | 0.263 | 0.127 |       |       |       |       |       |
| H3B    | 0.466 | 1.141 | 0.284 | 0.095 |       |       |       |       |       |

Atomic displacement parameters (Å²)

| Atom       | U11     | U22     | U33     | U12     | U13     | U23     |
|------------|---------|---------|---------|---------|---------|---------|
| Cl2        | 0.0694  | 0.0648  | 0.0496  | 0.0006  | 0.0170  | 0.0021  |
| Cl1        | 0.0642  | 0.1042  | 0.0982  | −0.0103 | 0.0502  | −0.0206 |
| O2         | 0.0539  | 0.0660  | 0.0463  | −0.0028 | 0.0111  | 0.0035  |
| O1         | 0.0471  | 0.0848  | 0.0534  | 0.0146  | 0.0229  | 0.0071  |
| N2         | 0.0415  | 0.0494  | 0.0429  | 0.0012  | 0.0168  | 0.0023  |
| N1         | 0.0375  | 0.0469  | 0.0463  | 0.0001  | 0.0138  | 0.0001  |
| O3         | 0.0801  | 0.0676  | 0.0748  | 0.0046  | 0.0331  | 0.0102  |
| N3         | 0.0397  | 0.0596  | 0.0591  | 0.0003  | 0.0195  | 0.0078  |
| C11        | 0.0363  | 0.0416  | 0.0427  | −0.0032 | 0.0089  | −0.0017 |
| C9         | 0.0394  | 0.0448  | 0.0431  | −0.0026 | 0.0128  | −0.0010 |
| C12        | 0.0385  | 0.0455  | 0.0454  | −0.0018 | 0.0130  | −0.0034 |
| C15        | 0.0373  | 0.0417  | 0.0445  | 0.0049  | 0.0107  | 0.0040  |
| C6         | 0.0431  | 0.0513  | 0.0468  | −0.0051 | 0.0153  | −0.0065 |
| C10        | 0.0424  | 0.0486  | 0.0396  | −0.0033 | 0.0116  | 0.0009  |
| C8         | 0.0402  | 0.0529  | 0.0479  | 0.0024  | 0.0123  | −0.0003 |
| C7         | 0.0390  | 0.0570  | 0.0463  | 0.0018  | 0.0119  | −0.0015 |
| C14        | 0.0458  | 0.0560  | 0.0423  | 0.0039  | 0.0154  | 0.0037  |
| C13        | 0.0397  | 0.0481  | 0.0552  | 0.0008  | 0.0085  | 0.0019  |
| C5         | 0.0495  | 0.0632  | 0.0496  | −0.0041 | 0.0171  | −0.0003 |
| C16        | 0.0483  | 0.0615  | 0.0473  | 0.0002  | 0.0200  | 0.0003  |
| C18        | 0.0437  | 0.0615  | 0.0592  | −0.0045 | 0.0062  | 0.0012  |
| C3         | 0.0494  | 0.0620  | 0.0662  | −0.0148 | 0.0297  | −0.0187 |
| C2         | 0.0414  | 0.0720  | 0.0589  | −0.0006 | 0.0133  | −0.0128 |
| C1         | 0.0500  | 0.0731  | 0.0453  | 0.0025  | 0.0163  | −0.0048 |
| C17        | 0.0588  | 0.0703  | 0.0449  | −0.0028 | 0.0125  | −0.0049 |
| C4         | 0.0611  | 0.0736  | 0.0527  | −0.0123 | 0.0290  | −0.0046 |

Geometric parameters (Å, °)

| Bond            | Length (Å) | Angle (°) |
|-----------------|------------|-----------|
| Cl1—C3          | 1.748 (2)  | C6—C1    | 1.389 (3) |
| O2—H2A          | 0.825 (18) | C6—C7    | 1.469 (3) |
| O2—H2B          | 0.837 (18) | C10—H10  | 0.9300    |
| O1—C12          | 1.237 (2)  | C8—C7    | 1.321 (3) |
N2—N1          1.351 (2) C8—H8          0.9300
N2—C12         1.354 (3) C7—H7          0.9300
N2—H2C         0.86 (2)  C14—H14        0.9300
N1—C9          1.313 (2) C13—H13A       0.9700
O3—H3A         0.81 (5)  C13—H13B       0.9700
O3—H3B         0.80 (4)  C5—C4           1.382 (3)
N3—C18         1.322 (3) C5—H5           0.9300
N3—C14         1.329 (3) C16—C17        1.376 (3)
N3—H3          0.80 (3)  C16—H16        0.9300
C11—C10        1.349 (3) C18—C17        1.361 (3)
C11—C12        1.453 (3) C18—H18        0.9300
C11—C13        1.503 (3) C3—C4           1.369 (4)
C9—C10         1.426 (3)  C3—C2           1.370 (3)
C9—C8          1.455 (3)  C2—C1           1.380 (3)
C15—C14        1.373 (3)  C2—H2           0.9300
C15—C16        1.388 (3)  C1—H1           0.9300
C15—C13        1.504 (3)  C17—H17         0.9300
C6—C5          1.386 (3)  C4—H4            0.9300

H2A—O2—H2B     107 (3)  N3—C14—C15       120.65 (18)
N1—N2—C12      128.25 (16) N3—C14—H14      119.7
N1—N2—H2C      116.0 (16) C15—C14—H14    119.7
C12—N2—H2C     115.7 (16)  C11—C13—C15    115.12 (17)
C9—N1—N2       116.31 (16) C11—C13—H13A   108.5
H3A—O3—H3B     109 (4)  C15—C13—H13A   108.5
C18—N3—C14     122.87 (19) C11—C13—H13B   108.5
C18—N3—H3      118 (2)  C15—C13—H13B   108.5
C14—N3—H3      119 (2)  H13A—C13—H13B  107.5
C10—C11—C12    118.06 (18) C4—C5—C6       121.6 (2)
C10—C11—C13    123.32 (18) C4—C5—H5       119.2
C12—C11—C13    118.51 (17) C6—C5—H5       119.2
N1—C9—C10      121.28 (17) C17—C16—C15   120.08 (19)
N1—C9—C8       115.79 (17) C17—C16—H16    120.0
C10—C9—C8      122.88 (17) C15—C16—H16    120.0
O1—C12—N2      120.86 (17) N3—C18—C17    119.2 (2)
O1—C12—C11     124.57 (18) N3—C18—H18    120.4
N2—C12—C11     114.55 (16) C17—C18—H18    120.4
C14—C15—C16    117.37 (19) C4—C3—C2       121.6 (2)
C14—C15—C13    121.23 (17) C4—C3—C11      119.49 (17)
C16—C15—C13    121.36 (18) C2—C3—C11      118.91 (19)
C5—C6—C1       117.58 (18) C3—C2—C1       118.8 (2)
C5—C6—C7       119.16 (19) C3—C2—H2       120.6
C1—C6—C7       123.26 (18) C1—C2—H2       120.6
C11—C10—C9     121.28 (17) C2—C1—C6       121.6 (2)
C11—C10—H10    119.4     C2—C1—H1       119.2
C9—C10—H10     119.4     C6—C1—H1       119.2
C7—C8—C9       125.74 (19) C18—C17—C16   119.8 (2)
C7—C8—H8       117.1     C18—C17—H17   120.1
C9—C8—H8  117.1  C16—C17—H17  120.1
C8—C7—C6  127.5 (2)  C3—C4—C5  118.8 (2)
C8—C7—H7  116.3  C3—C4—H4  120.6
C6—C7—H7  116.3  C5—C4—H4  120.6

C12—N2—N1—C9  −0.4 (3)  C13—C15—C14—N3  −178.22 (19)
N2—N1—C9—C10  −3.0 (3)  C10—C11—C13—C15  −100.2 (2)
N2—N1—C9—C8   179.47 (17)  C12—C11—C13—C15  83.7 (2)
N1—N2—C12—O1   −177.03 (19)  C14—C15—C13—C11  −92.5 (2)
N1—N2—C12—C11  4.6 (3)  C16—C15—C13—C11  90.2 (2)
C10—C11—C12—C11  176.3 (2)  C1—C6—C5—C4  0.5 (3)
C13—C11—C12—O1  −7.4 (3)  C7—C6—C5—C4  −179.8 (2)
C10—C11—C12—N2  −5.4 (3)  C14—C15—C16—C17  0.6 (3)
C13—C11—C12—N2  170.88 (18)  C13—C15—C16—C17  178.0 (2)
C12—C11—C10—C9   2.6 (3)  C14—N3—C18—C17  0.3 (4)
C13—C11—C10—C9  −173.49 (19)  C4—C3—C2—C1  0.0 (4)
N1—C9—C10—C11  1.8 (3)  C11—C3—C2—C1  179.66 (18)
C8—C9—C10—C11  179.15 (19)  C3—C2—C1—C6  0.9 (4)
N1—C9—C8—C7  179.9 (2)  C5—C6—C1—C2  −1.1 (3)
C10—C9—C8—C7  2.5 (3)  C7—C6—C1—C2  179.2 (2)
C9—C8—C7—C6  −174.2 (2)  N3—C18—C17—C16  −0.5 (4)
C5—C6—C7—C8  −174.2 (2)  C15—C16—C17—C18  0.0 (4)
C1—C6—C7—C8  5.4 (4)  C2—C3—C4—C5  −0.5 (4)
C18—N3—C14—C15  0.3 (3)  C11—C3—C4—C5  179.77 (19)
C16—C15—C14—N3  −0.8 (3)  C6—C5—C4—C3  0.3 (4)

Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H  | H···A  | D···A   | D—H···A |
|-----------|-------|--------|---------|---------|
| C10—H10···Cl2" | 0.93  | 2.72   | 3.6387 (19) | 168     |
| C18—H18···Cl2" | 0.93  | 2.94   | 3.622 (2)   | 132     |
| N3—H3···O2"   | 0.80 (3) | 2.35 (3) | 2.965 (2)   | 135 (2) |
| N3—H3···O1"   | 0.80 (3) | 2.25 (3) | 2.855 (2)   | 133 (3) |
| N2—H2C···O2   | 0.86 (2) | 1.97 (2) | 2.801 (2)   | 161 (2) |
| O2—H2A···Cl2  | 0.83 (2) | 2.35 (2) | 3.170 (2)   | 175 (3) |
| O2—H2B···O3   | 0.84 (2) | 1.92 (2) | 2.739 (3)   | 167 (3) |

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