In the title compound, C\textsubscript{17}H\textsubscript{14}Cl\textsubscript{2}N\textsubscript{4}, the dihedral angle between the aromatic rings is 50.09 (9)°. The central –N=N– unit shows an E configuration. In the crystal, C–H···N interactions, C–Cl···π and π–π stacking interactions [centroid-to-centroid distance = 3.7719 (14) Å] link the molecules, forming molecular layers approximately parallel to the (002) plane. Additional weak van der Waals interactions between the layers consolidate the three-dimensional packing. Hirshfeld surface analysis indicates that the most important contributions for the crystal packing are from H···H (33.6%), N···H/ H···N (17.2%), Cl···H/H···Cl (14.1%) and C···H/H···C (14.1%) contacts.

1. Chemical context

Azo dyes find numerous applications in a diversity of areas, including in molecular recognition, optical data storage, nonlinear optics and as molecular switches, antimicrobial agents, colour-changing materials, liquid crystals, dye-sensitized solar cells, mainly because of the ability for cis-to-trans isomerization and the chromophoric properties of the –N=N– synthon (Maharramov et al., 2018; Viswanathan et al., 2019). Not only isomerization, but azo-hydrazone tautomerism is also an important phenomenon in the coordination chemistry of azo dyes (Mahmoudi et al., 2018a, b). Modification of azo dyes with functional groups leads to multifunctional ligands, of which the corresponding metal complexes are effective catalysts in oxidation and in C–C coupling reactions (Ma et al., 2020, 2021; Mahmudov et al., 2013; Mizar et al., 2012). Moreover, the functional properties of azo dyes are dependent on non-covalent bond-donor or -acceptor site(s) attached to the –N=N– synthon (Gurbanov et al., 2020a, b; Kopylovich et al., 2011; Mahmudov et al., 2020; Shixaliyev et al., 2014). Thus, we have introduced halogen-bond-donor centres to the –N=N– moiety, leading to a new azo dye, (E)-4-((2,2-dichloro-1-[4-(dimethylamino)phenyl]ethenyl)diazenyl)benzonitrile, which provides multiple intermolecular non-covalent interactions.

2. Structural commentary

The aromatic rings C3–C8 and C11–C16 of the title compound (Fig. 1) form a dihedral angle of 50.09 (9)°. In the dimethyl-
amino group, the sum of bond angles about N3 is 357.02° and the nitrogen atom has a flattened trigonal–pyramidal conformation. The atoms of the dimethylamino group and those of its attached benzene ring (C3–C8) are nearly coplanar, with maximum deviations of 0.058 (2), 0.179 (2), and 0.087 (2) Å for N3, C9 and C10, respectively. The title molecule adopts an E configuration with respect to the N1
N2 bond. The N1/N2/C1–C3/Cl1/Cl2 unit is approximately planar with a maximum deviation of 0.102 (2) Å, and makes dihedral angles of 55.44 (9) and 5.36 (9)°, respectively, with the C3–C8 and C11–C16 benzene rings.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, molecules are linked by C—H···N interactions (Table 1), C—H···π [C12···Cg2ii] = 3.3910 (12) Å, C2···Cg2ii = 3.858 (2) Å, C2–Cl2···Cg2ii = 92.07 (7)°; symmetry code: (ii) x, 1 + y, z; where Cg2 is the centroid of the C11–C16 benzene ring] and π···π stacking interactions [Cg2···Cg1iii = 3.7719 (14) Å, slippage = 1.741 Å; Cg1···Cg2iv = 3.7719 (14) Å, slippage = 1.336 Å; symmetry codes: (iii) ½ – x, ½ – y, ½ – z; (iv) ½ – x, ½ + y, ½ – z; where Cg1 and Cg2 are the

Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level.

Figure 2
A general view of the C—H···N contacts, C—Cl···π interactions and π···π stacking interactions in the crystal packing of the title compound [symmetry codes: (a) –1 + x, y, z; (b) –1 + x, 1 + y, z; (c) x, 1 + y, z; (d) ½ – x, ½ + y, ½ – z; (e) ½ – x, ½ + y, ½ + z; (f) ½ – x, –½ + y, ½ – z; (g) ½ – x, ½ + y, ½ – z].

Figure 3
The crystal packing of the title compound, viewed along the a axis, showing the C—Cl···π interactions and π···π stacking interactions as dashed lines.

| Bond angle (°) | Table 1 Hydrogen-bond geometry (Å, °). |
|---------------|---------------------------------------|
| H1···N4       | 357.02                                |
| H···A         | 179                                   |
| C1···C9       | 92.07                                 |

Symmetry code: (i) –x + ½, y + ½, –z + ½.
centroids of the C3—C8 and C11–C16 benzene rings, respectively, forming molecular layers approximately parallel to the (002) plane with the molecules having a bellows-like shape when viewed along the \( a \) axis (Figs. 2 and 3). Weak van der Waals interactions between these layers increase the stability of the crystal structure.

Table 2
Summary of short interatomic contacts (\( \text{Å} \)) in the title compound.

| Contact     | Distance | Symmetry operation |
|-------------|----------|--------------------|
| Cl1···H4    | 2.86     | \( x, 1 + y, z \)  |
| Cl2···Cl1   | 3.60     | \( 2 - x, 3 - y, 1 - z \) |
| H9C···C7    | 2.95     | \( 1 - x, 2 - y, 1 - z \) |
| Cl2···H10B  | 3.01     | \( 1 + x, y, z \)   |
| C2···C2     | 3.47     | \( 2 - x, 2 - y, 1 - z \) |
| N4···H13    | 2.48     | \( \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z \) |
| N4···H7     | 2.70     | \( \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z \) |

To visualize the intermolecular interactions in the title molecule, CrystalExplorer17 (Turner et al., 2017) was used to compute Hirshfeld surfaces (McKinnon et al., 2007) and their corresponding two-dimensional fingerprint plots (Spackman & McKinnon, 2002). The Hirshfeld surface mapped over electrostatic potential (Spackman et al., 2008) is shown in Fig. 4. The positive electrostatic potential (blue region) over the surface indicates hydrogen-bond donors, whereas the hydrogen-bond acceptors are represented by a negative electrostatic potential (red region). In the Hirshfeld surface mapped over \( d_{\text{norm}} \) (Fig. 5), the bright-red spots near atoms H7, H13, N4 and Cl1 indicate the short C—H···Cl and C—H···N intermolecular contacts (Table 2). Other contacts are equal to or longer than the sum of van der Waals radii. The most important interaction is H···H, contributing 33.6% to the overall crystal packing, which is reflected in Fig. 6b as widely scattered
Table 3
Percentage contributions of interatomic contacts to the Hirshfeld surface for the title compound.

| Contact | Percentage contribution |
|---------|-------------------------|
| H··H   | 33.6                    |
| N··H/H··N | 17.2                |
| Cl··Cl | 14.1                    |
| C··C   | 14.1                    |
| Cl··C  | 6.7                     |
| Cl··Cl | 3.5                    |
| Cl··N  | 2.5                     |
| N··C   | 1.9                     |
| N··N   | 0.1                     |

points of high density due to the large hydrogen content of the molecule, with the tip at $d_c = d_l = 1.15$ Å. The reciprocal N··H/H··N interactions appear as two symmetrical broad wings with $d_c + d_l = 2.3$ Å and contribute 17.2% to the Hirshfeld surface (Fig. 6c). The reciprocal Cl··H/H··Cl interactions (14.1% contribution) are present as two symmetrical broad wings with $d_c + d_l = 2.7$ Å (Fig. 6d). The pair of characteristic wings in the fingerprint plot delineated into H··C/C··H contacts (Fig. 6e; 14.1% contribution) have the tips at $d_c + d_l = 2.8$ Å. The smaller percentage contributions to the Hirshfeld surface from the various other interatomic contact are comparatively listed in Table 3.

4. Database survey
A search of the Cambridge Structural Database (CSD, Version 5.40, update November 2018; Groom et al., 2016) for structures having an (E)-1-(2,2-dichloro-1-phenylethenyl)-2-phenyl diazene unit gave 25 hits. Six compounds closely resemble the title compound, viz. 4-(2,2-dichloro-1-[(E)-2-(4-methylphenyl)diazien-1-yl]ethenyl)-N,N-dimethylaniline [(I); Özkaraca et al., 2020], 4-(2,2-dichloro-1-[(E)-2-(4-fluorophenyl)diazilenyl]ethenyl)-N,N-dimethylaniline [(II); Özkaraca et al., 2020], 1-[(chlorophenyl)-2-[2,2-dichloro-1-(4-fluorophenyl)ethenyl]diazene [(III); Shikhaliyev et al., 2019], 1-(4-bromophenyl)-2-[2,2-dichloro-1-(4-nitrophenylethenyl)diazene [(IV); Akkurt et al., 2019], 1-(4-chlorophenyl)-2-[2,2-dichloro-1-(4-nitro phenylethenyl)diazene [(V); Akkurt et al., 2019] and 1-[2,2-dichloro-1-(4-nitrophenylethenyl]2-(4-fluorophenyl)diazene [(VI); Atioğlu et al., 2019].

In the crystal of (I), molecules are linked by pairs of C—Cl···π interactions, forming inversion dimers. A short intermolecular Cl···Cl contact [3.2555 (9) Å] links the dimers, forming a ribbon along the $c$ direction of the axis. The crystal structure of (II) is stabilized by C—Cl···π and van der Waals interactions. In (III), molecules are stacked in columns along the $a$ axis via weak C—H···Cl hydrogen bonds and face-to-face π···π stacking interactions. The packing is further stabilized by short Cl···Cl contacts. In the crystals of (IV) and (V), molecules are linked through weak X···Cl contacts [$X = Br$ for (IV) and Cl for (V)] and C—H···Cl and C—Cl···π interactions into sheets parallel to the $ab$ plane. In (VI), molecules are linked by C—H···O hydrogen bonds into zigzag chains running along the $c$-axis direction. The crystal packing is further stabilized by C—Cl···π, C—F···π and N—O···π interactions.

5. Synthesis and crystallization
The title compound was synthesized according to a reported method (Shikhaliyev et al., 2018, 2019). A 20 mL screw-neck vial was charged with DMSO (10 mL), (Z)-4-[2-[4-(dimethylamino)benzylidene]hydrazinyl]benzonitrile (264 mg, 1 mmol), tetramethylethlenediamine (TMEDA) (295 mg, 2.5 mmol), CuCl (2 mg, 0.02 mmol) and CCl₄ (20 mmol, 1 equiv). After 1–3 h (until TLC analysis showed complete consumption of the corresponding Schiff base), the reaction mixture was poured into ~0.01 M solution of HCl (100 mL, pH = 2–3), and extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with water (3 × 50 mL) and brine (30 mL), dried over anhydrous Na₂SO₄ and concentrated using a vacuum rotary evaporator. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and dichloromethane (3/1–1/1). Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution. Colourless solid (69%); m.p. 395 K. Analysis calculated for C₁₇H₁₄Cl₂N₄: C 59.15, H 4.02, N 16.19%. 1HN M R (75 MHz, CDCl₃) δ 2.30/2.36, 7.24/7.30/7.38 (1H, Me₃).
6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The C-bound H atoms were positioned geometrically and treated as riding atoms, C—H = 0.95 Å with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms and C—H = 0.98 Å with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.

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References

Akkurt, M., Shikhaliyev, N. Q., Suleymanova, G. T., Babayeva, G. V., Mammadova, G. Z., Niyazova, A. A., Shikhaliyeva, I. M. & Toze, F. A. A. (2019). Acta Cryst. E75, 1199–1204.

Atioglu, Z., Akkurt, M., Shikhaliyev, N. Q., Bagirova, K. N. & Toze, F. A. A. (2019). Acta Cryst. E75, 237–241.

Battye, T. G. G., Kontogiannis, L., Johnson, O., Powell, H. R. & Leslie, A. G. W. (2011). Acta Cryst. D67, 271–281.

Doyle, R. A. (2011). Marced software manual. Rayonix LLC, Evanston, IL 60201, USA.

Evans, P. (2006). Acta Cryst. D62, 72–82.

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.

Gurbanov, A. V., Kuznetsov, M. L., Demukhamedova, S. D., Alieva, I. N., Godjaev, N. M., Zubkov, F. I., Mahmudov, K. T. & Pomeirio, A. J. L. (2020). Coord. Chem. Rev.

Gurbanov, A. V., Kuznetsov, M. L., Mahmudov, K. T., Pomeirio, A. J. L. & Resnati, G. (2020b). Chem. Eur. J. 26, 14833–14837.

Kopylovich, M. N., Mahmudov, K. T., Mizar, A. & Pomeirio, A. J. L. (2011). Coord. Chem. Rev. 47, 7248–7250.

Ma, Z., Mahmudov, K. T., Aliyeva, V. A., Gurbanov, A. V., Guedes da Silva, M. F. C. & Pomeirio, A. J. L. (2021). Coord. Chem. Rev. 437, 213859.

Ma, Z., Mahmudov, K. T., Aliyeva, V. A., Gurbanov, A. V. & Pomeirio, A. J. L. (2020). Coord. Chem. Rev. 423, 213842.

Maharramov, A. M., Shikhaliyev, N. Q., Suleymanova, G. T., Gurbanov, A. V., Babayeva, G. V., Mammadova, G. Z., Zubkov, F. I., Nenajdenko, V. G., Mahmudov, K. T. & Pomeirio, A. J. L. (2018). Dyes Pigments, 159, 135–141.

Mahmoudi, G., Afkhami, F. A., Castiñeiras, A., Garcia-Santos, I., Gurbanov, A., Zubkov, F. I., Mitoraj, M. P., Kukulkka, M., Sagan, F., Szczepanik, D. W., Konyaeva, I. A. & Safin, D. A. (2018a). Inorg. Chem. 57, 4395–4408.

Mahmoudi, G., Zangrando, E., Mitoraj, M. P., Gurbanov, A. V., Zubkov, F. I., Moosavifar, M., Konyaeva, I. A., Kirillov, A. M. & Safin, D. A. (2018b). New J. Chem. 42, 4959–4971.

Mahmudov, K. T., Gurbanov, A. V., Aliyeva, V. A., Resnati, G. & Pomeirio, A. J. L. (2020). Coord. Chem. Rev. 418, 213381.

Mahmudov, K. T., Kopylovich, M. N., Haukka, M., Mahmudova, G. S., Esmaeila, E. F., Chyragov, F. M. & Pomeirio, A. J. L. (2013). J. Mol. Struct. 1048, 108–112.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). Chem. Commun. pp. 3814–3816.

Mizar, A., Guedes da Silva, M. F. C., Kopylovich, M. N., Mukherjee, S., Mahmudov, K. T. & Pomeirio, A. J. L. (2012). Eur. J. Inorg. Chem. pp. 2305–2313.

Ozkaraç, K., Akkurt, M., Shikhaliyev, N. Q., Askerova, U. F., Suleymanova, G. T., Shikhaliyev, I. M. & Bhattarai, A. (2020). Acta Cryst. E76, 811–815.

Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.

Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.

Shikhaliyev, N. Q., Ahmadova, N. E., Gurbanov, A. V., Maharramov, A. M., Mammadova, G. Z., Nenajdenko, V. G., Zubkov, F. I., Mahmudov, K. T. & Pomeirio, A. J. L. (2018). Dyes Pigments, 150, 377–381.

Shikhaliyev, N. Q., Celikesir, S. T., Akkurt, M., Bagirova, K. N., Suleymanova, G. T. & Toze, F. A. A. (2019). Acta Cryst. E75, 465–469.

Shikhaliyev, N. Q., Kuznetsov, M. L., Maharramov, A. M., Gurbanov, A. V., Ahmadova, N. E., Nenajdenko, V. G., Mahmudov, K. T. & Pomeirio, A. J. L. (2019). CrystEngComm, 21, 5032–5038.

Shikhaliyev, N. Q., Gurbanov, A. V., Maharramov, A. M., Mahmudov, K. T., Kopylovich, M. N., Martins, L. M. D. R. S., Muzalevskiy, V. M., Nenajdenko, V. G. & Pomeirio, A. J. L. (2014). New J. Chem. 38, 4807–4815.

Spackman, M. A. & McKinnon, J. J. (2002). Coord. Chem. Rev. 213, 75–82.

Spackman, M. A. & McKinnon, J. J. (2008). Coord. Chem. Rev. 252, 1483–14837.

Spackman, M. A., McKinnon, J. J. & Jayatilaka, D. (2008). Coord. Chem. Rev. 252, 14833–14837.

Spek, A. L. (2020). Acta Cryst. E76, 1–11.

Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). CrystalExplorer17. The University of Western Australia.

Viswanathan, A., Kute, D., Musa, A., Mani, S. K., Sipliä, V., Emmert-Streib, F., Zubkov, F. I., Gurbanov, A. V., Yli-Harja, O. & Kandhavelu, M. (2019). Eur. J. Med. Chem. 166, 291–303.
Crystal structure and Hirshfeld surface analysis of (E)-4-({2,2-dichloro-1-[4-(dimethylamino)phenyl]ethenyl}diazenyl)benzonitrile

Namiq Q. Shikhaliyev, Zeliha Atioğlu, Mehmet Akkurt, Gulnar T. Suleymanova, Gulnare V. Babayeva and Sixberth Mlowe

Computing details

Data collection: Marcdd (Doyle, 2011); cell refinement: iMosflm (Battye et al., 2011); data reduction: iMosflm (Battye et al., 2011); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2020).

(E)-4-({2,2-Dichloro-1-[4-(dimethylamino)phenyl]ethenyl}diazenyl)benzonitrile

Crystal data

C_{17}H_{14}Cl_{2}N_{4}  

$\rho = 1.409$ Mg m$^{-3}$  

Monoclinic, $P2_{1}/n$  

$V = 1627.1$ (5) Å$^3$  

$Z = 4$

Data collection

Rayonix SX165 CCD diffractometer  

Absorption correction: multi-scan  

$R_{min} = 0.939, R_{max} = 0.966$  

21540 measured reflections  

Data collection

Refinement

Refinement on $F^2$  

Least-squares matrix: full  

$R[F^2 > 2\sigma(F^2)] = 0.040$  

$wR(F^2) = 0.110$  

$S = 1.06$  

3712 reflections  

211 parameters  

0 restraints  

$F(000) = 712$  

Cell parameters from 600 reflections  

$\theta = 2.0$–28.0°  

$\mu = 0.54$ mm$^{-1}$  

$T = 100$ K  

Prism, colourless  

0.10 × 0.08 × 0.05 mm  

Primary atom site location: difference Fourier map  

Secondary atom site location: difference Fourier map  

Hydrogen site location: inferred from neighbouring sites  

H-atom parameters constrained  

$w = 1/[\sigma^2(F_c^2) + (0.0535P)^2 + 0.5596P]$  

where $P = (F_c^2 + 2F_e^2)/3$
(\Delta/\sigma)_{\text{max}} < 0.001
\Delta\rho_{\text{max}} = 0.34 \text{ e} \text{ Å}^{-3}
\Delta\rho_{\text{min}} = -0.36 \text{ e} \text{ Å}^{-3}

Extinction correction: SHELXL,
\[ F_c^* = k F_c [1 + 0.001 x F_c^2 / \sin(2\theta)]^{1/4} \]
Extinction coefficient: 0.0082 (8)

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          | U_{iso}*/U_{eq} |
|-------|------------|------------|------------|-----------------|
| Cl1   | 0.88106 (4)| 1.32286 (7)| 0.48668 (2)| 0.03392 (14)    |
| Cl2   | 1.05932 (4)| 1.18867 (7)| 0.43125 (2)| 0.03201 (14)    |
| N1    | 0.91524 (13)| 0.8624 (3)| 0.37007 (8)| 0.0292 (3)      |
| N2    | 0.85729 (13)| 0.7167 (3)| 0.33932 (8)| 0.0300 (3)      |
| N3    | 0.40040 (13)| 0.8913 (3)| 0.40216 (9)| 0.0380 (4)      |
| N4    | 1.13398 (14)| -0.0162 (3)| 0.21331 (9)| 0.0398 (4)      |
| C1    | 0.85825 (15)| 0.9987 (3)| 0.40327 (9)| 0.0284 (4)      |
| C2    | 0.92392 (15)| 1.1508 (3)| 0.43572 (9)| 0.0295 (4)      |
| C3    | 0.73981 (15)| 0.9728 (3)| 0.40425 (9)| 0.0291 (4)      |
| C4    | 0.70143 (15)| 0.7904 (3)| 0.42580 (9)| 0.0310 (4)      |
| H4    | 0.7525      | 0.6816     | 0.4404     | 0.037*          |
| C5    | 0.59082 (16)| 0.7638 (3)| 0.42649 (10)| 0.0330 (4)    |
| H5    | 0.5678      | 0.6384     | 0.4421     | 0.040*          |
| C6    | 0.51174 (15)| 0.9206 (3)| 0.40439 (9)| 0.0310 (4)      |
| C7    | 0.55024 (15)| 1.1054 (3)| 0.38262 (9)| 0.0312 (4)      |
| H7    | 0.4994      | 1.2145     | 0.3678     | 0.037*          |
| C8    | 0.66197 (15)| 1.1295 (3)| 0.38267 (9)| 0.0294 (4)      |
| H8    | 0.6859      | 1.2551     | 0.3677     | 0.035*          |
| C9    | 0.36642 (18)| 0.7158 (4)| 0.43561 (12)| 0.0434 (5)    |
| H9A   | 0.3835      | 0.5892     | 0.4148     | 0.065*          |
| H9B   | 0.2862      | 0.7231     | 0.4319     | 0.065*          |
| H9C   | 0.4067      | 0.7169     | 0.4826     | 0.065*          |
| C10   | 0.32281 (16)| 1.0620 (4)| 0.38642 (11)| 0.0410 (5)    |
| H10A  | 0.3390      | 1.1609     | 0.4231     | 0.061*          |
| H10B  | 0.2465      | 1.0113     | 0.3800     | 0.061*          |
| H10C  | 0.3307      | 1.1290     | 0.3456     | 0.061*          |
| C11   | 0.92081 (15)| 0.5780 (3)| 0.30993 (9)| 0.0291 (4)      |
| C12   | 1.03445 (15)| 0.6030 (3)| 0.31285 (9)| 0.0315 (4)      |
| H12   | 1.0731      | 0.7214     | 0.3330     | 0.038*          |
| C13   | 1.08971 (15)| 0.4540 (3)| 0.28610 (9)| 0.0318 (4)      |
| H13   | 1.1666      | 0.4692     | 0.2878     | 0.038*          |
| C14   | 1.03148 (15)| 0.2803 (3)| 0.25645 (9)| 0.0297 (4)      |
| C15   | 0.91773 (15)| 0.2583 (3)| 0.25146 (9)| 0.0308 (4)      |
| H15   | 0.8784      | 0.1423     | 0.2299     | 0.037*          |
| C16   | 0.86290 (15)| 0.4084 (3)| 0.27846 (9)| 0.0308 (4)      |
| H16   | 0.7855      | 0.3952     | 0.2754     | 0.037*          |
### Atomic displacement parameters (Å²)

|     | \(U_{11}\) | \(U_{22}\) | \(U_{33}\) | \(U_{12}\) | \(U_{13}\) | \(U_{23}\) |
|-----|------------|------------|------------|------------|------------|------------|
| Cl1 | 0.0306 (2) | 0.0350 (3) | 0.0359 (3) | 0.00155 (18)| 0.00763 (19)| −0.00490 (19)|
| Cl2 | 0.0255 (2) | 0.0375 (3) | 0.0326 (2) | −0.00150 (18)| 0.00657 (17)| 0.00029 (19) |
| N1  | 0.0276 (7) | 0.0326 (9) | 0.0261 (8) | 0.0018 (6)  | 0.0045 (6)  | 0.0004 (6)  |
| N2  | 0.0254 (7) | 0.0358 (9) | 0.0275 (8) | 0.0029 (6)  | 0.0043 (6)  | −0.0011 (7) |
| N3  | 0.0275 (8) | 0.0428 (10)| 0.0457 (10)| 0.0004 (7)  | 0.0126 (7)  | 0.0039 (8)  |
| N4  | 0.0316 (8) | 0.0444 (11)| 0.0441 (10)| 0.0004 (8)  | 0.0109 (7)  | −0.0063 (8) |
| C1  | 0.0270 (9) | 0.0323 (10)| 0.0254 (9) | 0.0026 (7)  | 0.0055 (7)  | 0.0026 (7)  |
| C2  | 0.0257 (9) | 0.0348 (10)| 0.0272 (9) | 0.0036 (7)  | 0.0052 (7)  | 0.0033 (7)  |
| C3  | 0.0271 (9) | 0.0333 (10)| 0.0261 (9) | 0.0017 (7)  | 0.0051 (7)  | −0.0007 (7)|
| C4  | 0.0284 (9) | 0.0334 (11)| 0.0300 (9) | 0.0034 (7)  | 0.0049 (7)  | 0.0010 (8)  |
| C5  | 0.0313 (9) | 0.0375 (11)| 0.0304 (10)| −0.0013 (8) | 0.0081 (8)  | 0.0007 (8)  |
| C6  | 0.0258 (9) | 0.0384 (11)| 0.0289 (9) | −0.0008 (8) | 0.0071 (7)  | −0.0017 (8) |
| C7  | 0.0276 (9) | 0.0352 (10)| 0.0301 (9) | 0.0048 (8)  | 0.0062 (7)  | −0.0010 (8)|
| C8  | 0.0269 (9) | 0.0326 (10)| 0.0277 (9) | 0.0013 (7)  | 0.0053 (7)  | 0.0000 (8)  |
| C9  | 0.0360 (11)| 0.0539 (14)| 0.0430 (12)| −0.0065 (10)| 0.0153 (9)  | 0.0035 (10)|
| C10 | 0.0251 (9) | 0.0503 (13)| 0.0475 (12)| 0.0022 (9)  | 0.0089 (8)  | −0.0047 (10)|
| C11 | 0.0258 (9) | 0.0345 (11)| 0.0264 (9) | 0.0030 (7)  | 0.0052 (7)  | 0.0024 (8)  |
| C12 | 0.0266 (9) | 0.0347 (10)| 0.0326 (10)| −0.0018 (8) | 0.0064 (7)  | 0.0001 (8)  |
| C13 | 0.0255 (9) | 0.0388 (11)| 0.0317 (10)| −0.0001 (8) | 0.0085 (7)  | 0.0016 (8)  |
| C14 | 0.0271 (9) | 0.0364 (11)| 0.0258 (9) | 0.0020 (7)  | 0.0069 (7)  | 0.0010 (8)  |
| C15 | 0.0274 (9) | 0.0355 (10)| 0.0287 (9) | −0.0008 (8) | 0.0057 (7)  | 0.0000 (8)  |
| C16 | 0.0231 (8) | 0.0403 (11)| 0.0283 (9) | −0.0002 (8) | 0.0052 (7)  | −0.0014 (8) |
| C17 | 0.0267 (9) | 0.0405 (11)| 0.0311 (9) | −0.0009 (8) | 0.0064 (7)  | −0.0002 (9) |

### Geometric parameters (Å, °)

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| C17 | 1.08914 (15) | 0.1179 (3) | 0.23155 (10) | 0.0329 (4) |     |     |
| C6—C7     | 1.412 (3) | C15—H15   | 0.9500 |
| C7—C8     | 1.394 (3) | C16—H16   | 0.9500 |
| N2—N1—C1  | 115.36 (15)| N3—C9—H9B | 109.5 |
| N1—N2—C11 | 112.77 (15)| H9A—C9—H9B | 109.5 |
| C6—N3—C10 | 120.00 (18)| N3—C9—H9C | 109.5 |
| C6—N3—C9  | 119.85 (18)| H9A—C9—H9C | 109.5 |
| C10—N3—C9 | 117.17 (17)| H9B—C9—H9C | 109.5 |
| C2—C1—N1  | 113.08 (16)| N3—C10—H10A | 109.5 |
| C2—C1—C3  | 123.52 (17)| N3—C10—H10B | 109.5 |
| N1—C1—C3  | 123.36 (17)| H10A—C10—H10B | 109.5 |
| C1—C2—C11 | 123.19 (15)| N3—C10—H10C | 109.5 |
| C1—C2—C12 | 123.55 (15)| H10A—C10—H10C | 109.5 |
| C11—C2—C12| 113.26 (11)| H10B—C10—H10C | 109.5 |
| C4—C3—C8  | 117.53 (17)| C16—C11—C12 | 120.54 (17) |
| C4—C3—C1  | 121.25 (17)| C16—C11—N2  | 115.41 (16) |
| C8—C3—C1  | 121.21 (18)| C12—C11—N2  | 124.03 (17) |
| C5—C4—C3  | 121.80 (18)| C13—C12—C11 | 119.48 (18) |
| C5—C4—H4  | 119.1     | C13—C12—H12 | 120.3 |
| C3—C4—H4  | 119.1     | C11—C12—H12 | 120.3 |
| C4—C5—C6  | 120.97 (19)| C12—C13—C14 | 119.54 (17) |
| C4—C5—H5  | 119.5     | C12—C13—H13 | 120.2 |
| C6—C5—C6  | 119.5     | C14—C13—H13 | 120.2 |
| N3—C6—C5  | 121.14 (18)| C15—C14—C13 | 121.10 (18) |
| N3—C6—C7  | 121.41 (18)| C15—C14—C17 | 118.60 (18) |
| C5—C6—C7  | 117.41 (17)| C13—C14—C17 | 120.29 (17) |
| C8—C7—C6  | 120.71 (18)| C16—C15—C14 | 118.99 (18) |
| C8—C7—H7  | 119.6     | C16—C15—H15 | 120.5 |
| C6—C7—H7  | 119.6     | C14—C15—H15 | 120.5 |
| C7—C8—C3  | 121.57 (19)| C15—C16—C11 | 120.29 (17) |
| C7—C8—H8  | 119.2     | C15—C16—H16 | 119.9 |
| C3—C8—H8  | 119.2     | C11—C16—H16 | 119.9 |
| N3—C9—H9A | 109.5     | N4—C17—C14 | 177.5 (2) |
| C1—N1—N2—C11 | −176.74 (15) | C4—C5—C6—C7 | −0.9 (3) |
| N2—N1—C1—C2 | 179.58 (16) | N3—C6—C7—C8 | −177.38 (18) |
| N2—N1—C1—C3 | 1.6 (3) | C5—C6—C7—C8 | 0.5 (3) |
| N1—C1—C2—C11 | −173.44 (13) | C6—C7—C8—C3 | −0.1 (3) |
| C3—C1—C2—C11 | 4.5 (3) | C4—C3—C8—C7 | 0.1 (3) |
| N1—C1—C2—C12 | 5.4 (2) | C1—C3—C8—C7 | 179.17 (17) |
| C3—C1—C2—C12 | −176.62 (14) | N1—N2—C11—C16 | 176.66 (16) |
| C2—C1—C3—C4 | −123.2 (2) | N1—N2—C11—C12 | −1.9 (3) |
| N1—C1—C3—C4 | 54.5 (3) | C16—C11—C12—C13 | −2.2 (3) |
| C2—C1—C3—C8 | 57.7 (3) | N2—C11—C12—C13 | 176.31 (17) |
| N1—C1—C3—C8 | −124.5 (2) | C11—C12—C13—C14 | 0.0 (3) |
| C8—C3—C4—C5 | −0.4 (3) | C12—C13—C14—C15 | 2.2 (3) |
| C1—C3—C4—C5 | −179.54 (18) | C12—C13—C14—C17 | −176.58 (18) |
| C3—C4—C5—C6 | 0.9 (3) | C13—C14—C15—C16 | −2.2 (3) |
| Bond                  | Angle (°)  | Bond                  | Angle (°)  |
|----------------------|------------|----------------------|------------|
| C10—N3—C6—C5        | 173.06 (19)| C17—C14—C15—C16     | 176.56 (18)|
| C9—N3—C6—C5         | 13.1 (3)   | C14—C15—C16—C11     | 0.0 (3)    |
| C10—N3—C6—C7        | −9.1 (3)   | C12—C11—C16—C15     | 2.1 (3)    |
| C9—N3—C6—C7         | −169.03 (19)| N2—C11—C16—C15      | −176.47 (17)|
| C4—C5—C6—N3         | 177.02 (18)|                      |            |

**Hydrogen-bond geometry (Å, °)**

| D—H···A              | D—H | H···A | D···A | D—H···A |
|----------------------|-----|-------|-------|---------|
| C13—H13···N4i        | 0.95| 2.48  | 3.428 (3) | 175     |

Symmetry code: (i) −x+5/2, y+1/2, −z+1/2.