

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

4-Ammoniobenzamidinium dichloride

Y. M. Legrand,* A. van der Lee and M. Barboiu

Institut Européen des Membranes, UMR 5635, CC 047 Université de Montpellier II, Montpellier, France

Correspondence e-mail: yves-marie.legrand@iemm.univ-montp2.fr

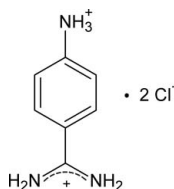
Received 8 April 2008; accepted 14 April 2008

 Key indicators: single-crystal X-ray study; $T = 175$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.027; wR factor = 0.034; data-to-parameter ratio = 19.4.

The crystal structure of the title compound, $\text{C}_7\text{H}_{11}\text{N}_3^{2+} \cdot 2\text{Cl}^-$, has been determined as part of a project focusing on the ability of the benzamidinium system to form strong hydrogen bonds in aqueous media. It is commonly used as a ligand in affinity chromatography for purification and immobilization of enzymes. A twofold rotation axis runs along the axis of the cation. The orientation of the amidinium group with respect to the benzene ring is indicated by the $\text{N}-\text{C}-\text{C}$ torsion angle of 40.2 (1)°. In the crystal structure, cations and anions are linked *via* hydrogen bonds. The chloride anion is surrounded by four ammonium cations in a tetrahedral environment. The aromatic rings of the amidinium cations are π -stacked, with a centroid-centroid distance of 4.178 (1) Å.

Related literature

For related literature, see: Boyd (1991); Nguyen & Loung (1990); Jarak *et al.* (2005); Hranjec *et al.* (2003); Danan *et al.* (1997); Del Poeta, Schell, Dykstra, Jones, Tidwell, Czarny *et al.* (1998); Del Poeta, Schell, Dykstra, Jones, Tidwell, Kumar *et al.*, (1998); Janiak (2000); Fujita *et al.* (1995); Müller *et al.* (2006); Kimata *et al.* (1990). For examples of related tubular superstructures, see: Barboiu *et al.* (2003); Blondeau *et al.* (2005).



Experimental

Crystal data

 $\text{C}_7\text{H}_{11}\text{N}_3^{2+} \cdot 2\text{Cl}^-$
 $M_r = 208.09$
 Monoclinic, $C2/c$
 $a = 4.1779$ (2) Å
 $b = 20.9388$ (10) Å
 $c = 11.6260$ (5) Å

 $\beta = 94.920$ (4)°
 $V = 1013.30$ (8) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

 $\mu = 0.59$ mm⁻¹
 $T = 175$ K
 $0.49 \times 0.09 \times 0.05$ mm

Data collection

 Oxford Diffraction XCalibur diffractometer
 Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
 $T_{\min} = 0.95$, $T_{\max} = 0.97$

 7752 measured reflections
 1750 independent reflections
 1144 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.034$
 $S = 1.00$
 1144 reflections
 59 parameters

 2 restraints
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.34$ e Å⁻³
 $\Delta\rho_{\min} = -0.20$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N2}-\text{H9} \cdots \text{Cl1}^{\text{i}}$	0.90	2.35	3.2247 (13)	166
$\text{N2}-\text{H10} \cdots \text{Cl1}$	0.92	2.32	3.2142 (13)	162
$\text{N8}-\text{H13} \cdots \text{Cl1}^{\text{ii}}$	0.85	2.26	3.1031 (6)	173
$\text{N8}-\text{H14} \cdots \text{Cl1}^{\text{iii}}$	0.94	2.20	3.1369 (6)	176
$\text{C5}-\text{H11} \cdots \text{Cl1}^{\text{iv}}$	1.00	2.70	3.6806 (13)	165

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2003); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *CRYSTALS*.

This work, conducted as part of the award 'Dynamic Adaptive Materials for Separation and Sensing Microsystems' (to MB) made under the European Heads of Research Councils and European Science Foundation EURYI (European Young Investigator) Awards Scheme in 2004, was supported by funds from the Participating Organizations of EURYI and the EC Sixth Framework Program (see <http://www.esf.org/euryi>). This research was also supported in part by the CNRS and the University of Montpellier II.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2252).

References

- Barboiu, M., Vaughan, G. & van der Lee, A. (2003). *Org. Lett.* **5**, 3073–3076.
 Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
 Blondeau, P., van der Lee, A. & Barboiu, M. (2005). *Inorg. Chem.* **44**, 5649–5653.
 Boyd, V. (1991). *The Chemistry of Amidines and Imidates*, Vol. 2, edited by S. Patai, pp. 339–366. New York: John Wiley.
 Burla, M. C., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Polidori, G. & Spagna, R. (2003). *J. Appl. Cryst.* **36**, 1103.

- Danan, A., Charon, D., Kirkiacharian, S., Bories, K. & Loiseau, P. M. (1997). *Farmaco*, **52**, 227–229.
- Del Poeta, M., Schell, W. A., Dykstra, C. C., Jones, S. K., Tidwell, R. R., Czarny, A., Bajić, M., Kumar, A., Boykin, D. W. & Perfect, J. R. (1998). *Antimicrob. Agents Chemother.* **42**, 2495–2502.
- Del Poeta, M., Schell, W. A., Dykstra, C. C., Jones, S. K., Tidwell, R. R., Kumar, A., Boykin, D. W. & Perfect, J. R. (1998). *Antimicrob. Agents Chemother.* **42**, 2503–2510.
- Fujita, M., Oguro, D., Miyazawa, M., Oka, H., Yamaguchi, K. & Ogura, K. (1995). *Nature (London)*, **378**, 469–471.
- Hranjec, M., Grdisa, M., Pavelić, K., Boykin, D. W. & Karminski-Zamola, G. (2003). *Farmaco*, **58**, 1319–1324.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Jarak, I., Karminski-Zamola, G., Pavlović, G. & Popović, Z. (2005). *Acta Cryst. C61*, o98–o100.
- Kimata, K., Tsuboi, R., Hosoya, K., Tanaka, N. & Araki, T. (1990). *J. Chromatogr. A*, **515**, 73–84.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Müller, A., Zhou, Y. S., Bogge, H., Schmidtman, M., Mitra, T., Haupt, E. T. K. & Berkle, A. (2006). *Angew. Chem. Int. Ed.* **45**, 460–465.
- Nguyen, A. L. & Loung, J. H. T. (1990). *Enzyme Microb. Technol.* **12**, 663–668.
- Oxford Diffraction (2007). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

supporting information

Acta Cryst. (2008). E64, o967–o968 [doi:10.1107/S1600536808010179]

4-Ammoniobenzamidinium dichloride

Y. M. Legrand, A. van der Lee and M. Barboiu

S1. Comment

Several types of heteroditopic receptors, including the title compound, are being used in our group as bricks for supramolecular construction (Barboiu *et al.*, 2003, Blondeau *et al.*, 2005). Among other functions, amidine compounds have shown antiparasitic (Danan *et al.*, 1997) and antifungal activity (Del Poeta, Schell, Dykstra, Jones, Tidwell, Czarny *et al.*, 1998; Del Poeta, Schell, Dykstra, Jones, Tidwell, Kumar *et al.*, 1998). Indeed, this class of compounds has been widely studied for its biological activities. Surprisingly, only one crystal structure of an aminobenzamidine derivative has been published so far (Jarak *et al.*, 2005). Our project deals with the construction of supramolecular architectures based on hydrogen bonding in aqueous media. This is possible due to the strength of the bonds formed between the very electrophilic amidinium unit and the nucleophilic character of acids, for example. Superstructures made of co-crystals have been designed and surprising results have been achieved by Fujita *et al.* (1995) and Müller *et al.* (2006). The amidine group also forms a well recognized class of anticancer compounds (Boyd, 1991, Hranjec *et al.*, 2003) and, based on the same properties, can also be used as ligands in affinity chromatography to immobilize enzymes (Nguyen & Loung, 1990 and Kimata *et al.*, 1990).

The molecule of the title compound (Fig. 1) is not planar. The amidinium group has a synclinal disposition with respect to the benzene ring ($N2-C3-C4-C5 = -40.2 (1)^\circ$). A twofold rotation axis runs along the axis of the cation. The observed deviation from coplanarity might serve to accommodate the formation of intermolecular hydrogen bonds with chloride ions. The three ammonium protons are free to rotate about the $C7-N8$ bond. These protons were found by Fourier difference maps at four positions (2 + 2 by symmetry) which appears to be in line with the four chloride anions surrounding the ammonium group ($N\cdots Cl = 3.103 \text{ \AA}$). The site occupation factors of the four ammonium protons was set at 0.75, as there are, in fact, only three protons attached to this ammonium nitrogen. As Fig. 2 shows, rows of head-to-tail benzamidine are stacked alternately. Interestingly, three of four nitrogen atoms form a plane on which the chloride atom sits, almost perfectly. Each chloride anion is bound to four nitrogen cations by weak hydrogen bonds ($N\cdots Cl = 3.103 (1) - 3.225 (1) \text{ \AA}$), while each amidinium unit is bound to eight chloride anions (four times through the ammonium site, twice through each amidinium nitrogen). This produces a singular pyramidal architecture, as depicted in Fig. 3. The packing is determined by these hydrogen bonds, but also by π -stacking. The aromatic rings of the amidinium cations adopt a parallel offset conformation. The distance $Cg\cdots Cg$ between the centroids of two adjacent rings is $4.178 (1) \text{ \AA}$, whereas the angle between the ring-centroid vector and the ring normal of one of the amidine rings is $27.7 (1)^\circ$ (with a perpendicular interplanar distance of 3.7 \AA). The angle between the two benzene rings is 0.02° . These values can be considered to be normal for π - π interactions (Janiak, 2000). Fig. 3 also shows both the hydrogen bonding pattern and the interactions between the aromatic groups held together by π - π non-covalent intermolecular interactions.

S2. Experimental

The title compound is commercially available. To purify it, it has been crystallized from a mixture of water and methanol (10:2). The crystals formed over a period of one week.

S3. Refinement

The H atoms, including those attached to nitrogen atoms, were all located in a difference map, and then repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.99-1.00, N—H = 0.85-0.94 Å) and $U_{\text{iso}}(\text{H})$ (in the range 1.3-1.8 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

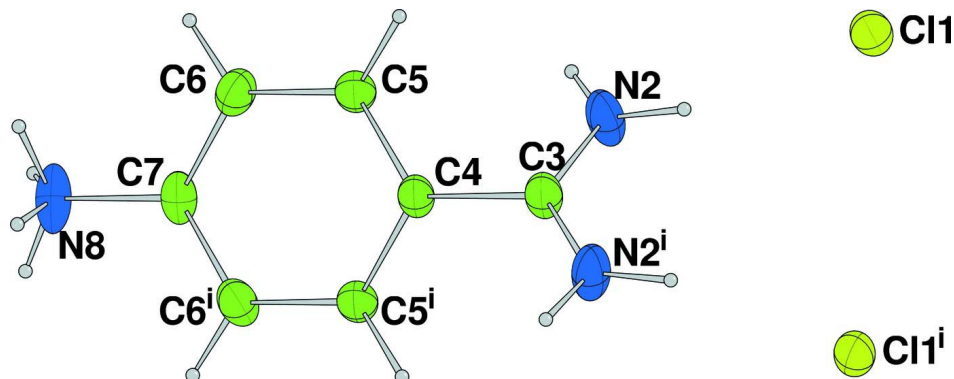


Figure 1

Representation of the structure of the title compound, with the numbering scheme adopted. The Cl atoms is light-green, the C atom green, the N atoms blue and the H atoms in grey. Displacement ellipsoids are drawn at the 50% probability level [symmetry code: (i) $-x, y, -z + 3/2$].

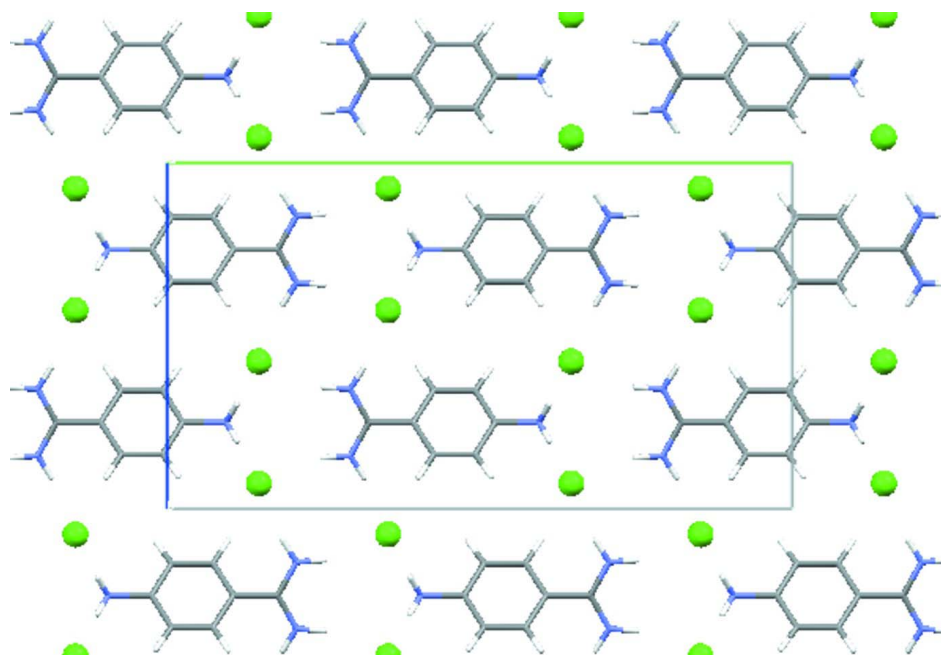


Figure 2

The two-dimensional framework of the title compound, viewed down the a cell direction.

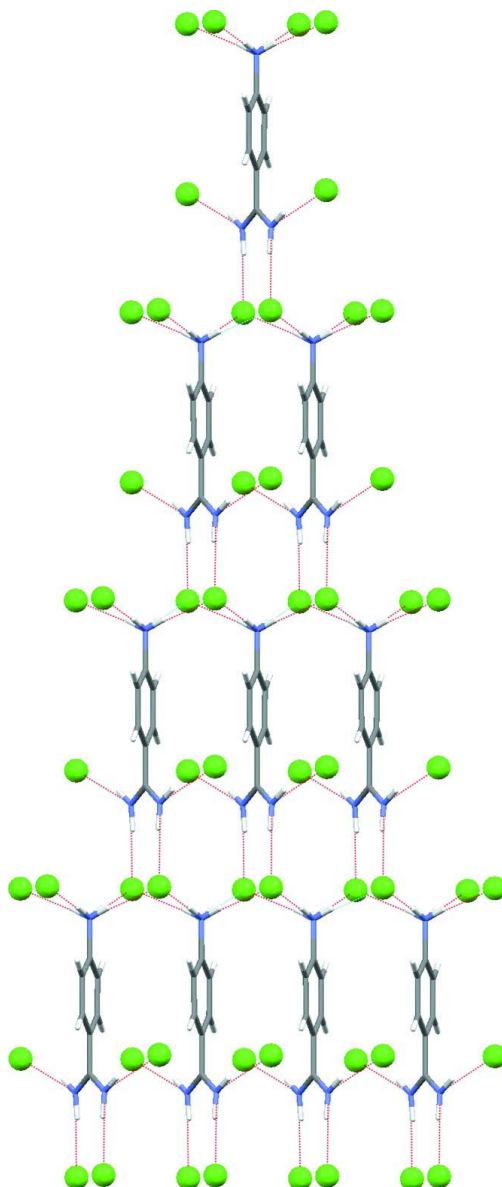


Figure 3

Representation of the hydrogen bonding network between the cations and the chloride anions, giving rise to a pyramidal scaffold architecture. Hydrogen bonds are denoted by dotted lines.

4-Ammoniobenzamidineium dichloride

Crystal data

$C_7H_{11}N_3^{2+} \cdot 2Cl^-$

$M_r = 208.09$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 4.1779 (2) \text{ \AA}$

$b = 20.9388 (10) \text{ \AA}$

$c = 11.6260 (5) \text{ \AA}$

$\beta = 94.920 (4)^\circ$

$V = 1013.30 (8) \text{ \AA}^3$

$Z = 4$

$F(000) = 432$

$D_x = 1.364 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 4424 reflections

$\theta = 4\text{--}32^\circ$

$\mu = 0.59 \text{ mm}^{-1}$

$T = 175$ K
Stick, colourless

$0.49 \times 0.09 \times 0.05$ mm

Data collection

Oxford Diffraction XCALIBUR
diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0143 pixels mm^{-1}
 ω scans

Absorption correction: multi-scan
(*CrysAlis RED*; Oxford Diffraction, 2007);
empirical (using intensity measurements)
absorption correction using spherical
harmonics, implemented in SCALE3
ABSPACK scaling algorithm

$T_{\min} = 0.95$, $T_{\max} = 0.97$

7752 measured reflections

1750 independent reflections

1144 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\max} = 32.7^\circ$, $\theta_{\min} = 3.9^\circ$

$h = -5 \rightarrow 6$

$k = -31 \rightarrow 29$

$l = -17 \rightarrow 15$

Refinement

Refinement on F

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.034$

$S = 1.01$

1144 reflections

59 parameters

2 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

Method, part 1, Chebychev polynomial [Watkin,
D. J. (1994). *Acta Cryst.* A50, 411-437. Prince,
E. (1982). *Mathematical Techniques in
Crystallography and Materials Science*. New
York: Springer-Verlag.] [weight] =
 $1.0/[A_0 * T_0(x) + A_1 * T_1(x) \dots + A_{n-1} * T_{n-1}(x)]$
where A_i are the Chebychev coefficients listed
below and $x = F / F_{\max}$ Method = Robust
Weighting (Prince, 1982) $W = [\text{weight}] * [1 - (\Delta F / 6 * \sigma F)^2]^2$ A_i are 20.0 -14.7 15.4

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C11	0.03602 (8)	0.146532 (14)	0.92627 (3)	0.0297	
N2	0.0839 (4)	0.29292 (6)	0.84632 (10)	0.0380	
C3	0.0000	0.32303 (8)	0.7500	0.0271	
C4	0.0000	0.39368 (8)	0.7500	0.0236	
C5	-0.1109 (3)	0.42664 (6)	0.84251 (11)	0.0282	
C6	-0.1138 (3)	0.49282 (6)	0.84200 (11)	0.0296	
C7	0.0000	0.52485 (8)	0.7500	0.0264	
N8	0.000000 (10)	0.59418 (7)	0.750000 (10)	0.0381	
H9	0.1600	0.3149	0.9089	0.0500*	
H10	0.0659	0.2491	0.8520	0.0500*	
H11	-0.1867	0.4022	0.9091	0.0500*	
H12	-0.1892	0.5181	0.9058	0.0500*	
H13	0.1342	0.6109	0.8006	0.0500*	0.7500
H14	-0.1333	0.6116	0.8033	0.0500*	0.7500

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.04130 (17)	0.02485 (14)	0.02214 (13)	-0.00435 (13)	-0.00233 (9)	-0.00073 (11)
N2	0.0652 (9)	0.0209 (5)	0.0252 (5)	-0.0030 (5)	-0.0122 (5)	0.0038 (4)
C3	0.0386 (9)	0.0198 (7)	0.0218 (7)	0.0000	-0.0043 (6)	0.0000
C4	0.0324 (9)	0.0184 (6)	0.0191 (6)	0.0000	-0.0030 (6)	0.0000
C5	0.0403 (7)	0.0236 (5)	0.0208 (5)	0.0006 (5)	0.0021 (4)	0.0000 (4)
C6	0.0379 (7)	0.0238 (6)	0.0265 (5)	0.0036 (5)	-0.0011 (4)	-0.0043 (4)
C7	0.0275 (8)	0.0180 (6)	0.0319 (8)	0.0000	-0.0074 (6)	0.0000
N8	0.0296 (8)	0.0177 (7)	0.0651 (12)	0.0000	-0.0072 (8)	0.0000

Geometric parameters (\AA , $^\circ$)

N2—C3	1.3064 (13)	C6—C7	1.3810 (16)
N2—H9	0.896	C6—H12	0.985
N2—H10	0.923	C7—N8	1.452 (2)
C3—C4	1.479 (2)	N8—H14 ⁱ	0.942
C4—C5	1.3904 (15)	N8—H13 ⁱ	0.852
C5—C6	1.3859 (18)	N8—H13	0.852
C5—H11	1.002	N8—H14	0.942
C3—N2—H9	120.0	C6—C7—N8	119.05 (8)
C3—N2—H10	121.5	C6 ⁱ —C7—N8	119.05 (8)
H9—N2—H10	118.5	C7—N8—H14 ⁱ	112.8
N2—C3—N2 ⁱ	122.30 (16)	C7—N8—H13 ⁱ	114.3
N2—C3—C4	118.85 (8)	H14 ⁱ —N8—H13 ⁱ	77.2
C3—C4—C5	119.75 (8)	C7—N8—H13	114.3
C5 ⁱ —C4—C5	120.49 (16)	H14 ⁱ —N8—H13	84.5
C4—C5—C6	119.76 (13)	H13 ⁱ —N8—H13	131.5
C4—C5—H11	119.5	C7—N8—H14	112.8
C6—C5—H11	120.7	H14 ⁱ —N8—H14	134.3
C5—C6—C7	119.04 (13)	H13 ⁱ —N8—H14	84.5
C5—C6—H12	122.5	H13—N8—H14	77.2
C7—C6—H12	118.5		
C(4)—C(5)—C(6)—C(7)	-1.2 (1)	C(5)—C(6)—C(7)—N(8)	-179.4 (1)
C(5)—C(4)—C(3)—N(2)	-40.2 (1)		

Symmetry code: (i) $-x, y, -z+3/2$.Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H9 \cdots C11 ⁱⁱ	0.90	2.35	3.2247 (13)	166
N2—H10 \cdots C11	0.92	2.32	3.2142 (13)	162
N8—H13 \cdots C11 ⁱⁱⁱ	0.85	2.26	3.1031 (6)	173

N8—H14···C11 ^{iv}	0.94	2.20	3.1369 (6)	176
C5—H11···C11 ^v	1.00	2.70	3.6806 (13)	165

Symmetry codes: (ii) $-x+1/2, -y+1/2, -z+2$; (iii) $x+1/2, y+1/2, z$; (iv) $x-1/2, y+1/2, z$; (v) $-x-1/2, -y+1/2, -z+2$.