



Crystal structure, Hirshfeld surface analysis and frontier molecular orbital analysis of (*E*)-4-bromo-*N'*-(2,3-dichlorobenzylidene)benzohydrazide

Palaniyappan Sivajeyanthi, Muthaiah Jeevaraj, Bellarmin Edison and Kasthuri Balasubramani*

Received 3 December 2018
Accepted 31 January 2019

Department of Chemistry, Government Arts College (Autonomous), Thanthonimalai, Karur- 639 005, Tamil Nadu, India.
*Correspondence e-mail: manavaibala@gmail.com

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; Schiff base; hydrogen bonding; Hirshfeld surface analysis.

CCDC reference: 1587252

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

The title Schiff base compound, $C_{14}H_9BrCl_2N_2O$, displays a *trans* or *E* configuration with respect to the $C=N$ bond, with a dihedral angle $15.7 (2)^\circ$ formed between the benzene rings. In the crystal, molecules are linked by $N-H \cdots O$ and $C-H \cdots O$ hydrogen bonds, forming chains along $[001]$ which enclose $R_2^1(6)$ loops. The intermolecular interactions were investigated by Hirshfeld surfaces analysis and two-dimensional fingerprint plots. The DFT-B3LYP/6-311 G++(d,p) method was used to determine the HOMO–LUMO energy levels.

1. Chemical context

Schiff bases are nitrogen-containing compounds that were first obtained by the condensation reactions of aromatic amines and aldehydes (Schiff, 1864). A wide range of these compounds, with the general formula $RHC=NR_1$ (R and R_1 can be alkyl, aryl, cycloalkyl or heterocyclic groups) have been synthesized. They are of great importance in the field of coordination chemistry as they are able to form stable complexes with many metal ions (Souza *et al.*, 1985). The chemical and biological significance of Schiff bases can be attributed to the presence of a lone electron pair in the sp^2 -hybridized orbital of the nitrogen atom of the azomethine group (Singh *et al.*, 1975). These compounds are used in the fields of organic synthesis, chemical catalysis, medicine and pharmacy as well as other new technologies (Tanaka *et al.*, 2010). Schiff bases are also used as probes in investigating the structure of DNA (Tiwari *et al.*, 2011) and have gained special attention in pharmacophore research and in the development of several bioactive lead molecules (Muralisankar *et al.*, 2016). They also exhibit photochromic and thermochromic properties and have been used in information storage, electronic display systems, optical switching devices, and ophthalmic glasses (Amimoto & Kawato, 2005). Herein, we report on the crystal structure, the Hirshfeld surface analysis and the molecular orbital analysis of the title compound, (*E*)-4-bromo-*N'*-(2,3-dichlorobenzylidene)benzohydrazide.

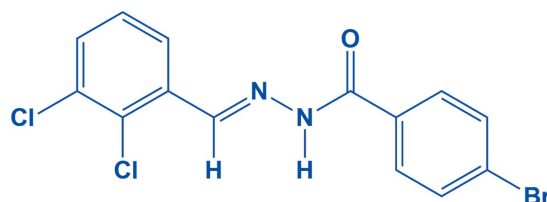
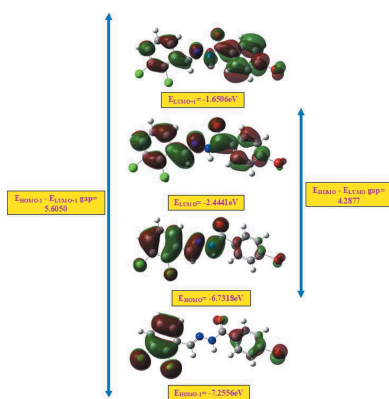


Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N1\cdots O1^i$	0.86	2.20	3.003 (4)	155
$C8-H8\cdots O1^i$	0.93	2.42	3.234 (5)	146

Symmetry code: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

2. Structural commentary

The molecular structure of the title compound is illustrated in Fig. 1. The configuration about the $C8=N2$ bond, which has a bond length of 1.271 (5) Å, is *E*. The benzene rings ($C1-C6$ and $C9-C14$) are inclined to each other by 15.7 (2)°. The bond lengths and angles and the overall conformation of the molecule are close to those reported for a very similar compound, (*E*)-4-bromo-*N'*-(2-chlorobenzylidene)benzohydrazide (Shu *et al.*, 2009).

3. Supramolecular features

In the crystal, molecules are linked by $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds, forming chains that propagate along the [001] direction and which enclose $R_2^1(6)$ ring motifs (Fig. 2 and Table 1). Here the oxygen atom O1 acts as a bifurcated acceptor. There are no other significant intermolecular interactions present (see Table 2 in *Hirshfeld surface analysis*).

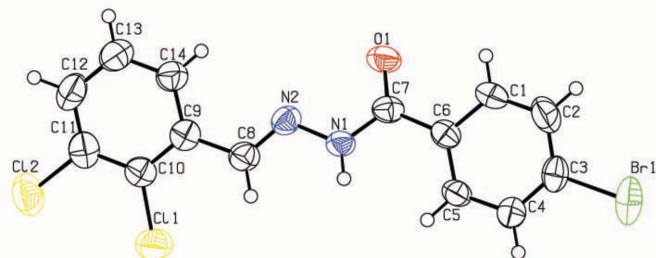


Figure 1
A view of the molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

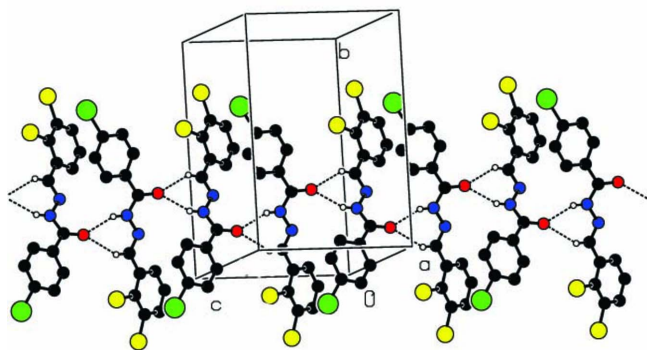


Figure 2
A partial view along the *a* axis of the crystal packing of the title compound. Hydrogen bonds (Table 1) are shown as dashed lines, and only the H atoms involved in hydrogen bonding have been included.

Table 2
Intermolecular contacts (Å) for the title compound.

Atom1 \cdots Atom2	Length	Length – vdW radii	Symm. op. 2
$H1M1\cdots H5$	2.136	–0.264	x, y, z
$O1\cdots H1N1$	2.200	–0.520	$x, \frac{1}{2} - y, z - \frac{1}{2}$
$H1M1\cdots H8$	2.242	–0.158	x, y, z
$O1\cdots H8$	2.421	–0.299	$x, \frac{1}{2} - y, z - \frac{1}{2}$
$O1\cdots H1$	2.520	–0.200	x, y, z
$N2\cdots H14$	2.523	–0.227	x, y, z
$H1M1\cdots C5$	2.608	–0.292	x, y, z
$N1\cdots H5$	2.652	–0.098	x, y, z
$Cl1\cdots H8$	2.733	–0.217	x, y, z
$H1\cdots Cl1$	2.931	–0.019	$x, \frac{1}{2} - y, z - \frac{1}{2}$
$O1\cdots N1$	3.003 (4)	–0.067	$x, -y, z - \frac{1}{2}$
$H12\cdots Cl2$	3.024	0.074	$x, -y, z - \frac{1}{2}$
$O1\cdots C8$	3.234 (5)	0.014	$x, -y, z - \frac{1}{2}$
$N2\cdots C5$	3.262 (5)	0.012	$x, -y, z - \frac{1}{2}$
$Cl2\cdots Cl2$	3.440 (5)	–0.010	$x, -y, z - \frac{1}{2}$
$C9\cdots C4$	3.468 (6)	0.068	$x, -y, z - \frac{1}{2}$
$C8\cdots Cl2$	3.475 (5)	0.075	$-x, 1 - y, -z$

4. Hirshfeld surface analysis

Crystal Explorer (Wolff *et al.*, 2012) was used to generate the Hirshfeld surface and two-dimensional fingerprint plots (Rohl *et al.*, 2008). The three-dimensional d_{norm} surface is a useful tool for analysing and visualizing the intermolecular interactions, which are given in Table 2. The d_{norm} values are negative or positive depending on whether the intermolecular contact is shorter or longer than the sum of the van der Waals radii (Spackman & Jayatilaka, 2009; McKinnon *et al.*, 2007). The total d_{norm} surface of the title compound is shown in Fig. 3. The red spots correspond to the $N-H\cdots O$ and $C-H\cdots O$ interactions, the most significant interactions in the crystal (Tables 1 and 2).

The two-dimensional fingerprint plots from the Hirshfeld surface analysis are shown in Fig. 4. They indicate the percentage contributions of the various intermolecular contacts to the Hirshfeld surface, the most significant are $Cl\cdots H/H\cdots Cl$ (22.5%), $H\cdots H$ (15.7%), $C\cdots H/H\cdots C$ (13.2%), $Br\cdots H/H\cdots Br$ (11.5%), $C\cdots C$ (9.8%), $O\cdots H/H\cdots O$ (9.0%), $N\cdots H/H\cdots N$ (4.9%), and $Br\cdots Cl/Cl\cdots Br$ (3.3%), as shown in Fig. 4, *cf* Table 2.

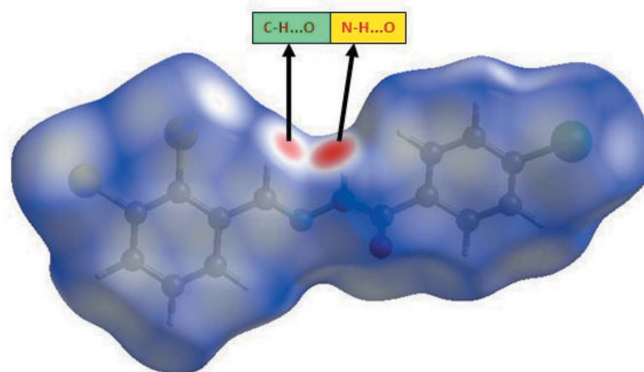


Figure 3
Hirshfeld surface mapped over d_{norm} for the title compound. [add range of d_{norm} to legend]

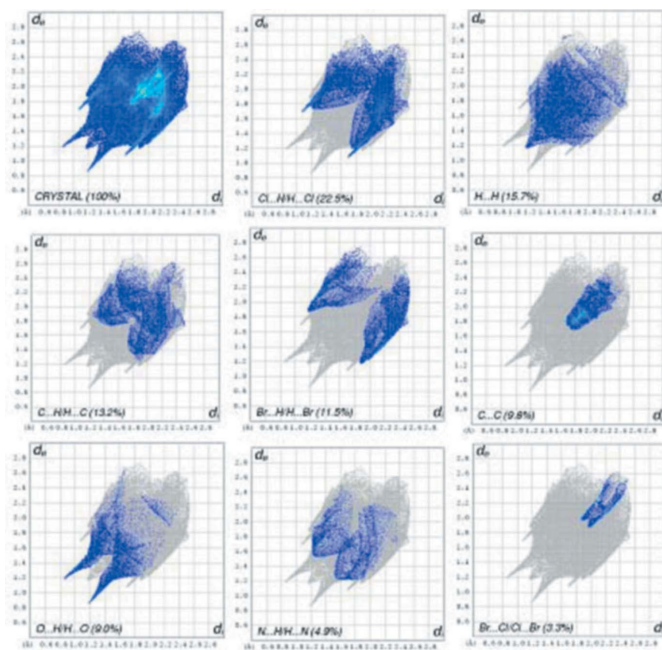


Figure 4 Two-dimensional fingerprint plots of the crystal with the relative contributions of the atom pairs to the Hirshfeld surface.

5. Frontier molecular orbital calculations

The HOMO (highest occupied molecular orbital) acts as an electron donor and the LUMO (lowest occupied molecular orbital) as an electron acceptor. If the energy gap is small then the molecule is highly polarizable and has high chemical reactivity. The energy levels of the title compound were computed using the DFT-B3LYP/6-311G++(d,p) method (Sivajeyanthi *et al.*, 2017). The energy gap between HOMO–LUMO orbitals, which determines the chemical stability, chemical hardness, chemical potential, electronegativity and the electrophilicity index are shown in Fig. 5 and details are given in Table 3. The frontier molecular orbital LUMO is located over the whole of the molecule. The energy gap of the molecule clearly shows the charge-transfer interaction involving donor and acceptor groups. The chemical hardness and softness of a molecule is a sign of its chemical stability. From the HOMO–LUMO energy gap, we can see whether or not the molecule is hard or soft. If the energy gap is large, the molecule is hard and if small the molecule is soft. Soft molecules are more polarizable than hard ones because they need less energy for excitation. From the data presented in Table 3, we conclude that the energy gap is large, hence the title molecule is a hard material and will be difficult to polarize.

6. Database survey

A search of the Cambridge Structural Database (CSD, version 5.39, last update August 2018; Groom *et al.*, 2016) for 4-bromo-(benzylidene)benzohydrazides yielded six structures. They include the following analogues: 2,4-dihydroxybenzylidene [ATOSEJ (Mohanraj *et al.*, 2016) and ATOSEJ01 (Arunagiri

Table 3

Calculated frontier molecular orbital analysis of the title compound.

EHOMO	−6.7318 eV
ELUMO	−2.4441 eV
EHOMO−1	−7.2556 eV
ELUMO+1	−1.6506 eV
EHOMO–ELUMO gap	4.2877 eV
EHOMO−1 ELUMO+1 gap	5.6050 eV
Chemical hardness (η)	2.1438 eV
Chemical potential (μ)	4.5879 eV
Electronegativity (χ)	−4.5879 eV
Electrophilicity index (ω)	4.9092 eV

et al., 2018)], 2-nitrobenzylidene (EGUSEF; Zhang *et al.*, 2009), 2-chlorobenzylidene (HOTDAW; Shu *et al.*, 2009), 2-hydroxy-1-naphthylmethylene (IFUSEI; Diao *et al.*, 2008), 2-hydroxy-5-methoxybenzylidene (OBUBUL; Wang *et al.*, 2017) and 4-hydroxy-3-methoxybenzylidene (YAWXOL; Horkaew *et al.*, 2012). They all have an *E* configuration about the C=N bond. The N–N bond lengths vary from 1.366 (4) to 1.396 (5) Å while the C=N bond lengths vary from 1.264 (4) to 1.285 (2) Å. The values observed for the title compound, respectively, 1.391 (4) and 1.271 (5) Å, fall within these limits. The dihedral angle between the two benzene rings varies from as little as 4.12 (17)° in EGUSEF to 49.08 (18)° in ATOSEJ01. In the title compound this dihedral angle is 15.7 (2)°, similar to the values observed for HOTDAW, the 2-chlorobenzylidene analogue, and for YAWXOL, the 4-hydroxy-3-methoxybenzylidene analogue, for which the dihedral angles are 11.43 (16) and 13.92 (6)°, respectively.

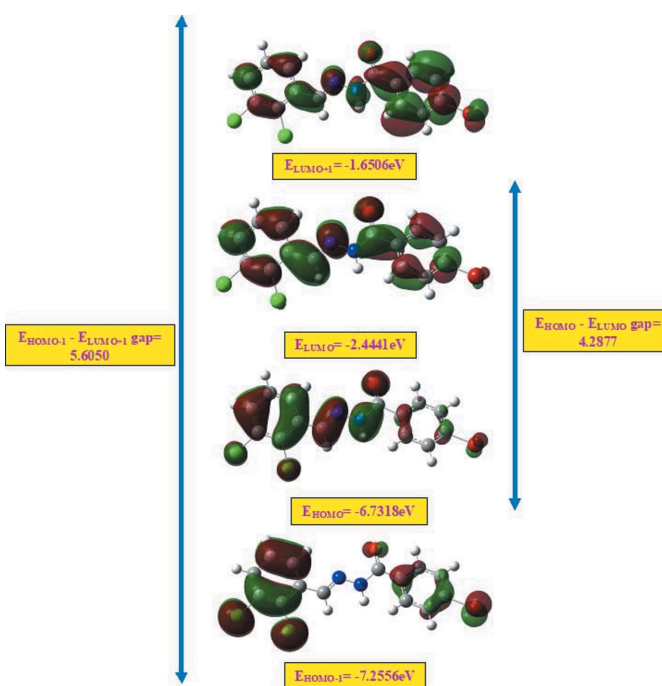


Figure 5 Molecular orbital energy levels of the title compound.

7. Synthesis and crystallization

The title compound was synthesized by the reaction of 1:1 molar ratio mixture of a hot ethanolic solution (20 ml) of 4-bromobenzohydrazide (0.213 mg, Aldrich) and 2,3-dichlorobenzaldehyde (0.175 mg, Aldrich), which was refluxed for 8 h. The solution was then cooled and kept at room temperature. The powder obtained was recrystallized from dimethyl sulfoxide (DMSO). Colourless block-like crystals suitable for the X-ray diffraction analysis were obtained in a few days.

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The hydrogen atoms were positioned geometrically and refined using a riding model: C—H = 0.93 Å, N—H = 0.86 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{C})$.

Funding information

KB and PS thank the Department of Science and Technology (DST—SERB), grant No. SB/FT/CS-058/2013, New Delhi, India, for financial support.

References

Altomare, A., Casciarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
 Amimoto, K. & Kawato, T. (2005). *J. Photochem. Photobiol. Photochem. Rev.* **6**, 207–226.
 Arunagiri, C., Anitha, A. G., Subashini, A. & Selvakumar, S. (2018). *J. Mol. Struct.* **1163**, 368–378.
 Bruker (2004). *SAINTE, APEX2, XPREP and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Diao, Y.-P., Zhang, Q.-H., Wang, D.-C. & Deng, X.-M. (2008). *Acta Cryst.* **E64**, o2070.
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Horkaew, J., Chantrapromma, S., Anantapong, T., Kanjana-Opas, A. & Fun, H.-K. (2012). *Acta Cryst.* **E68**, o1069–o1070.
 McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* 3814–3816.
 Mohanraj, M., Ayyannan, G., Raja, G. & Jayabalakrishnan, C. (2016). *Mater. Sci. Eng. C*, **69**, 1297–1306.
 Muralisankar, M., Haribabu, J., Bhuvanesh, N. S. P., Karvembu, R. & Sreekanth, A. (2016). *Inorg. Chim. Acta*, **449**, 82–95.
 Rohl, A. L., Moret, M., Kaminsky, W., Claborn, K., McKinnon, J. J. & Kahr, B. (2008). *Cryst. Growth Des.* **8**, 4517–4525.
 Schiff, H. (1864). *Justus Liebigs Ann. Chem.* **131**, 118–119.
 Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.

Table 4

Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₉ BrCl ₂ N ₂ O
<i>M_r</i>	372.04
Crystal system, space group	Monoclinic, <i>P</i> ₂ / <i>c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.1952 (18), 14.055 (2), 9.3050 (12)
β (°)	96.446 (6)
<i>V</i> (Å ³)	1454.8 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.19
Crystal size (mm)	0.30 × 0.20 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2004)
<i>T</i> _{min} , <i>T</i> _{max}	0.448, 0.568
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	11392, 3363, 1724
<i>R</i> _{int}	0.050
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.666
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.051, 0.173, 0.94
No. of reflections	3363
No. of parameters	181
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.70, -0.63

Computer programs: *APEX2*, *SAINTE* and *XPREP* (Bruker, 2004), *SIR92* (Altomare *et al.*, 1993), *SHELXL2017* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

Shu, X.-H., Diao, Y.-P., Li, M.-L., Yan, X. & Liu, J. (2009). *Acta Cryst.* **E65**, o1034.
 Singh, P., Goel, R. L. & Singh, B. P. (1975). *J. Indian Chem. Soc.* **52**, 958–959.
 Sivajeyanthi, P., Jeevaraj, M., Balasubramani, K., Viswanathan, V. & Velmurugan, D. (2017). *Chem. Data Collect.* **11–12**, 220–231.
 Souza, P., Garcia-Vazquez, J. A. & Masaguer, J. R. (1985). *Transition Met. Chem.* **10**, 410–412.
 Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Tanaka, K., Shimoura, R. & Caira, M. R. (2010). *Tetrahedron Lett.* **51**, 449–452.
 Tiwari, A. D., Mishra, A. K., Mishra, B. B., Mamba, B. B., Maji, B. & Bhattacharya, S. (2011). *Spectrochim. Acta A*, **79**, 1050–1056.
 Wang, J., Qu, D., Lei, J.-X. & You, Z. (2017). *J. Coord. Chem.* **70**, 544–555.
 Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Turner, M. J., Jayatilaka, D. & Spackman, M. A. (2012). *Crystal Explorer*. University of Western Australia, Australia.
 Zhang, M.-J., Yin, L.-Z., Wang, D.-C., Deng, X.-M. & Liu, J.-B. (2009). *Acta Cryst.* **E65**, o508.

supporting information

Acta Cryst. (2019). E75, 324-327 [https://doi.org/10.1107/S2056989019001816]

Crystal structure, Hirshfeld surface analysis and frontier molecular orbital analysis of (*E*)-4-bromo-*N'*-(2,3-dichlorobenzylidene)benzohydrazide

Palaniyappan Sivajeyanthi, Muthaiah Jeevaraj, Bellarmin Edison and Kasthuri Balasubramani

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINTE* (Bruker, 2004); data reduction: *SAINTE* and *XPREF* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2017* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

(*E*)-4-Bromo-*N'*-(2,3-dichlorobenzylidene)benzohydrazide

Crystal data

C₁₄H₉BrCl₂N₂O
M_r = 372.04
 Monoclinic, *P2₁/c*
a = 11.1952 (18) Å
b = 14.055 (2) Å
c = 9.3050 (12) Å
 β = 96.446 (6)°
V = 1454.8 (4) Å³
Z = 4

F(000) = 736
D_x = 1.699 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 3186 reflections
 θ = 4.7–47.5°
 μ = 3.19 mm⁻¹
T = 296 K
 Block, colourless
 0.30 × 0.20 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 ω and ϕ scan
 Absorption correction: multi-scan
 (SADABS; Bruker, 2004)
T_{min} = 0.448, *T_{max}* = 0.568
 11392 measured reflections

3363 independent reflections
 1724 reflections with *I* > 2σ(*I*)
R_{int} = 0.050
 θ_{\max} = 28.3°, θ_{\min} = 2.6°
h = -14→14
k = -18→18
l = -8→12

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.051
wR(*F*²) = 0.173
S = 0.94
 3363 reflections
 181 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.70 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.63 \text{ e \AA}^{-3}$

Special details

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

Refinement. 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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.45376 (6)	-0.17154 (4)	0.33892 (7)	0.0891 (3)
Cl1	0.24263 (13)	0.60728 (9)	0.12531 (12)	0.0749 (4)
Cl2	0.11288 (14)	0.77291 (9)	-0.05544 (15)	0.0843 (5)
O1	0.2713 (3)	0.1659 (2)	-0.1706 (3)	0.0628 (9)
N1	0.2462 (3)	0.2532 (2)	0.0288 (3)	0.0456 (9)
H1N1	0.253851	0.257938	0.121571	0.055*
N2	0.1988 (3)	0.3275 (2)	-0.0585 (4)	0.0478 (9)
C6	0.3268 (4)	0.0931 (3)	0.0576 (4)	0.0439 (10)
C9	0.1358 (4)	0.4878 (3)	-0.0799 (4)	0.0470 (10)
C7	0.2801 (4)	0.1731 (3)	-0.0370 (4)	0.0452 (10)
C5	0.3717 (4)	0.1033 (3)	0.2017 (4)	0.0473 (10)
H5	0.375456	0.163419	0.243713	0.057*
C10	0.1524 (4)	0.5818 (3)	-0.0321 (4)	0.0483 (10)
C3	0.4067 (4)	-0.0633 (3)	0.2236 (5)	0.0527 (11)
C4	0.4112 (4)	0.0249 (3)	0.2838 (5)	0.0539 (11)
H4	0.440892	0.032600	0.380460	0.065*
C8	0.1896 (4)	0.4073 (3)	0.0037 (4)	0.0496 (11)
H8	0.216763	0.414398	0.101258	0.060*
C11	0.0950 (5)	0.6564 (3)	-0.1127 (5)	0.0569 (12)
C12	0.0226 (5)	0.6387 (4)	-0.2402 (5)	0.0663 (14)
H12	-0.015996	0.688339	-0.292702	0.080*
C14	0.0639 (4)	0.4716 (3)	-0.2103 (5)	0.0555 (12)
H14	0.053241	0.409731	-0.244882	0.067*
C1	0.3261 (5)	0.0017 (3)	-0.0023 (5)	0.0636 (13)
H1	0.299196	-0.006402	-0.099732	0.076*
C13	0.0084 (5)	0.5456 (4)	-0.2885 (5)	0.0674 (14)
H13	-0.039161	0.533003	-0.374844	0.081*
C2	0.3643 (5)	-0.0761 (3)	0.0792 (6)	0.0716 (15)
H2	0.361649	-0.136545	0.038188	0.086*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0922 (5)	0.0604 (4)	0.1158 (6)	0.0313 (3)	0.0164 (4)	0.0248 (3)
Cl1	0.1014 (11)	0.0608 (7)	0.0589 (8)	-0.0126 (7)	-0.0069 (7)	0.0007 (6)
Cl2	0.1127 (13)	0.0482 (7)	0.0933 (10)	0.0101 (7)	0.0175 (9)	0.0065 (6)

O1	0.094 (3)	0.0564 (19)	0.0371 (17)	-0.0015 (16)	0.0027 (16)	-0.0063 (13)
N1	0.062 (2)	0.0421 (19)	0.0319 (17)	-0.0021 (17)	0.0032 (16)	0.0005 (14)
N2	0.052 (2)	0.047 (2)	0.0430 (19)	-0.0024 (17)	0.0010 (17)	0.0065 (16)
C6	0.042 (3)	0.042 (2)	0.048 (2)	-0.0064 (19)	0.0082 (19)	-0.0053 (18)
C9	0.044 (3)	0.052 (2)	0.047 (2)	-0.001 (2)	0.012 (2)	0.0049 (19)
C7	0.049 (3)	0.046 (2)	0.041 (2)	-0.0128 (19)	0.004 (2)	-0.0007 (19)
C5	0.060 (3)	0.040 (2)	0.041 (2)	-0.003 (2)	0.005 (2)	-0.0070 (17)
C10	0.050 (3)	0.052 (2)	0.044 (2)	-0.003 (2)	0.013 (2)	0.0009 (18)
C3	0.041 (3)	0.052 (2)	0.066 (3)	0.013 (2)	0.013 (2)	0.008 (2)
C4	0.061 (3)	0.050 (2)	0.050 (2)	0.009 (2)	0.004 (2)	0.002 (2)
C8	0.059 (3)	0.047 (2)	0.043 (2)	-0.004 (2)	0.007 (2)	0.0023 (19)
C11	0.062 (3)	0.053 (3)	0.060 (3)	0.003 (2)	0.025 (3)	0.010 (2)
C12	0.068 (4)	0.069 (3)	0.062 (3)	0.017 (3)	0.005 (3)	0.019 (3)
C14	0.058 (3)	0.061 (3)	0.047 (3)	0.006 (2)	0.004 (2)	-0.002 (2)
C1	0.085 (4)	0.051 (3)	0.051 (3)	0.000 (3)	-0.008 (2)	-0.018 (2)
C13	0.069 (4)	0.078 (4)	0.053 (3)	0.012 (3)	-0.004 (3)	0.002 (3)
C2	0.076 (4)	0.043 (3)	0.093 (4)	0.006 (2)	-0.004 (3)	-0.017 (3)

Geometric parameters (Å, °)

Br1—C3	1.901 (4)	C5—H5	0.9300
Cl1—C10	1.721 (4)	C10—C11	1.402 (6)
Cl2—C11	1.727 (5)	C3—C4	1.359 (6)
O1—C7	1.240 (5)	C3—C2	1.385 (6)
N1—C7	1.356 (5)	C4—H4	0.9300
N1—N2	1.391 (4)	C8—H8	0.9300
N1—H1N1	0.8600	C11—C12	1.383 (7)
N2—C8	1.271 (5)	C12—C13	1.386 (7)
C6—C5	1.385 (5)	C12—H12	0.9300
C6—C1	1.400 (5)	C14—C13	1.377 (6)
C6—C7	1.486 (6)	C14—H14	0.9300
C9—C14	1.398 (6)	C1—C2	1.372 (7)
C9—C10	1.400 (6)	C1—H1	0.9300
C9—C8	1.464 (6)	C13—H13	0.9300
C5—C4	1.385 (6)	C2—H2	0.9300
C7—N1—N2	117.8 (3)	C3—C4—H4	119.9
C7—N1—H1N1	121.1	C5—C4—H4	119.9
N2—N1—H1N1	121.1	N2—C8—C9	119.3 (4)
C8—N2—N1	116.2 (3)	N2—C8—H8	120.3
C5—C6—C1	117.7 (4)	C9—C8—H8	120.3
C5—C6—C7	124.1 (4)	C12—C11—C10	120.9 (4)
C1—C6—C7	118.2 (4)	C12—C11—Cl2	118.2 (4)
C14—C9—C10	118.2 (4)	C10—C11—Cl2	121.0 (4)
C14—C9—C8	119.9 (4)	C11—C12—C13	118.9 (4)
C10—C9—C8	121.9 (4)	C11—C12—H12	120.6
O1—C7—N1	121.7 (4)	C13—C12—H12	120.6
O1—C7—C6	121.0 (4)	C13—C14—C9	121.2 (4)

N1—C7—C6	117.3 (3)	C13—C14—H14	119.4
C4—C5—C6	120.7 (4)	C9—C14—H14	119.4
C4—C5—H5	119.7	C2—C1—C6	121.6 (4)
C6—C5—H5	119.7	C2—C1—H1	119.2
C9—C10—C11	120.0 (4)	C6—C1—H1	119.2
C9—C10—C11	120.7 (3)	C14—C13—C12	120.9 (5)
C11—C10—C11	119.3 (3)	C14—C13—H13	119.6
C4—C3—C2	120.7 (4)	C12—C13—H13	119.6
C4—C3—Br1	120.1 (3)	C1—C2—C3	118.9 (4)
C2—C3—Br1	119.1 (3)	C1—C2—H2	120.5
C3—C4—C5	120.3 (4)	C3—C2—H2	120.5
C7—N1—N2—C8	-166.9 (4)	C14—C9—C8—N2	19.2 (6)
N2—N1—C7—O1	1.1 (6)	C10—C9—C8—N2	-162.0 (4)
N2—N1—C7—C6	-178.0 (4)	C9—C10—C11—C12	-0.6 (7)
C5—C6—C7—O1	160.5 (4)	C11—C10—C11—C12	179.5 (4)
C1—C6—C7—O1	-19.2 (6)	C9—C10—C11—C12	179.5 (3)
C5—C6—C7—N1	-20.4 (6)	C11—C10—C11—C12	-0.4 (5)
C1—C6—C7—N1	160.0 (4)	C10—C11—C12—C13	-0.7 (7)
C1—C6—C5—C4	-1.8 (6)	C12—C11—C12—C13	179.2 (4)
C7—C6—C5—C4	178.5 (4)	C10—C9—C14—C13	-1.4 (7)
C14—C9—C10—C11	1.6 (6)	C8—C9—C14—C13	177.5 (4)
C8—C9—C10—C11	-177.3 (4)	C5—C6—C1—C2	2.4 (7)
C14—C9—C10—C11	-178.5 (3)	C7—C6—C1—C2	-177.9 (4)
C8—C9—C10—C11	2.6 (6)	C9—C14—C13—C12	0.1 (7)
C2—C3—C4—C5	0.9 (7)	C11—C12—C13—C14	0.9 (8)
Br1—C3—C4—C5	-177.0 (3)	C6—C1—C2—C3	-1.4 (8)
C6—C5—C4—C3	0.3 (7)	C4—C3—C2—C1	-0.3 (7)
N1—N2—C8—C9	-177.5 (3)	Br1—C3—C2—C1	177.6 (4)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N1...O1 ⁱ	0.86	2.20	3.003 (4)	155
C8—H8...O1 ⁱ	0.93	2.42	3.234 (5)	146

Symmetry code: (i) *x*, -*y*+1/2, *z*+1/2.