

The hydrochloride and hydrobromide salt forms of (S)-amphetamine

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Abstract

(S)-Amphetamine hydrochloride, $C_9H_{14}ClN$, has a $Z' = 6$ structure with six independent cation, anion pairs. That these are indeed crystallographically independent is supported by different packing orientations of the cations and by observation of a wide range of cation conformations generated by rotation about the phenyl- CH_2 bond. The supramolecular contacts about the anions also differ such that both a wide variation in the geometry of the three $N-H\cdots Cl$ hydrogen bonds formed by each chloride anion and differences in $C-H\cdots Cl$ contacts are apparent. (S)-Amphetamine hydrobromide, $C_9H_{14}BrN$, is broadly similar to the chloride in terms of cation conformation, the existence of three $N-H\cdots X$ hydrogen bond contacts per anion and the overall 2 dimensional hydrogen bonded sheet motif. However, only the chloride structure features organic bilayers and $Z' > 1$.

1. Comment

Salt selection or salt screening is a common technique used in the pharmaceutical industry to improve the physicochemical properties of potential Active Pharmaceutical Ingredients (APIs, Stahl & Wermuth 2008). Studies on systematic series of crystal structures of phenylethylamine salts have been instigated with a view to determining relationships between crystal structure and the physicochemical properties of APIs (see for example Kennedy *et al.*, 2011; Black *et al.*, 2007; Briggs *et al.*, 2012; Cruickshank *et al.*, 2013). The ultimate goal of such studies is to understand and improve the pharmaceutical salt selection process. A member of the phenylethylamine class of molecules, amphetamine is popularly known as a stimulant and as a drug of abuse (Kilminster *et al.*, 1977), but it also has legitimate pharmaceutical roles for instance in the treatment of attention deficit hyperactivity disorder and of narcolepsy (Wood *et al.*, 2014). Despite the high profile of amphetamine, there have been relatively few structural studies of its salt forms. The sulfate has been crystallographically characterised and has been shown to undergo a temperature dependent phase transition (Pogorzelec-Glaser *et al.*, 2009) and additionally the crystal structures of a dihydrogen phosphate salt and a salt formed with a pyrazol derivative are known (Hebert, 1978; Reviriego *et al.*, 2006). The lack of any halide salt forms is surprising as the typical synthetic route for amphetamine initially produces the chloride salt. Additionally, the chloride salt is sometimes found in general circulation, although the sulfate salt is that most commonly seized by law enforcement agencies (United Nations, 2006). Structures are known for the chloride salts of structurally related drugs of abuse such as methylamphetamine (Hakey *et al.*, 2008) and the more complex, ring substituted species methylenedioxymethamphetamine (MDMA or ecstasy) and ethylone (Morimoto *et al.*, 1998 ; Cameron *et al.*, 2015).

Reaction of (S)-amphetamine free base with aqueous HCl or HBr gave (S)-amphetamine hydrochloride (I) and (S)-amphetamine hydrobromide (II), respectively. (I) is unusual in that it crystallises with six cations and six anions per unit cell in the space group P 1 ($Z = Z' = 6$), Figure 1. Structures with $Z' > 1$ have drawn much attention for their ability to shed light on fundamental aspects of crystal theory (Steed & Steed, 2015; Bernstein *et al.*, 2008). As discussed in the review by Steed and Steed (2015), (I) is in some ways a typical example of the type of species that gives $Z' > 1$ structures, being as it is a relatively small and enantiopure organic compound that crystallises in space group P1. Note that the diffraction data for (I) were non-merohedrally twinned by a 180° rotation about 001. This could be worrying as the presence of unidentified twinning can lead to false identification of structures with $Z' > 1$ (see for example Herstein, 1964).

However, inspection of Figure 2 shows that a $Z' = 1$ structure is not correct here. The cations in the layers parallel to the ac plane form two independent rows parallel to the c direction. In each row every third cation has a different orientation from the others, being rotated by approximately 180° along its phenyl to NH_3 axis.

The six independent cations of (I) also show distinct conformational variation. This is most easily seen with the C2C3C4C5 and C2C3C4C9 torsion angles (and their equivalents in other ions) which have ranges of -61.9 (5) to -69.3 (4) and 106.9 (4) to 115.4 (4) $^\circ$ for five of the six cations, see Table 2. The geometry of the sixth cation, that containing atom N5, lies significantly outside this range with equivalent angles of -52.7 (4) and 127.5 (3) $^\circ$. The cations all have *anti* conformations with NCCC torsion angles that lie within 3.5° of 180° . The previously described crystal structures of salt forms of amphetamine all have similar *anti* conformations (Herbert, 1978; Pogorzelec-Glaser *et al.*, 2009; Reviriego *et al.*, 2006) as does solution phase amphetamine (Neville *et al.*, 1971). The structure of the bromide salt (II) is shown in Figure 3. Here the torsion angles C2C3C4C5 and C2C3C4C9 are -75.2 (2) and 104.5 (2) $^\circ$. These values lie out-with the range seen for (I). The angle N1C2C3C4 is 158.84 (17) $^\circ$ for (II) and this too shows a modest conformational change from the range found for the cations of (I). These small differences do not however amount to evidence of two or more dramatically distinct conformer geometries as has been previously described for salt forms of related phenylethylamine species such as methylephedrine, pseudoephedrine and tyramine (Kennedy *et al.*, 2011; Black *et al.*, 2007; Briggs *et al.*, 2012).

All six crystallographically independent NH_3 groups in structure (I) utilise all three H atoms as single hydrogen bond donors. Both the H_2PO_4 salt and the room temperature phase of the SO_4 salt show similar hydrogen-bonding behaviour by the amphetamine cation (Pogorzelec-Glaser *et al.*, 2009; Hebert, 1978). Each NH_3 group in (I) thus bonds to three chloride anions, two of which are related to each other by translational symmetry with the third being independent, see Table 3. Although each anion and each cation is involved in three hydrogen bonding interactions, there are subtle differences in geometry. These are best shown by comparing the environment of C11 with that of C15. The N–H \cdots Cl angles of C15 are all near linear (169.4 to 171.3°) whilst the three angles about C11 are 145.0 , 158.9 and 167.9° . There are further small differences, for instance C12 makes a much shorter contact with a phenyl ring than any other chloride anion (C19–H19 \cdots C12 2.72 and 3.562 (5) \AA for H \cdots Cl and C \cdots Cl distances respectively). C15 has a similar but longer interaction whilst the other four anions do not make any such contact. The N–H \cdots Cl hydrogen bonds link all six fragments parallel to the crystallographic a and c directions. Both cations and anions act as three-connected nodes and so each 2 dimensional hydrogen bonded sheet can be described as a net with (6,3) topology. The packing structure can be seen in Figure 2, note the organic bilayers and the hydrophobic and hydrophilic layers that alternate parallel to the b axis.

Despite the larger size of bromide as compared to chloride, each bromide anion in (II) also makes three hydrogen bonds to three amphetamine cations, Table 4. As the cations also act as three-connected nodes this structure, like that of (I), features a net with (6,3) topology. In this case the 2 dimensional hydrogen bonded sheets are parallel to the ab plane. In contrast to (I) there are no C–H \cdots X contacts of less than the sum of van der Waals radii in (II). Figure 4 shows the resulting packing. Like (I) there are alternating hydrophobic and hydrophilic layers but the structure of (II) lacks the organic bilayers found in (I).

There are now structures available for five mineral acid derived salt forms of (S)-amphetamine, the chloride, bromide and dihydrogen phosphate forms together with the high and low temperature sulfate forms. All are layer structures with two dimensional hydrogen bonded hydrophilic layers alternating with organic, hydrophobic layers. A MERCURY packing analysis of the cation positions of the five structures suggests that on this basis only the two sulfate structures are related, having 18 matching cation positions from a cluster of 20 cations (RMS 0.791, Macrae *et al.*, 2008). The difference between the two sulfate structures is as follows. Like (I), both sulfate structures consist of organic bilayers. However, the low temperature sulfate structure has two structurally distinct organic bilayers constructed from four crystallographically

independent amphetamine cations (see Figure 5) whereas in the high temperature form all cations and hence all the organic layers are identical. The MERCURY packing analysis is thus highlighting the close match between the high temperature form's cation packing and the cation packing in only one of the two organic bilayers of the low temperature form. The packing in the second bilayer is different. Whilst (I) and the sulfate salt structures all feature organic bilayers, structure (II) and the H₂PO₄ salt structure do not. It is interesting that of the three bilayer structures, two have $Z' > 1$ and the third is disordered. Both the other structures have $Z' = 1$ and are well ordered. Within these five structures, the formation of organic bilayers is correlated with an inability to form simple $Z' = 1$ ordered structures.

Although in all five salt structures each hydrophilic layer is interconnected by hydrogen bonds between cations and anions (and for the H₂PO₄ salt between anions and anions too), there are few strong or close contacts within the organic layers. There are some weak C—H \cdots π contacts which seem to be influential in the transformation between the two sulfate phases (see Pogorzelec-Glaser *et al.*, 2009 for a discussion). All structures form cation stacks within the organic layers but the constituent cations in each case are too far apart to form a bonded supramolecular motif. The exception is the bromide salt, (II). Here a close $\pi\cdots\pi$ contact does exist (shortest C \cdots C distance 3.388 (3) Å for C6 to C9', ' = x+1, y, z) and this connects stacks of cations parallel to the crystallographic *a* direction.

2. Synthesis and crystallization

(S)-Amphetamine sulfate (0.25 g) was dissolved in 3 cm³ of deionized water. The pH of the solution was raised to approximately 12.5 by addition of sodium hydroxide solution and the organic product extracted into 5 cm³ of diethyl ether. Allowing the ether to evaporate yielded amphetamine free base as an oily residue. This oil was mixed with 2 cm² of water and a few drops of either concentrated HCl or HBr were added and the resulting solution was warmed slightly. After several days of slow evaporation, colourless crystals of (I) and (II) had developed.

3. Refinement

Crystallographic measurements for (I) and (II) were carried out by the National Crystallography Service (Coles & Gale, 2012). The data for (I) was treated as a non-merohedral twin by 180 ° rotation about 001. Applying the twin matrix -1 0 0 0 -1 0.682 0 0 1 within the *CrystalClear* software gave a reflection file in the *SHELX* hklf 5 format. The BASF parameter refined to 0.4431 (6). For both structures, H atoms bound to C atoms were placed in the expected geometric positions and treated in riding modes with C—H = 0.95, 0.98, 0.99 and 1.00 Å for *sp*² CH, methyl, CH₂ and *sp*³ CH respectively. $U(H)_{iso} = 1.5U(C)_{eq}$ for methyl groups and $1.2U(C)_{eq}$ for other CH groups. In (I) The H atoms of the NH₃ groups were similarly modeled with N—H = 0.91 Å and $U(H)_{iso} = 1.5U(N)_{eq}$. However, for (II) the H atoms bound to N were refined isotropically, see Tables 3 and 4.

Table 1

Experimental details

	(I)	(II)
Crystal data		
Chemical formula	C ₉ H ₁₄ N·Cl	C ₉ H ₁₄ N·Br
<i>M</i> _r	171.66	216.12
Crystal system, space group	Triclinic, <i>P</i> 1	Monoclinic, <i>P</i> 2 ₁
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.6396 (4), 16.3917 (11), 16.9602 (12)	5.2366 (4), 8.4264 (5), 11.3895 (8)
α , β , γ (°)	69.427 (4), 89.995 (5), 87.286 (5)	90, 94.079 (2), 90
<i>V</i> (Å ³)	1465.98 (18)	501.30 (6)
<i>Z</i>	6	2

Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.33	4.04
Crystal size (mm)	0.18 × 0.06 × 0.01	0.25 × 0.18 × 0.12
Data collection		
Diffractometer	Rigaku Saturn724+ (2x2 bin mode) diffractometer	Rigaku Saturn724+ (2x2 bin mode) diffractometer
Absorption correction	Multi-scan <i>CrystalClear</i> -SM Expert 3.1 (Rigaku, 2013)	Multi-scan <i>CrystalClear</i> -SM Expert 3.1 (Rigaku, 2013)
T_{\min} , T_{\max}	0.593, 1.000	0.711, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19328, 19328, 17180	5432, 2383, 2343
R_{int}	0.0000	0.019
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.699	0.705
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.129, 1.03	0.020, 0.052, 1.08
No. of reflections	19328	2383
No. of parameters	608	115
No. of restraints	3	1
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.60, -0.31	0.29, -0.39
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881	Flack H D (1983), Acta Cryst. A39, 876-881
Absolute structure parameter	0.01 (4)	0.003 (10)

Computer programs: *CrystalClear*-SM Expert 3.1 b27 (Rigaku, 2012), *SIR92* (Altomare *et al.*, 1994, *SIR97* (Altomare *et al.*, 1994, *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) & *Mercury* (Macrae *et al.*, 2008), *SHELXL97*.

Table 2

Selected torsion angles (°) for (I)

N1—C2—C3—C4	-177.0 (3)	N4—C32—C33—C34	-179.0 (3)
C2—C3—C4—C5	-69.3 (4)	C31—C32—C33—C34	-57.9 (4)
C2—C3—C4—C9	106.9 (4)	C32—C33—C34—C39	109.7 (4)
N2—C12—C13—C14	176.7 (3)	N5—C52—C53—C54	179.3 (3)
C12—C13—C14—C15	115.4 (4)	C52—C53—C54—C59	-52.7 (4)
C12—C13—C14—C19	-61.9 (5)	C52—C53—C54—C55	127.5 (3)
N3—C22—C23—C24	177.6 (3)	N6—C62—C63—C64	178.6 (3)
C21—C22—C23—C24	-61.3 (4)	C62—C63—C64—C65	-63.9 (4)
C22—C23—C24—C29	113.2 (4)	C62—C63—C64—C69	114.7 (4)

Table 3

Hydrogen-bond geometry (Å, °) for (I)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots Cl5 ⁱ	0.91	2.40	3.304 (3)	171
N1—H1B \cdots Cl5 ⁱⁱ	0.91	2.27	3.177 (3)	171
N1—H1C \cdots Cl6 ⁱ	0.91	2.28	3.181 (3)	169
N2—H2A \cdots Cl6 ⁱⁱⁱ	0.91	2.27	3.179 (3)	174
N2—H2B \cdots Cl1 ^{iv}	0.91	2.43	3.215 (3)	145
N2—H2C \cdots Cl6 ⁱ	0.91	2.37	3.233 (3)	158

N3—H3A···Cl1 ^{iv}	0.91	2.28	3.151 (3)	159
N3—H3B···Cl1	0.91	2.22	3.118 (3)	168
N3—H3C···Cl2	0.91	2.27	3.171 (3)	169
N4—H4A···Cl2	0.91	2.25	3.149 (3)	168
N4—H4B···Cl3	0.91	2.26	3.164 (3)	172
N4—H4C···Cl2 ^v	0.91	2.37	3.271 (3)	171
N5—H5A···Cl3	0.91	2.27	3.159 (3)	165
N5—H5B···Cl4	0.91	2.36	3.196 (3)	153
N5—H5C···Cl3 ^{iv}	0.91	2.33	3.233 (3)	170
N6—H6A···Cl4	0.91	2.22	3.117 (3)	167
N6—H6B···Cl5 ^v	0.91	2.27	3.168 (3)	169
N6—H6C···Cl4 ^v	0.91	2.29	3.158 (3)	161

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

Table 4

Hydrogen-bond geometry (Å, °) for (II)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N···Br1 ⁱ	0.83 (3)	2.54 (3)	3.3080 (19)	154 (2)
N1—H2N···Br1 ⁱⁱ	0.93 (3)	2.36 (3)	3.2656 (19)	165 (3)
N1—H3N···Br1	0.94 (3)	2.44 (3)	3.3296 (18)	157 (3)

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

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Figure 1

Figure 1. The molecular structure of (I) with non-H atoms shown as 50% probability ellipsoids.

Figure 2

Figure 2. Packing structure of (I) viewed down the crystallographic a direction. The red and blue ellipsoids highlight the different cation orientations found in a cation row parallel to c . The neighbouring cation row of the same organic bilayer has a similar 2 to 1 arrangement of cation orientations.

Figure 3

Figure 3. The molecular structure of (II) with non-H atoms shown as 50% probability ellipsoids.

Figure 4

Figure 4. Packing structure of (II) viewed down the crystallographic a direction. Note that the organic bilayers shown in Figure 3 are absent here.

Figure 5

Figure 5. Packing structure of the low temperature form of (s)-amphetamine sulfate drawn from AMPETS01. Note that the organic bilayers at $c = 0$ and $c = 1$ differ from the bilayer at $c = 0.5$.

supplementary materials

The hydrochloride and hydrobromide salt forms of (S)-amphetamine

Computing details

For both compounds, data collection: *CrystalClear-SM Expert 3.1 b27* (Rigaku, 2012); cell refinement: *CrystalClear-SM Expert 3.1 b27* (Rigaku, 2012); data reduction: *CrystalClear-SM Expert 3.1 b27* (Rigaku, 2012). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994 for (I); *SIR97* (Altomare *et al.*, 1994 for (II). For both compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) & *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

(I)

Crystal data

$C_9H_{14}N \cdot Cl$	$Z = 6$
$M_r = 171.66$	$F(000) = 552$
Triclinic, $P1$	$D_x = 1.167 \text{ Mg m}^{-3}$
Hall symbol: $P1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 5.6396 (4) \text{ \AA}$	Cell parameters from 24532 reflections
$b = 16.3917 (11) \text{ \AA}$	$\theta = 2.1\text{--}27.5^\circ$
$c = 16.9602 (12) \text{ \AA}$	$\mu = 0.33 \text{ mm}^{-1}$
$\alpha = 69.427 (4)^\circ$	$T = 100 \text{ K}$
$\beta = 89.995 (5)^\circ$	Blade, colourless
$\gamma = 87.286 (5)^\circ$	$0.18 \times 0.06 \times 0.01 \text{ mm}$
$V = 1465.98 (18) \text{ \AA}^3$	

Data collection

Rigaku Saturn724+ (2x2 bin mode) diffractometer	19328 measured reflections
Radiation source: fine-focus sealed tube	19328 independent reflections
Graphite monochromator	17180 reflections with $I > 2\sigma(I)$
Detector resolution: $28.5714 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.0000$
profile data from ω -scans	$\theta_{\text{max}} = 29.8^\circ$, $\theta_{\text{min}} = 1.5^\circ$
Absorption correction: multi-scan	$h = -7 \rightarrow 7$
CrystalClear-SM Expert 3.1 (Rigaku, 2013)	$k = -22 \rightarrow 22$
$T_{\text{min}} = 0.593$, $T_{\text{max}} = 1.000$	$l = -23 \rightarrow 22$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.055$	$w = 1/[\sigma^2(F_o^2) + (0.070P)^2 + 0.9426P]$
$wR(F^2) = 0.129$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{\text{max}} = 0.001$
19328 reflections	$\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$
608 parameters	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
3 restraints	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.01 (4)
Secondary atom site location: difference Fourier map	

Special details

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) for (I)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	-0.06769 (12)	1.62848 (5)	0.75422 (6)	0.02168 (17)
Cl2	0.53180 (13)	1.80851 (5)	0.53529 (6)	0.02264 (18)
Cl3	0.06999 (12)	1.61130 (5)	0.42734 (5)	0.01902 (16)
Cl4	0.41074 (12)	1.78429 (5)	0.20307 (5)	0.01911 (16)
Cl5	0.80481 (13)	1.59774 (5)	0.10755 (5)	0.02096 (17)
Cl6	0.27312 (12)	1.80318 (5)	-0.14216 (5)	0.02188 (17)
N1	0.2889 (5)	1.61990 (18)	1.00800 (18)	0.0206 (6)
H1A	0.4237	1.6091	1.0403	0.031*
H1B	0.1600	1.6125	1.0417	0.031*
H1C	0.2850	1.6757	0.9708	0.031*
N2	0.7768 (5)	1.81575 (18)	0.76431 (19)	0.0231 (6)
H2A	0.9174	1.8162	0.7905	0.035*
H2B	0.7879	1.7752	0.7390	0.035*
H2C	0.6596	1.8023	0.8030	0.035*
N3	0.4294 (5)	1.62596 (18)	0.67440 (17)	0.0176 (6)
H3A	0.5599	1.6148	0.7088	0.026*
H3B	0.2964	1.6246	0.7051	0.026*
H3C	0.4372	1.6796	0.6338	0.026*
N4	0.0460 (5)	1.79490 (17)	0.45030 (18)	0.0189 (6)
H4A	0.1729	1.8016	0.4803	0.028*
H4B	0.0523	1.7398	0.4491	0.028*
H4C	-0.0906	1.8043	0.4751	0.028*
N5	0.5642 (5)	1.60012 (17)	0.34301 (17)	0.0172 (6)
H5A	0.4378	1.6004	0.3763	0.026*
H5B	0.5403	1.6431	0.2919	0.026*
H5C	0.6984	1.6095	0.3677	0.026*
N6	-0.0844 (5)	1.77880 (17)	0.12398 (17)	0.0182 (6)
H6A	0.0471	1.7787	0.1551	0.027*
H6B	-0.0951	1.7253	0.1196	0.027*
H6C	-0.2158	1.7913	0.1496	0.027*
C1	0.5080 (7)	1.5677 (3)	0.9095 (3)	0.0304 (9)
H1D	0.5137	1.6283	0.8710	0.046*
H1E	0.5085	1.5288	0.8770	0.046*
H1F	0.6469	1.5529	0.9476	0.046*
C2	0.2852 (6)	1.5573 (2)	0.9602 (2)	0.0203 (7)
H2	0.1446	1.5733	0.9209	0.024*
C3	0.2596 (6)	1.4649 (2)	1.0243 (2)	0.0228 (7)
H3D	0.3895	1.4511	1.0670	0.027*
H3E	0.1072	1.4628	1.0538	0.027*
C4	0.2671 (6)	1.3968 (2)	0.9828 (2)	0.0203 (7)
C5	0.0827 (6)	1.3923 (2)	0.9303 (2)	0.0218 (7)
H5	-0.0537	1.4309	0.9220	0.026*
C6	0.0963 (6)	1.3318 (2)	0.8898 (2)	0.0233 (8)
H6	-0.0311	1.3290	0.8543	0.028*

C7	0.2959 (6)	1.2751 (2)	0.9009 (3)	0.0226 (8)
H7	0.3054	1.2338	0.8732	0.027*
C8	0.4794 (7)	1.2797 (2)	0.9526 (2)	0.0244 (8)
H8	0.6153	1.2410	0.9608	0.029*
C9	0.4681 (6)	1.3400 (2)	0.9928 (2)	0.0215 (8)
H9	0.5974	1.3430	1.0274	0.026*
C11	0.6831 (8)	1.9714 (3)	0.7410 (3)	0.0401 (10)
H11A	0.8307	1.9747	0.7700	0.060*
H11B	0.5562	1.9535	0.7821	0.060*
H11C	0.6392	2.0288	0.6990	0.060*
C12	0.7190 (7)	1.9059 (3)	0.6978 (2)	0.0289 (8)
H12	0.5661	1.9034	0.6691	0.035*
C13	0.9113 (7)	1.9288 (3)	0.6319 (2)	0.0299 (8)
H13A	0.9293	1.8826	0.6070	0.036*
H13B	1.0646	1.9319	0.6589	0.036*
C14	0.8476 (7)	2.0172 (2)	0.5618 (2)	0.0292 (8)
C15	0.9846 (8)	2.0886 (3)	0.5489 (3)	0.0479 (12)
H15	1.1239	2.0830	0.5822	0.057*
C16	0.9201 (9)	2.1672 (3)	0.4881 (3)	0.0502 (13)
H16	1.0156	2.2156	0.4798	0.060*
C17	0.7193 (7)	2.1771 (3)	0.4391 (2)	0.0342 (9)
H17	0.6785	2.2315	0.3962	0.041*
C18	0.5783 (7)	2.1078 (2)	0.4525 (3)	0.0368 (9)
H18	0.4352	2.1150	0.4207	0.044*
C19	0.6437 (7)	2.0277 (2)	0.5121 (3)	0.0356 (9)
H19	0.5489	1.9793	0.5194	0.043*
C21	0.6330 (6)	1.5667 (2)	0.5781 (2)	0.0235 (8)
H21A	0.6239	1.6241	0.5331	0.035*
H21B	0.6340	1.5210	0.5532	0.035*
H21C	0.7789	1.5604	0.6115	0.035*
C22	0.4206 (6)	1.5584 (2)	0.6341 (2)	0.0157 (6)
H22	0.2732	1.5702	0.5983	0.019*
C23	0.4086 (6)	1.4677 (2)	0.7034 (2)	0.0227 (7)
H23A	0.5530	1.4557	0.7396	0.027*
H23B	0.2697	1.4678	0.7390	0.027*
C24	0.3889 (6)	1.3964 (2)	0.6675 (2)	0.0192 (7)
C25	0.1894 (6)	1.3917 (2)	0.6201 (3)	0.0270 (8)
H25	0.0620	1.4341	0.6117	0.032*
C26	0.1718 (6)	1.3279 (2)	0.5856 (2)	0.0272 (8)
H26	0.0332	1.3263	0.5544	0.033*
C27	0.3570 (6)	1.2656 (2)	0.5963 (2)	0.0230 (8)
H27	0.3461	1.2215	0.5723	0.028*
C28	0.5574 (6)	1.2685 (2)	0.6422 (2)	0.0261 (8)
H28	0.6856	1.2266	0.6495	0.031*
C29	0.5706 (6)	1.3334 (2)	0.6780 (2)	0.0235 (7)
H29	0.7077	1.3342	0.7102	0.028*
C31	-0.1718 (7)	1.8495 (2)	0.3151 (2)	0.0286 (9)
H31A	-0.1736	1.7897	0.3151	0.043*
H31B	-0.1710	1.8905	0.2569	0.043*
H31C	-0.3133	1.8620	0.3432	0.043*
C32	0.0519 (6)	1.8592 (2)	0.3622 (2)	0.0173 (7)
H32	0.1942	1.8440	0.3340	0.021*
C33	0.0743 (6)	1.9512 (2)	0.3631 (2)	0.0214 (7)
H33A	-0.0604	1.9657	0.3941	0.026*

H33B	0.2228	1.9533	0.3933	0.026*
C34	0.0766 (6)	2.0180 (2)	0.2751 (2)	0.0201 (7)
C35	0.2649 (6)	2.0187 (2)	0.2217 (2)	0.0243 (8)
H35	0.3973	1.9786	0.2420	0.029*
C36	0.2624 (7)	2.0769 (2)	0.1395 (3)	0.0281 (8)
H36	0.3936	2.0767	0.1044	0.034*
C37	0.0690 (6)	2.1358 (2)	0.1077 (2)	0.0244 (8)
H37	0.0669	2.1752	0.0511	0.029*
C38	-0.1205 (7)	2.1360 (2)	0.1599 (2)	0.0252 (8)
H38	-0.2535	2.1757	0.1392	0.030*
C39	-0.1148 (6)	2.0778 (2)	0.2431 (2)	0.0214 (7)
H39	-0.2443	2.0789	0.2786	0.026*
C51	0.6355 (6)	1.4427 (2)	0.4188 (2)	0.0221 (7)
H51A	0.7810	1.4542	0.4438	0.033*
H51B	0.6528	1.3852	0.4131	0.033*
H51C	0.5011	1.4437	0.4551	0.033*
C52	0.5907 (5)	1.5130 (2)	0.3317 (2)	0.0169 (6)
H52	0.7312	1.5129	0.2957	0.020*
C53	0.3662 (6)	1.5002 (2)	0.2866 (2)	0.0210 (7)
H53A	0.2261	1.5023	0.3212	0.025*
H53B	0.3453	1.5488	0.2319	0.025*
C54	0.3771 (6)	1.4147 (2)	0.2712 (2)	0.0199 (7)
C55	0.1915 (6)	1.3571 (2)	0.2974 (2)	0.0270 (8)
H55	0.0617	1.3712	0.3268	0.032*
C56	0.1967 (6)	1.2795 (2)	0.2806 (2)	0.0302 (8)
H56	0.0693	1.2416	0.2980	0.036*
C57	0.3853 (6)	1.2574 (2)	0.2389 (2)	0.0264 (8)
H57	0.3864	1.2053	0.2264	0.032*
C58	0.5734 (6)	1.3121 (2)	0.2154 (2)	0.0234 (7)
H58	0.7063	1.2961	0.1886	0.028*
C59	0.5690 (6)	1.3899 (2)	0.2307 (2)	0.0212 (7)
H59	0.6982	1.4270	0.2134	0.025*
C61	-0.2773 (6)	1.8390 (2)	-0.0155 (2)	0.0241 (8)
H61A	-0.2662	1.7821	-0.0225	0.036*
H61B	-0.2750	1.8855	-0.0708	0.036*
H61C	-0.4257	1.8448	0.0126	0.036*
C62	-0.0668 (6)	1.8463 (2)	0.0380 (2)	0.0181 (7)
H62	0.0833	1.8338	0.0120	0.022*
C63	-0.0560 (6)	1.9360 (2)	0.0462 (2)	0.0202 (7)
H63A	-0.2022	1.9480	0.0734	0.024*
H63B	0.0807	1.9354	0.0831	0.024*
C64	-0.0316 (6)	2.0087 (2)	-0.0382 (2)	0.0187 (7)
C65	0.1685 (6)	2.0117 (2)	-0.0867 (3)	0.0257 (8)
H65	0.2927	1.9680	-0.0661	0.031*
C66	0.1908 (6)	2.0772 (2)	-0.1647 (3)	0.0265 (9)
H66	0.3303	2.0780	-0.1963	0.032*
C67	0.0122 (6)	2.1413 (2)	-0.1967 (3)	0.0222 (8)
H67	0.0275	2.1860	-0.2500	0.027*
C68	-0.1906 (6)	2.1390 (2)	-0.1493 (3)	0.0231 (8)
H68	-0.3157	2.1821	-0.1708	0.028*
C69	-0.2120 (6)	2.0741 (2)	-0.0708 (2)	0.0219 (8)
H69	-0.3504	2.0740	-0.0388	0.026*

Atomic displacement parameters (\AA^2) for (I)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0149 (4)	0.0286 (4)	0.0238 (4)	-0.0002 (3)	0.0020 (3)	-0.0123 (4)
Cl2	0.0184 (4)	0.0175 (4)	0.0292 (5)	-0.0041 (3)	-0.0007 (3)	-0.0042 (4)
Cl3	0.0159 (4)	0.0193 (4)	0.0221 (4)	-0.0018 (3)	0.0022 (3)	-0.0074 (3)
Cl4	0.0146 (3)	0.0194 (4)	0.0205 (4)	0.0010 (3)	-0.0025 (3)	-0.0038 (4)
Cl5	0.0218 (4)	0.0171 (4)	0.0239 (4)	-0.0034 (3)	0.0064 (3)	-0.0067 (4)
Cl6	0.0176 (4)	0.0209 (4)	0.0259 (4)	-0.0021 (3)	0.0013 (3)	-0.0065 (4)
N1	0.0214 (14)	0.0191 (14)	0.0227 (16)	0.0005 (11)	0.0057 (12)	-0.0092 (13)
N2	0.0184 (14)	0.0227 (15)	0.0293 (17)	-0.0036 (11)	0.0017 (12)	-0.0104 (13)
N3	0.0147 (13)	0.0219 (14)	0.0170 (14)	-0.0023 (11)	0.0035 (11)	-0.0075 (12)
N4	0.0147 (13)	0.0175 (14)	0.0252 (16)	-0.0031 (10)	-0.0018 (12)	-0.0083 (12)
N5	0.0137 (13)	0.0159 (13)	0.0195 (14)	-0.0023 (10)	-0.0036 (11)	-0.0028 (11)
N6	0.0137 (13)	0.0166 (13)	0.0226 (15)	0.0022 (10)	-0.0021 (11)	-0.0053 (12)
C1	0.032 (2)	0.028 (2)	0.034 (2)	-0.0059 (16)	0.0145 (18)	-0.0135 (18)
C2	0.0263 (18)	0.0133 (15)	0.0204 (18)	-0.0026 (13)	0.0025 (14)	-0.0047 (14)
C3	0.0308 (19)	0.0196 (17)	0.0169 (17)	0.0021 (14)	0.0065 (14)	-0.0055 (14)
C4	0.0230 (18)	0.0187 (17)	0.0184 (18)	-0.0029 (14)	0.0075 (15)	-0.0054 (14)
C5	0.0167 (16)	0.0210 (17)	0.0236 (19)	0.0006 (13)	0.0034 (14)	-0.0030 (15)
C6	0.0200 (17)	0.0263 (19)	0.0244 (19)	-0.0064 (14)	0.0043 (14)	-0.0094 (16)
C7	0.0276 (18)	0.0171 (17)	0.026 (2)	-0.0047 (14)	0.0118 (16)	-0.0115 (15)
C8	0.0225 (18)	0.0213 (18)	0.030 (2)	0.0026 (14)	0.0007 (16)	-0.0103 (16)
C9	0.0218 (17)	0.0197 (17)	0.0224 (19)	-0.0027 (14)	0.0014 (15)	-0.0067 (15)
C11	0.052 (3)	0.022 (2)	0.042 (3)	-0.0041 (18)	0.003 (2)	-0.0064 (19)
C12	0.0269 (19)	0.035 (2)	0.0187 (18)	-0.0052 (15)	-0.0022 (14)	-0.0008 (16)
C13	0.0233 (18)	0.036 (2)	0.028 (2)	-0.0033 (15)	0.0006 (15)	-0.0084 (17)
C14	0.0292 (19)	0.032 (2)	0.0250 (19)	-0.0063 (15)	0.0063 (15)	-0.0074 (16)
C15	0.050 (3)	0.045 (3)	0.039 (2)	-0.022 (2)	-0.018 (2)	0.001 (2)
C16	0.065 (3)	0.034 (2)	0.045 (3)	-0.024 (2)	-0.017 (2)	-0.004 (2)
C17	0.047 (2)	0.0264 (19)	0.029 (2)	0.0000 (16)	-0.0053 (17)	-0.0091 (16)
C18	0.036 (2)	0.0252 (19)	0.046 (2)	0.0041 (15)	-0.0166 (18)	-0.0090 (18)
C19	0.036 (2)	0.0243 (19)	0.044 (2)	-0.0054 (16)	-0.0046 (18)	-0.0087 (18)
C21	0.0243 (18)	0.0213 (18)	0.0258 (19)	-0.0052 (14)	0.0102 (15)	-0.0089 (15)
C22	0.0164 (15)	0.0149 (15)	0.0163 (16)	0.0003 (12)	0.0004 (13)	-0.0063 (13)
C23	0.0258 (17)	0.0212 (17)	0.0195 (18)	-0.0011 (13)	0.0060 (14)	-0.0052 (15)
C24	0.0252 (17)	0.0140 (15)	0.0161 (16)	-0.0050 (12)	0.0053 (14)	-0.0020 (13)
C25	0.0191 (17)	0.0233 (18)	0.035 (2)	0.0036 (14)	-0.0019 (16)	-0.0069 (17)
C26	0.0180 (17)	0.0275 (19)	0.034 (2)	-0.0032 (14)	-0.0056 (15)	-0.0077 (17)
C27	0.0261 (18)	0.0172 (17)	0.024 (2)	-0.0054 (14)	0.0044 (15)	-0.0044 (15)
C28	0.0272 (18)	0.0183 (17)	0.031 (2)	0.0024 (14)	-0.0023 (16)	-0.0065 (16)
C29	0.0214 (17)	0.0222 (17)	0.0235 (18)	0.0033 (13)	-0.0071 (15)	-0.0042 (15)
C31	0.0279 (19)	0.029 (2)	0.027 (2)	-0.0052 (16)	-0.0126 (16)	-0.0062 (17)
C32	0.0166 (15)	0.0174 (16)	0.0160 (16)	0.0004 (12)	-0.0020 (14)	-0.0034 (14)
C33	0.0229 (17)	0.0184 (17)	0.0240 (19)	0.0016 (13)	-0.0013 (14)	-0.0091 (14)
C34	0.0237 (17)	0.0141 (16)	0.0232 (19)	-0.0033 (13)	-0.0020 (15)	-0.0072 (15)
C35	0.0197 (17)	0.0196 (18)	0.031 (2)	0.0003 (14)	-0.0020 (15)	-0.0051 (16)
C36	0.0265 (19)	0.0261 (19)	0.031 (2)	-0.0034 (15)	0.0041 (16)	-0.0087 (17)
C37	0.0303 (19)	0.0176 (17)	0.024 (2)	-0.0077 (14)	0.0029 (16)	-0.0051 (15)
C38	0.0291 (19)	0.0161 (17)	0.029 (2)	0.0020 (14)	-0.0066 (16)	-0.0070 (15)
C39	0.0215 (17)	0.0181 (17)	0.0256 (19)	0.0027 (13)	0.0030 (14)	-0.0093 (15)
C51	0.0283 (18)	0.0178 (16)	0.0175 (17)	0.0020 (13)	-0.0015 (14)	-0.0030 (14)
C52	0.0154 (15)	0.0163 (15)	0.0186 (16)	0.0002 (12)	0.0015 (12)	-0.0060 (13)
C53	0.0213 (16)	0.0190 (16)	0.0238 (18)	0.0003 (12)	-0.0024 (13)	-0.0089 (14)

C54	0.0198 (16)	0.0241 (17)	0.0138 (15)	0.0016 (13)	-0.0068 (13)	-0.0044 (13)
C55	0.0155 (16)	0.030 (2)	0.038 (2)	0.0026 (14)	-0.0013 (15)	-0.0166 (17)
C56	0.0223 (18)	0.0277 (19)	0.043 (2)	-0.0042 (14)	-0.0064 (16)	-0.0151 (18)
C57	0.0308 (19)	0.0200 (17)	0.030 (2)	0.0026 (14)	-0.0103 (16)	-0.0118 (15)
C58	0.0292 (17)	0.0209 (16)	0.0196 (17)	0.0050 (13)	-0.0034 (14)	-0.0074 (14)
C59	0.0231 (16)	0.0242 (17)	0.0160 (16)	-0.0005 (13)	-0.0016 (13)	-0.0067 (14)
C61	0.0254 (18)	0.0212 (18)	0.0227 (19)	-0.0039 (14)	-0.0039 (15)	-0.0038 (15)
C62	0.0202 (16)	0.0149 (16)	0.0173 (17)	0.0004 (12)	-0.0047 (14)	-0.0033 (13)
C63	0.0266 (18)	0.0129 (16)	0.0189 (17)	0.0009 (13)	-0.0033 (14)	-0.0032 (13)
C64	0.0205 (16)	0.0107 (15)	0.0245 (19)	0.0004 (12)	-0.0031 (15)	-0.0056 (14)
C65	0.0183 (17)	0.0172 (17)	0.036 (2)	0.0031 (13)	-0.0027 (16)	-0.0028 (16)
C66	0.0209 (18)	0.0183 (18)	0.039 (2)	-0.0041 (13)	0.0080 (16)	-0.0077 (16)
C67	0.0259 (19)	0.0143 (17)	0.024 (2)	-0.0054 (13)	0.0019 (15)	-0.0033 (15)
C68	0.0200 (17)	0.0156 (17)	0.030 (2)	0.0054 (13)	-0.0030 (15)	-0.0048 (15)
C69	0.0218 (17)	0.0144 (16)	0.030 (2)	-0.0026 (13)	0.0062 (15)	-0.0081 (15)

Geometric parameters (Å, °) for (I)

N1—C2	1.515 (4)	C23—H23B	0.9900
N1—H1A	0.9100	C24—C29	1.385 (5)
N1—H1B	0.9100	C24—C25	1.403 (5)
N1—H1C	0.9100	C25—C26	1.374 (5)
N2—C12	1.531 (5)	C25—H25	0.9500
N2—H2A	0.9100	C26—C27	1.391 (5)
N2—H2B	0.9100	C26—H26	0.9500
N2—H2C	0.9100	C27—C28	1.385 (5)
N3—C22	1.494 (4)	C27—H27	0.9500
N3—H3A	0.9100	C28—C29	1.403 (5)
N3—H3B	0.9100	C28—H28	0.9500
N3—H3C	0.9100	C29—H29	0.9500
N4—C32	1.497 (4)	C31—C32	1.537 (5)
N4—H4A	0.9100	C31—H31A	0.9800
N4—H4B	0.9100	C31—H31B	0.9800
N4—H4C	0.9100	C31—H31C	0.9800
N5—C52	1.508 (4)	C32—C33	1.525 (4)
N5—H5A	0.9100	C32—H32	1.0000
N5—H5B	0.9100	C33—C34	1.511 (5)
N5—H5C	0.9100	C33—H33A	0.9900
N6—C62	1.495 (4)	C33—H33B	0.9900
N6—H6A	0.9100	C34—C35	1.394 (5)
N6—H6B	0.9100	C34—C39	1.395 (5)
N6—H6C	0.9100	C35—C36	1.385 (5)
C1—C2	1.505 (5)	C35—H35	0.9500
C1—H1D	0.9800	C36—C37	1.395 (5)
C1—H1E	0.9800	C36—H36	0.9500
C1—H1F	0.9800	C37—C38	1.389 (5)
C2—C3	1.537 (4)	C37—H37	0.9500
C2—H2	1.0000	C38—C39	1.397 (5)
C3—C4	1.514 (5)	C38—H38	0.9500
C3—H3D	0.9900	C39—H39	0.9500
C3—H3E	0.9900	C51—C52	1.534 (4)
C4—C5	1.390 (5)	C51—H51A	0.9800
C4—C9	1.404 (5)	C51—H51B	0.9800
C5—C6	1.391 (5)	C51—H51C	0.9800

C5—H5	0.9500	C52—C53	1.539 (4)
C6—C7	1.394 (5)	C52—H52	1.0000
C6—H6	0.9500	C53—C54	1.511 (5)
C7—C8	1.378 (6)	C53—H53A	0.9900
C7—H7	0.9500	C53—H53B	0.9900
C8—C9	1.382 (5)	C54—C59	1.401 (5)
C8—H8	0.9500	C54—C55	1.408 (5)
C9—H9	0.9500	C55—C56	1.397 (5)
C11—C12	1.504 (5)	C55—H55	0.9500
C11—H11A	0.9800	C56—C57	1.381 (5)
C11—H11B	0.9800	C56—H56	0.9500
C11—H11C	0.9800	C57—C58	1.388 (5)
C12—C13	1.521 (5)	C57—H57	0.9500
C12—H12	1.0000	C58—C59	1.388 (5)
C13—C14	1.543 (5)	C58—H58	0.9500
C13—H13A	0.9900	C59—H59	0.9500
C13—H13B	0.9900	C61—C62	1.528 (5)
C14—C15	1.385 (5)	C61—H61A	0.9800
C14—C19	1.393 (5)	C61—H61B	0.9800
C15—C16	1.370 (6)	C61—H61C	0.9800
C15—H15	0.9500	C62—C63	1.529 (4)
C16—C17	1.374 (6)	C62—H62	1.0000
C16—H16	0.9500	C63—C64	1.518 (5)
C17—C18	1.369 (5)	C63—H63A	0.9900
C17—H17	0.9500	C63—H63B	0.9900
C18—C19	1.380 (5)	C64—C65	1.389 (5)
C18—H18	0.9500	C64—C69	1.403 (5)
C19—H19	0.9500	C65—C66	1.391 (5)
C21—C22	1.511 (5)	C65—H65	0.9500
C21—H21A	0.9800	C66—C67	1.382 (5)
C21—H21B	0.9800	C66—H66	0.9500
C21—H21C	0.9800	C67—C68	1.392 (5)
C22—C23	1.542 (4)	C67—H67	0.9500
C22—H22	1.0000	C68—C69	1.392 (5)
C23—C24	1.505 (5)	C68—H68	0.9500
C23—H23A	0.9900	C69—H69	0.9500
C2—N1—H1A	109.5	C29—C24—C25	116.9 (3)
C2—N1—H1B	109.5	C29—C24—C23	121.3 (3)
H1A—N1—H1B	109.5	C25—C24—C23	121.8 (3)
C2—N1—H1C	109.5	C26—C25—C24	122.3 (3)
H1A—N1—H1C	109.5	C26—C25—H25	118.8
H1B—N1—H1C	109.5	C24—C25—H25	118.8
C12—N2—H2A	109.5	C25—C26—C27	119.9 (3)
C12—N2—H2B	109.5	C25—C26—H26	120.0
H2A—N2—H2B	109.5	C27—C26—H26	120.0
C12—N2—H2C	109.5	C28—C27—C26	119.4 (4)
H2A—N2—H2C	109.5	C28—C27—H27	120.3
H2B—N2—H2C	109.5	C26—C27—H27	120.3
C22—N3—H3A	109.5	C27—C28—C29	119.8 (3)
C22—N3—H3B	109.5	C27—C28—H28	120.1
H3A—N3—H3B	109.5	C29—C28—H28	120.1
C22—N3—H3C	109.5	C24—C29—C28	121.7 (3)
H3A—N3—H3C	109.5	C24—C29—H29	119.2

H3B—N3—H3C	109.5	C28—C29—H29	119.2
C32—N4—H4A	109.5	C32—C31—H31A	109.5
C32—N4—H4B	109.5	C32—C31—H31B	109.5
H4A—N4—H4B	109.5	H31A—C31—H31B	109.5
C32—N4—H4C	109.5	C32—C31—H31C	109.5
H4A—N4—H4C	109.5	H31A—C31—H31C	109.5
H4B—N4—H4C	109.5	H31B—C31—H31C	109.5
C52—N5—H5A	109.5	N4—C32—C33	110.3 (3)
C52—N5—H5B	109.5	N4—C32—C31	107.9 (3)
H5A—N5—H5B	109.5	C33—C32—C31	113.3 (3)
C52—N5—H5C	109.5	N4—C32—H32	108.4
H5A—N5—H5C	109.5	C33—C32—H32	108.4
H5B—N5—H5C	109.5	C31—C32—H32	108.4
C62—N6—H6A	109.5	C34—C33—C32	111.7 (3)
C62—N6—H6B	109.5	C34—C33—H33A	109.3
H6A—N6—H6B	109.5	C32—C33—H33A	109.3
C62—N6—H6C	109.5	C34—C33—H33B	109.3
H6A—N6—H6C	109.5	C32—C33—H33B	109.3
H6B—N6—H6C	109.5	H33A—C33—H33B	107.9
C2—C1—H1D	109.5	C35—C34—C39	117.8 (3)
C2—C1—H1E	109.5	C35—C34—C33	120.8 (3)
H1D—C1—H1E	109.5	C39—C34—C33	121.2 (3)
C2—C1—H1F	109.5	C36—C35—C34	121.1 (3)
H1D—C1—H1F	109.5	C36—C35—H35	119.4
H1E—C1—H1F	109.5	C34—C35—H35	119.4
C1—C2—N1	107.8 (3)	C35—C36—C37	120.6 (3)
C1—C2—C3	114.1 (3)	C35—C36—H36	119.7
N1—C2—C3	108.1 (3)	C37—C36—H36	119.7
C1—C2—H2	108.9	C38—C37—C36	119.1 (4)
N1—C2—H2	108.9	C38—C37—H37	120.4
C3—C2—H2	108.9	C36—C37—H37	120.4
C4—C3—C2	112.0 (3)	C37—C38—C39	119.8 (3)
C4—C3—H3D	109.2	C37—C38—H38	120.1
C2—C3—H3D	109.2	C39—C38—H38	120.1
C4—C3—H3E	109.2	C34—C39—C38	121.5 (3)
C2—C3—H3E	109.2	C34—C39—H39	119.3
H3D—C3—H3E	107.9	C38—C39—H39	119.3
C5—C4—C9	118.6 (3)	C52—C51—H51A	109.5
C5—C4—C3	121.1 (3)	C52—C51—H51B	109.5
C9—C4—C3	120.2 (3)	H51A—C51—H51B	109.5
C4—C5—C6	120.5 (3)	C52—C51—H51C	109.5
C4—C5—H5	119.7	H51A—C51—H51C	109.5
C6—C5—H5	119.7	H51B—C51—H51C	109.5
C5—C6—C7	120.4 (3)	N5—C52—C51	107.9 (3)
C5—C6—H6	119.8	N5—C52—C53	108.6 (2)
C7—C6—H6	119.8	C51—C52—C53	113.5 (3)
C8—C7—C6	119.2 (4)	N5—C52—H52	108.9
C8—C7—H7	120.4	C51—C52—H52	108.9
C6—C7—H7	120.4	C53—C52—H52	108.9
C7—C8—C9	120.9 (3)	C54—C53—C52	112.6 (3)
C7—C8—H8	119.6	C54—C53—H53A	109.1
C9—C8—H8	119.6	C52—C53—H53A	109.1
C8—C9—C4	120.5 (3)	C54—C53—H53B	109.1
C8—C9—H9	119.8	C52—C53—H53B	109.1

C4—C9—H9	119.8	H53A—C53—H53B	107.8
C12—C11—H11A	109.5	C59—C54—C55	117.7 (3)
C12—C11—H11B	109.5	C59—C54—C53	121.9 (3)
H11A—C11—H11B	109.5	C55—C54—C53	120.4 (3)
C12—C11—H11C	109.5	C56—C55—C54	120.6 (3)
H11A—C11—H11C	109.5	C56—C55—H55	119.7
H11B—C11—H11C	109.5	C54—C55—H55	119.7
C11—C12—C13	113.4 (3)	C57—C56—C55	120.6 (3)
C11—C12—N2	109.1 (3)	C57—C56—H56	119.7
C13—C12—N2	110.1 (3)	C55—C56—H56	119.7
C11—C12—H12	108.0	C56—C57—C58	119.4 (3)
C13—C12—H12	108.0	C56—C57—H57	120.3
N2—C12—H12	108.0	C58—C57—H57	120.3
C12—C13—C14	110.6 (3)	C59—C58—C57	120.6 (3)
C12—C13—H13A	109.5	C59—C58—H58	119.7
C14—C13—H13A	109.5	C57—C58—H58	119.7
C12—C13—H13B	109.5	C58—C59—C54	121.1 (3)
C14—C13—H13B	109.5	C58—C59—H59	119.5
H13A—C13—H13B	108.1	C54—C59—H59	119.5
C15—C14—C19	118.5 (4)	C62—C61—H61A	109.5
C15—C14—C13	121.3 (4)	C62—C61—H61B	109.5
C19—C14—C13	120.2 (3)	H61A—C61—H61B	109.5
C16—C15—C14	120.3 (4)	C62—C61—H61C	109.5
C16—C15—H15	119.9	H61A—C61—H61C	109.5
C14—C15—H15	119.9	H61B—C61—H61C	109.5
C15—C16—C17	121.0 (4)	N6—C62—C61	108.3 (3)
C15—C16—H16	119.5	N6—C62—C63	108.9 (3)
C17—C16—H16	119.5	C61—C62—C63	113.5 (3)
C18—C17—C16	119.5 (4)	N6—C62—H62	108.7
C18—C17—H17	120.2	C61—C62—H62	108.7
C16—C17—H17	120.2	C63—C62—H62	108.7
C17—C18—C19	120.1 (4)	C64—C63—C62	112.7 (3)
C17—C18—H18	120.0	C64—C63—H63A	109.1
C19—C18—H18	120.0	C62—C63—H63A	109.1
C18—C19—C14	120.6 (4)	C64—C63—H63B	109.1
C18—C19—H19	119.7	C62—C63—H63B	109.1
C14—C19—H19	119.7	H63A—C63—H63B	107.8
C22—C21—H21A	109.5	C65—C64—C69	117.7 (3)
C22—C21—H21B	109.5	C65—C64—C63	121.0 (3)
H21A—C21—H21B	109.5	C69—C64—C63	121.3 (3)
C22—C21—H21C	109.5	C64—C65—C66	121.4 (3)
H21A—C21—H21C	109.5	C64—C65—H65	119.3
H21B—C21—H21C	109.5	C66—C65—H65	119.3
N3—C22—C21	108.4 (3)	C67—C66—C65	120.7 (4)
N3—C22—C23	109.1 (3)	C67—C66—H66	119.7
C21—C22—C23	113.6 (3)	C65—C66—H66	119.7
N3—C22—H22	108.5	C66—C67—C68	118.7 (4)
C21—C22—H22	108.5	C66—C67—H67	120.6
C23—C22—H22	108.5	C68—C67—H67	120.6
C24—C23—C22	112.2 (3)	C69—C68—C67	120.7 (3)
C24—C23—H23A	109.2	C69—C68—H68	119.7
C22—C23—H23A	109.2	C67—C68—H68	119.7
C24—C23—H23B	109.2	C68—C69—C64	120.8 (3)
C22—C23—H23B	109.2	C68—C69—H69	119.6

H23A—C23—H23B	107.9	C64—C69—H69	119.6
C1—C2—C3—C4	-57.2 (4)	N4—C32—C33—C34	-179.0 (3)
N1—C2—C3—C4	-177.0 (3)	C31—C32—C33—C34	-57.9 (4)
C2—C3—C4—C5	-69.3 (4)	C32—C33—C34—C35	-66.7 (4)
C2—C3—C4—C9	106.9 (4)	C32—C33—C34—C39	109.7 (4)
C9—C4—C5—C6	1.0 (5)	C39—C34—C35—C36	0.1 (5)
C3—C4—C5—C6	177.3 (3)	C33—C34—C35—C36	176.6 (3)
C4—C5—C6—C7	-0.4 (5)	C34—C35—C36—C37	-0.8 (6)
C5—C6—C7—C8	0.1 (6)	C35—C36—C37—C38	0.7 (6)
C6—C7—C8—C9	-0.5 (6)	C36—C37—C38—C39	0.1 (5)
C7—C8—C9—C4	1.2 (6)	C35—C34—C39—C38	0.7 (5)
C5—C4—C9—C8	-1.4 (5)	C33—C34—C39—C38	-175.8 (3)
C3—C4—C9—C8	-177.7 (3)	C37—C38—C39—C34	-0.8 (5)
C11—C12—C13—C14	-60.7 (4)	N5—C52—C53—C54	179.3 (3)
N2—C12—C13—C14	176.7 (3)	C51—C52—C53—C54	-60.8 (4)
C12—C13—C14—C15	115.4 (4)	C52—C53—C54—C59	-52.7 (4)
C12—C13—C14—C19	-61.9 (5)	C52—C53—C54—C55	127.5 (3)
C19—C14—C15—C16	-0.4 (7)	C59—C54—C55—C56	-2.2 (5)
C13—C14—C15—C16	-177.8 (5)	C53—C54—C55—C56	177.6 (3)
C14—C15—C16—C17	0.1 (8)	C54—C55—C56—C57	0.8 (6)
C15—C16—C17—C18	1.6 (8)	C55—C56—C57—C58	1.5 (6)
C16—C17—C18—C19	-3.0 (7)	C56—C57—C58—C59	-2.4 (5)
C17—C18—C19—C14	2.8 (7)	C57—C58—C59—C54	1.0 (5)
C15—C14—C19—C18	-1.1 (6)	C55—C54—C59—C58	1.3 (5)
C13—C14—C19—C18	176.3 (4)	C53—C54—C59—C58	-178.5 (3)
N3—C22—C23—C24	177.6 (3)	N6—C62—C63—C64	178.6 (3)
C21—C22—C23—C24	-61.3 (4)	C61—C62—C63—C64	-60.7 (4)
C22—C23—C24—C29	113.2 (4)	C62—C63—C64—C65	-63.9 (4)
C22—C23—C24—C25	-65.1 (4)	C62—C63—C64—C69	114.7 (4)
C29—C24—C25—C26	0.2 (5)	C69—C64—C65—C66	0.3 (5)
C23—C24—C25—C26	178.6 (3)	C63—C64—C65—C66	179.0 (3)
C24—C25—C26—C27	-0.7 (6)	C64—C65—C66—C67	-0.6 (6)
C25—C26—C27—C28	0.3 (6)	C65—C66—C67—C68	0.1 (6)
C26—C27—C28—C29	0.6 (5)	C66—C67—C68—C69	0.8 (6)
C25—C24—C29—C28	0.7 (5)	C67—C68—C69—C64	-1.1 (6)
C23—C24—C29—C28	-177.7 (3)	C65—C64—C69—C68	0.5 (5)
C27—C28—C29—C24	-1.1 (6)	C63—C64—C69—C68	-178.1 (3)

Hydrogen-bond geometry (\AA , $^\circ$) for (I)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots Cl5 ⁱ	0.91	2.40	3.304 (3)	171
N1—H1B \cdots Cl5 ⁱⁱ	0.91	2.27	3.177 (3)	171
N1—H1C \cdots Cl6 ⁱ	0.91	2.28	3.181 (3)	169
N2—H2A \cdots Cl6 ⁱⁱⁱ	0.91	2.27	3.179 (3)	174
N2—H2B \cdots Cl1 ^{iv}	0.91	2.43	3.215 (3)	145
N2—H2C \cdots Cl6 ⁱ	0.91	2.37	3.233 (3)	158
N3—H3A \cdots Cl1 ^{iv}	0.91	2.28	3.151 (3)	159
N3—H3B \cdots Cl1	0.91	2.22	3.118 (3)	168
N3—H3C \cdots Cl2	0.91	2.27	3.171 (3)	169
N4—H4A \cdots Cl2	0.91	2.25	3.149 (3)	168
N4—H4B \cdots Cl3	0.91	2.26	3.164 (3)	172
N4—H4C \cdots Cl2 ^v	0.91	2.37	3.271 (3)	171

N5—H5A···Cl3	0.91	2.27	3.159 (3)	165
N5—H5B···Cl4	0.91	2.36	3.196 (3)	153
N5—H5C···Cl3 ^{iv}	0.91	2.33	3.233 (3)	170
N6—H6A···Cl4	0.91	2.22	3.117 (3)	167
N6—H6B···Cl5 ^v	0.91	2.27	3.168 (3)	169
N6—H6C···Cl4 ^v	0.91	2.29	3.158 (3)	161

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

(II)

Crystal data

$C_9H_{14}N \cdot Br$	$F(000) = 220$
$M_r = 216.12$	$D_x = 1.432 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$
Hall symbol: P 2yb	Cell parameters from 5999 reflections
$a = 5.2366 (4) \text{ \AA}$	$\theta = 3.0\text{--}27.5^\circ$
$b = 8.4264 (5) \text{ \AA}$	$\mu = 4.04 \text{ mm}^{-1}$
$c = 11.3895 (8) \text{ \AA}$	$T = 100 \text{ K}$
$\beta = 94.079 (2)^\circ$	Blade, colourless
$V = 501.30 (6) \text{ \AA}^3$	$0.25 \times 0.18 \times 0.12 \text{ mm}$
$Z = 2$	

Data collection

Rigaku Saturn724+ (2x2 bin mode) diffractometer	5432 measured reflections
Radiation source: fine-focus sealed tube	2383 independent reflections
Graphite monochromator	2343 reflections with $I > 2\sigma(I)$
Detector resolution: $28.5714 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.019$
profile data from ω -scans	$\theta_{\text{max}} = 30.1^\circ$, $\theta_{\text{min}} = 3.0^\circ$
Absorption correction: multi-scan	$h = -7 \rightarrow 7$
CrystalClear-SM Expert 3.1 (Rigaku, 2013)	$k = -11 \rightarrow 10$
$T_{\text{min}} = 0.711$, $T_{\text{max}} = 1.000$	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 0.1173P]$
$R[F^2 > 2\sigma(F^2)] = 0.020$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.052$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
2383 reflections	$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$
115 parameters	Extinction correction: SHELXL,
1 restraint	$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.045 (3)
Secondary atom site location: difference Fourier map	Absolute structure: Flack H D (1983), Acta Cryst.
Hydrogen site location: inferred from neighbouring sites	A39, 876-881
	Absolute structure parameter: 0.003 (10)

Special details

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) for (II)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.08467 (3)	0.71309 (4)	0.418045 (13)	0.02270 (7)
N1	0.6129 (4)	0.5569 (2)	0.55110 (15)	0.0206 (3)
C1	0.6190 (5)	0.7824 (3)	0.6887 (2)	0.0267 (5)
H1A	0.7315	0.8410	0.6389	0.040*
H1B	0.6541	0.8148	0.7709	0.040*
H1C	0.4400	0.8055	0.6636	0.040*
C2	0.6679 (4)	0.6056 (3)	0.67731 (19)	0.0198 (4)
H2	0.8533	0.5854	0.6994	0.024*
C3	0.5097 (3)	0.5028 (2)	0.75640 (17)	0.0202 (4)
H3A	0.3326	0.5442	0.7546	0.024*
H3B	0.5024	0.3927	0.7260	0.024*
C4	0.6258 (3)	0.5028 (2)	0.88157 (17)	0.0187 (3)
C5	0.8463 (4)	0.4144 (2)	0.91057 (17)	0.0209 (4)
H5	0.9208	0.3539	0.8514	0.025*
C6	0.9585 (4)	0.4134 (3)	1.02495 (18)	0.0237 (4)
H6	1.1085	0.3524	1.0435	0.028*
C7	0.8511 (4)	0.5017 (3)	1.11225 (19)	0.0262 (4)
H7	0.9281	0.5019	1.1903	0.031*
C8	0.6311 (4)	0.5894 (3)	1.08438 (19)	0.0269 (4)
H8	0.5567	0.6492	1.1439	0.032*
C9	0.5187 (4)	0.5905 (3)	0.97025 (18)	0.0240 (4)
H9	0.3680	0.6511	0.9522	0.029*
H1N	0.649 (5)	0.461 (4)	0.542 (2)	0.030 (7)*
H2N	0.724 (5)	0.604 (4)	0.501 (3)	0.033 (7)*
H3N	0.442 (6)	0.576 (4)	0.524 (3)	0.038 (8)*

Atomic displacement parameters (\AA^2) for (II)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02399 (10)	0.02052 (10)	0.02300 (10)	-0.00361 (9)	-0.00246 (6)	0.00244 (9)
N1	0.0249 (8)	0.0182 (8)	0.0183 (7)	0.0019 (6)	-0.0017 (6)	0.0003 (6)
C1	0.0379 (14)	0.0202 (11)	0.0209 (10)	-0.0013 (9)	-0.0059 (9)	-0.0007 (8)
C2	0.0210 (9)	0.0203 (10)	0.0174 (9)	-0.0024 (8)	-0.0029 (7)	0.0023 (8)
C3	0.0175 (8)	0.0216 (9)	0.0210 (8)	-0.0022 (7)	-0.0029 (6)	0.0018 (7)
C4	0.0185 (8)	0.0185 (9)	0.0191 (8)	-0.0040 (7)	0.0015 (6)	0.0013 (7)
C5	0.0217 (9)	0.0221 (9)	0.0190 (8)	0.0006 (7)	0.0018 (7)	0.0017 (7)
C6	0.0218 (9)	0.0271 (10)	0.0218 (9)	-0.0007 (7)	-0.0021 (7)	0.0038 (7)
C7	0.0318 (10)	0.0258 (10)	0.0204 (8)	-0.0069 (8)	-0.0030 (8)	0.0029 (8)
C8	0.0374 (11)	0.0222 (10)	0.0217 (9)	-0.0001 (8)	0.0055 (8)	-0.0024 (8)
C9	0.0257 (9)	0.0206 (9)	0.0258 (10)	0.0035 (7)	0.0029 (8)	0.0015 (8)

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

N1—C2	1.503 (3)	C3—H3B	0.9900
N1—H1N	0.83 (3)	C4—C5	1.394 (3)
N1—H2N	0.93 (3)	C4—C9	1.400 (3)
N1—H3N	0.94 (3)	C5—C6	1.391 (3)
C1—C2	1.519 (3)	C5—H5	0.9500
C1—H1A	0.9800	C6—C7	1.392 (3)
C1—H1B	0.9800	C6—H6	0.9500
C1—H1C	0.9800	C7—C8	1.386 (3)

C2—C3	1.534 (3)	C7—H7	0.9500
C2—H2	1.0000	C8—C9	1.388 (3)
C3—C4	1.509 (3)	C8—H8	0.9500
C3—H3A	0.9900	C9—H9	0.9500
C2—N1—H1N	110.3 (19)	C4—C3—H3B	109.5
C2—N1—H2N	112.5 (18)	C2—C3—H3B	109.5
H1N—N1—H2N	100 (2)	H3A—C3—H3B	108.1
C2—N1—H3N	112.6 (19)	C5—C4—C9	118.60 (18)
H1N—N1—H3N	110 (3)	C5—C4—C3	119.65 (18)
H2N—N1—H3N	111 (3)	C9—C4—C3	121.76 (18)
C2—C1—H1A	109.5	C6—C5—C4	120.84 (18)
C2—C1—H1B	109.5	C6—C5—H5	119.6
H1A—C1—H1B	109.5	C4—C5—H5	119.6
C2—C1—H1C	109.5	C5—C6—C7	120.05 (19)
H1A—C1—H1C	109.5	C5—C6—H6	120.0
H1B—C1—H1C	109.5	C7—C6—H6	120.0
N1—C2—C1	109.1 (2)	C8—C7—C6	119.52 (19)
N1—C2—C3	109.44 (17)	C8—C7—H7	120.2
C1—C2—C3	113.74 (19)	C6—C7—H7	120.2
N1—C2—H2	108.1	C7—C8—C9	120.5 (2)
C1—C2—H2	108.1	C7—C8—H8	119.7
C3—C2—H2	108.1	C9—C8—H8	119.7
C4—C3—C2	110.88 (16)	C8—C9—C4	120.46 (19)
C4—C3—H3A	109.5	C8—C9—H9	119.8
C2—C3—H3A	109.5	C4—C9—H9	119.8
N1—C2—C3—C4	158.84 (17)	C4—C5—C6—C7	-0.1 (3)
C1—C2—C3—C4	-78.9 (2)	C5—C6—C7—C8	0.5 (3)
C2—C3—C4—C5	-75.2 (2)	C6—C7—C8—C9	-0.4 (3)
C2—C3—C4—C9	104.5 (2)	C7—C8—C9—C4	0.1 (3)
C9—C4—C5—C6	-0.3 (3)	C5—C4—C9—C8	0.3 (3)
C3—C4—C5—C6	179.42 (19)	C3—C4—C9—C8	-179.38 (18)

Hydrogen-bond geometry (\AA , $^\circ$) for (II)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N \cdots Br1 ⁱ	0.83 (3)	2.54 (3)	3.3080 (19)	154 (2)
N1—H2N \cdots Br1 ⁱⁱ	0.93 (3)	2.36 (3)	3.2656 (19)	165 (3)
N1—H3N \cdots Br1	0.94 (3)	2.44 (3)	3.3296 (18)	157 (3)

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