

## Salt forms of the amide dihydrocarbamazepine.

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### Abstract

Reaction of the pharmaceutical amide dihydrocarbamazepine with strong acids results in protonation of the amide functionality at the O atom and gives the salt forms dihydrocarbamazepine hydrochloride, dihydrocarbamazepine hydrochloride monohydrate and dihydrocarbamazepine hydrobromide monohydrate (formal names [(10,11-dihydro-5H-dibenzo[b.f]azepin-5-yl)(hydroxy)methylidene]azanium chloride,  $C_{15}H_{15}ClN_2O$ , [(10,11-dihydro-5H-dibenzo[b.f]azepin-5-yl)(hydroxy)methylidene]azanium chloride monohydrate,  $C_{15}H_{17}ClN_2O_2$ , and [(10,11-dihydro-5H-dibenzo[b.f]azepin-5-yl)(hydroxy)methylidene]azanium bromide monohydrate,  $C_{15}H_{17}BrN_2O_2$ , respectively). The anhydrous hydrochloride has a structures with two crystallographically independent ion pairs ( $Z' = 2$ ) wherein both cations adopt *syn* conformations, whilst the two hydrated species are mutually isostructural and have cations with anti conformations. Compared to neutral dihydrocarbamazepine structures, protonation of the amide is shown to cause changes to both molecular structure (C=O lengthening and C–N shortening) and to supramolecular structure. The amide to amide and dimeric hydrogen bonding motifs seen for neutral polymorphs and cocrystalline species are replaced here by one-dimensional polymeric constructs with no direct amide to amide bonds. The structures are also compared with, and shown to be closely related to, those of salt forms of the structurally similar pharmaceutical carbamazepine.

### 1. Comment

Carbamazepine (CBZ) is an anti-epileptic drug that is well known to the crystallographic community as a model Active Pharmaceutical Ingredient (API) that has been widely used in the study of polymorphism and the generation and comparison of cocrystal forms (*e.g.* Gelbrich & Hursthouse, 2006; Fleischman *et al.*, 2003). Recently it has been shown that despite the relatively non-basic nature of amides, it is possible to protonate the O atom of the amide group of CBZ using strong acids, thus generating salt forms (Perumalla & Sun, 2012; Eberlin *et al.*, 2013; Buist *et al.*, 2013; Buist *et al.*, 2015). Comparison of the structures of neutral CBZ species with those of cationic CBZ(H) species show that protonation is accompanied both by changes to molecular structure (lengthening of the C=O bond and shortening of the C–N bonds) and by changes to packing structure (*e.g.* the typical R2,2(8) homodimer found in CBZ structures does not occur in the salt forms). Low pH conditions have also been shown to allow easy access to Ionic Cocrystalline (ICC) forms of CBZ, including hydronium, ammonium and Na(I) species (Buist *et al.*, 2013; Buist & Kennedy, 2014; Buist *et al.*, 2015). Dihydrocarbamazepine (DCBZ) is a less well known material and is largely of interest here as a structural congener of CBZ. The structures of four polymorphs of DCBZ have been described (Bandoli *et al.*, 1992; Harrison *et al.*, 2006; Leech *et al.*, 2007; Arlin *et al.*, 2010) as have the structures of 5 cocrystalline or solvate forms (Cruz Cabeza *et al.*, 2006; Johnston *et al.*, 2007 & 2007a & 2007b; Oliveira *et al.*, 2011). A single salt form of DCBZ, the methylsulfonate, has also been reported (Eberlin *et al.*, 2013). The two compounds, CBZ and DCBZ, have broadly similar sizes and shapes and the same single polar functional group. Despite this similarity, it has been noted that their packing behaviours differ. Discussion of these differences has centred about the tendency of CBZ to form R2,2(8) hydrogen bonded homodimers rather than catemeric chains, whilst the opposite is true of DCBZ (Arlin *et al.*, 2010). Herein we report 3 salt forms of DCBZ and thus extend the previous work comparing neutral CBZ and DCBZ structures to a comparison of the cationic CBZ(H) and DCBZ(H).

HCl was generated *in situ* by adding acetyl chloride to a methanol solution of DCBZ. The initial product was anhydrous [DCBZ(H)][Cl] (I), Figure 1. Leaving crystalline (I) in the mother liquor allowed a transformation to occur and after 5 days crystals of the hydrated form [DCBZ(H)][Cl]·H<sub>2</sub>O (II) were recovered, Figure 2. A similar hydration on exposure to atmospheric moisture is known to cause the transformation of [CBZ(H)][Br] to [CBZ(H)][Br]·H<sub>2</sub>O (Buist *et al.*, 2013). In contrast [CBZ(H)][Cl] interacts in a more complex fashion with atmospheric moisture, simultaneously losing HCl and absorbing water to give the ICC hydronium compound CBZ<sub>2</sub>[H<sub>3</sub>O][Cl] (Buist *et al.*, 2013). Reactions of DCBZ with HBr, whether through a similar *in situ* generation of acid as described above or simply through use of aqueous HBr, gave only the hydrate [DCBZ(H)][Br]·H<sub>2</sub>O (III), Figure 3. Examination of the unit-cell dimensions and the structures of (II) and (III) show that they are isostructural. Isostructurality is relatively common for Cl and Br salts of API materials and other examples of isostructurality are found amongst the multiple known phases of Cl and Br salt forms of CBZ (Buist *et al.*, 2013 & 2015). Interestingly (I), [DCBZ(H)][Cl], is isostructural with one of the known forms of [CBZ(H)][Br] but not with any hydrochloride phase of CBZ (Buist *et al.*, 2013). The double change in chemical identity with no structural change invites speculation that there could be similar, currently unknown, phases of [CBZ(H)][Cl] and [DCBZ(H)][Br] that also have the same structure as (I).

There are two crystallographically independent ion pairs in (I),  $Z' = 2$ , and the acidic H atom of each cation was clearly located and refined as being bonded to the amide O atom. Both DCBZ(H) cations in (I) adopt the *syn* conformation where the C–O vector is parallel to the CH<sub>2</sub>–CH<sub>2</sub> vector. For neutral DCBZ this *syn* conformation has been shown to be slightly energetically disfavoured (by  $< 2 \text{ kJ mol}^{-1}$ ) when compared to the alternative anti conformation where the C–NH<sub>2</sub> vector is parallel to the CH<sub>2</sub>–CH<sub>2</sub> vector (Arlin *et al.*, 2010). The higher energy *syn* conformation is also less commonly seen in the crystalline state, Table 8. The DCBZ(H) cations of hydrated structures (II) and (III) both have anti conformations and their acidic protons were again freely refined and located as being bonded to the amide O atoms. As shown in Table 8, protonation of the amide has a significant effect on the C=O and C–N distances with the former lengthening and the latter shortening. Comparing all 4 known DCBZ(H) structures with the known neutral DCBZ structures it can be seen that the C=O bonds are 0.05 to 0.09 Å longer for the protonated DCBZ ions, whereas the C–NH<sub>2</sub> and C–N<sub>ring</sub> bonds shorten by 0.01 to 0.04 and by 0.03 to 0.06 Å respectively. The larger change for C–N<sub>ring</sub> as compared to C–NH<sub>2</sub> suggests a significant role for resonance form C as shown in the Scheme. Similar changes to bond length are seen on comparing CBZ with CBZ(H). Averaging 47 well modelled CBZ structures from the CSD (Allen, 2002) gives values of 1.242, 1.342 and 1.373 Å for C=O, C–NH<sub>2</sub> and C–N<sub>ring</sub> in neutral CBZ species, whereas the equivalent ranges for the known fully protonated CBZ(H) structures are 1.285–1.312, 1.304–1.326 and 1.323–1.348 Å (Eberlin *et al.*, 2013; Buist *et al.*, 2015). For CBZ, these bond length differences are so well established that species with C=O and C–N distances intermediate to the two groupings given have convincingly been shown to have structures intermediate between salt and cocrystalline forms (Eberlin *et al.*, 2013). Such dynamic equilibria where protons move between two sites are well known (*e.g.* Cruickshank *et al.*, 2013; Wilson *et al.*, 2006) but have extra significance for ionisable APIs due to the potential for classification/regulation issues. For instance, the FDA Guidance for Industry on the Regulatory Classification of Pharmaceutical Co-Crystals does not consider materials that are in such intermediate states between salt and cocrystalline forms (Eberlin *et al.*, 2013). One such intermediate species is [CBZ(H)][Br]·H<sub>2</sub>O, where the acidic H is shared by the CBZ and water molecules (Buist *et al.*, 2013). Despite being directly analogous in composition to this hydrated species, neither (II) nor (III) show any sign of having bond lengths that indicate intermediate salt-cocrystal character. Note that the two forms of cocrystalline DCBZ in Table 8 that have acid cofomers do have the longest C=O bonds and shortest N–C bonds of any of the given neutral species, but these differences are very small compared to those found for the CBZ(H) cations.

Arlin *et al.* (2010) compare and contrast the hydrogen bonding motifs found in the polymorphic forms of CBZ and DCBZ. The CBZ structures are dominated by a R2,2(8) homodimer formed by bonding between two amide units. This motif is only seen for one of the four known phases of DCBZ, with the others instead having catenated chain amide-to-amide structures. This structural difference is not repeated for cocrystal and solvate forms of CBZ and DCBZ. CBZ is well studied and two hydrogen bonded motifs are known to be common. The first is an extension of the R2,2(8) homodimer where the coformer molecules hydrogen bond to the edges of the core CBZ dimeric group. The second is a heterodimer, again R2,2(8), where a COOH bearing coformer replaces one of the amide units (Gelbrich & Hursthouse, 2006; Fleischman *et al.*, 2003). The known DCBZ cocrystals also display these two motifs with solvated homodimers present in the DMSO and saccharine species (Johnston *et al.*, 2007b; Oliveira *et al.*, 2011) and the heterodimer present in the acetic acid, formic acid and formamide structures (Cruz Cabeza *et al.*, 2006; Johnston *et al.*, 2007; Johnston *et al.* 2007a). The homodimer motif is not, however, seen in protonated CBZ(H) species as the new OH group makes this unfavourable (Buist *et al.*, 2013 & 2015). Equivalents of the heterodimer motif are seen for CBZ(H) with some sulfonate counterions, albeit with the proton bound to the O atom of the amide rather than remaining on an acidic coformer (Buist *et al.*, 2015; Eberlin *et al.*, 2013). None of the new DCBZ(H) species structures described herein adopt any of these well known R2,2(8) hydrogen bonding motifs and so structures of DCBZ(H) can be differentiated from those of DCBZ both by differences in molecular structure (above) and by differences in packing structure. Both (II) and (III) are found to have structures based about cation/anion [DCBZ(H)]<sub>2</sub>[X]<sub>2</sub> dimers that have the R2,4(8) graph set. The water molecules interact with both cation and anion to give a further ring motif, R2,3(8) see Figure 4. The [DCBZ(H)]<sub>2</sub>[X]<sub>2</sub> dimers connect through the hydrogen bonds between halide ions and water molecules to give 1 dimensional constructs parallel to the crystallographic *a* direction, see Figure 5. The largest difference in unit-cell length between (II) and (III) is for the *a* axes and is thus associated with small differences in spacing for this hydrogen bonded motif. In contrast the only strong hydrogen bond acceptors in the structure of (I) are the chloride anions. These each accept hydrogen bonds from an O–H group and from two N–H groups, see Table 3. One O–H and one N–H donor per chloride ion are from a single DCBZ(H) cation (giving a *R* 1,2(6) motif) but the second N–H donor is from an independent cation and thus the hydrogen bonding propagates to give 1 dimensional motifs parallel to the crystallographic *a* axis, see Figure 6. As (I) is isostructural with Form 1 of [CBZ(H)][Br], this is obviously a hydrogen bonding system that is common to both DCBZ(H) and CBZ(H) species. The hydrogen bonding structure in (II) and (III) also has precedence in CBZ(H) chemistry as similar supramolecular structures are present in both [CBZ(H)][Cl]·H<sub>2</sub>O and [CBZ(H)][Br]·H<sub>2</sub>O, (Buist *et al.*, 2013 & 2015). Thus, although the polymorphic forms of CBZ display different supramolecular chemistry from the polymorphic forms of DCBZ, the salt forms (as with the cocrystalline forms) of the two APIs have structures based around the same intermolecular hydrogen bonding.

## 2. Synthesis and crystallization

Synthesis of hydrochloride salts of DCBZ; DCBZ (0.208 g, 0.87 mmol) and NaI (0.0656 g, 0.44 mmol) were dissolved in 4 cm<sup>3</sup> of warm methanol. Once the solution had cooled to room temperature, 1 cm<sup>3</sup> of acetyl chloride was slowly added. The reaction vial was covered with a perforated parafilm seal. Crystals of [DCBZ(H)][Cl] were deposited within 48 h. Some of the crystals with their mother liquor were then left in the unsealed vial. After 5 days, the solid present was found to be [DCBZ(H)][Cl]·H<sub>2</sub>O.

Synthesis of [DCBZ(H)][Br]·H<sub>2</sub>O; 0.198 g (0.83 mmol) of DCBZ was dissolved in 4 cm<sup>3</sup> of methanol. The solution was heated in a water bath until the DCBZ had dissolved. Once the solution had cooled to room temperature, 1 cm<sup>3</sup> of concentrated hydrobromic acid was slowly added. The reaction's test tube was sealed with parafilm. Small holes were made in the parafilm to aid evaporation. Crystals formed over a period of 10 days. The same product was also isolated on reacting a methanol solution of DCBZ with acetyl bromide in the presence of ammonium bromide. Ammonium bromide

(here) and NaI (above) were included in attempts to form Ionic Cocrystalline forms of DCBZ as described for CBZ by Buist & Kennedy, 2014.

### 3. Refinement

For all structures, H atoms bound to C atoms were placed in the expected geometric positions and treated in riding modes with C–H = 0.95, and 0.99 Å for  $sp^2$  CH and CH<sub>2</sub> groups respectively,  $U(H)_{iso} = 1.2U(C)_{eq}$ . In (I) and (II) all H atoms bound to N or to O atoms were located by difference synthesis and refined isotropically. The H atoms bound to N or to O atoms in structure (III) were located and treated similarly, with the exception that it was found necessary to restrain the N–H and O–H distances of the NH<sub>2</sub> and OH<sub>2</sub> groups to 0.88 (2) Å.

**Table 1**

Experimental details

	(I)	(II)	(III)
Crystal data			
Chemical formula	C <sub>15</sub> H <sub>15</sub> N <sub>2</sub> O·Cl	C <sub>15</sub> H <sub>15</sub> N <sub>2</sub> O·Cl·H <sub>2</sub> O	C <sub>15</sub> H <sub>15</sub> N <sub>2</sub> O·Br·H <sub>2</sub> O
$M_r$	274.74	292.76	337.22
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	123	123	123
$a, b, c$ (Å)	5.4867 (17), 9.8381 (3), 50.3061 (17)	5.3048 (3), 24.4966 (14), 11.0163 (6)	5.4857 (2), 24.5526 (9), 10.9796 (4)
$\alpha, \beta, \gamma$ (°)	90, 90, 90	90, 96.731 (5), 90	90, 96.931 (3), 90
$V$ (Å <sup>3</sup> )	2715.5 (9)	1421.70 (14)	1468.02 (9)
$Z$	8	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.27	0.27	2.80
Crystal size (mm)	0.28 × 0.20 × 0.18	0.25 × 0.22 × 0.18	0.25 × 0.20 × 0.15
Data collection			
Diffractometer	Oxford Diffraction Xcalibur E	Oxford Diffraction Xcalibur E	Oxford Diffraction Xcalibur E
Absorption correction	Multi-scan <i>CrysAlis PRO</i> , Oxford Diffraction Ltd., Version 1.171.34.40 (release 27-08-2010 CrysAlis171 .NET) (compiled Aug 27 2010,11:50:40)	Multi-scan <i>CrysAlis PRO</i> , Oxford Diffraction Ltd., Version 1.171.34.40 (release 27-08-2010 CrysAlis171 .NET) (compiled Aug 27 2010,11:50:40)	Multi-scan <i>CrysAlis PRO</i> , Oxford Diffraction Ltd., Version 1.171.34.40 (release 27-08-2010 CrysAlis171 .NET) (compiled Aug 27 2010,11:50:40)
	Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
$T_{min}, T_{max}$	0.907, 1.000	0.967, 1.000	0.794, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	28541, 6173, 5189	7044, 3507, 2477	6786, 3324, 2687
$R_{int}$	0.058	0.032	0.028
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.665	0.682	0.650
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.049, 0.093, 1.06	0.044, 0.099, 1.03	0.036, 0.078, 1.02
No. of reflections	6173	3507	3324
No. of parameters	367	201	201

No. of restraints	0	0	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e $\text{\AA}^{-3}$ )	0.29, -0.24	0.27, -0.27	0.67, -0.39
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881	–	–
Absolute structure parameter	0.00 (5)	–	–

Computer programs: *CrysAlis PRO* (Agilent, 2014), *CrysAlis PRO, SIR92* (Altomare *et al.*, 1994), *SHELXS* (Sheldrick, 2015), *SHELXL97* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) & *ORTEP-3* (Farrugia, 2012), *ORTEP-3* (Farrugia, 2012), *SHELXL*, *SHELXL97*.

**Table 2**Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I)

O1—C15	1.300 (3)	N2—C15	1.323 (3)
O2—C30	1.309 (3)	N3—C30	1.333 (3)
N1—C15	1.331 (3)	N3—C20	1.442 (3)
N1—C1	1.443 (3)	N3—C16	1.450 (3)
N1—C6	1.446 (3)	N4—C30	1.318 (3)
C15—N1—C1	120.0 (2)	O1—C15—N2	120.6 (2)
C15—N1—C6	121.51 (19)	O1—C15—N1	116.5 (2)
C1—N1—C6	117.80 (19)	N2—C15—N1	122.9 (2)
C30—N3—C20	122.1 (2)	O2—C30—N4	120.8 (2)
C30—N3—C16	121.4 (2)	O2—C30—N3	116.7 (2)
C20—N3—C16	116.08 (19)	N4—C30—N3	122.5 (2)

**Table 3**Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ Cl1	0.91 (3)	1.96 (3)	2.865 (2)	174 (3)
N2—H1N $\cdots$ Cl1	0.93 (3)	2.49 (3)	3.254 (2)	139 (2)
N2—H2N $\cdots$ Cl2 <sup>i</sup>	0.89 (3)	2.44 (3)	3.208 (2)	145 (2)
O2—H2 $\cdots$ Cl2	1.03 (4)	1.86 (4)	2.889 (2)	173 (3)
N4—H3N $\cdots$ Cl2	0.90 (3)	2.42 (3)	3.192 (2)	144 (2)
N4—H4N $\cdots$ Cl1 <sup>ii</sup>	0.95 (3)	2.34 (3)	3.179 (2)	148 (2)

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

**Table 4**Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II)

O1—C15	1.297 (2)	N1—C1	1.449 (2)
N1—C15	1.339 (2)	N2—C15	1.314 (2)
N1—C6	1.444 (2)		
C15—N1—C6	120.69 (14)	O1—C15—N2	121.44 (17)
C15—N1—C1	122.19 (15)	O1—C15—N1	117.00 (16)
C6—N1—C1	116.77 (14)	N2—C15—N1	121.53 (17)

**Table 5**

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

<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>
O1—H1...O1 <i>W</i>	0.97 (3)	1.51 (3)	2.4807 (18)	173 (3)
N2—H1 <i>N</i> ...C11	0.86 (2)	2.42 (3)	3.2151 (19)	153 (2)
N2—H2 <i>N</i> ...C11 <sup>i</sup>	0.89 (2)	2.45 (2)	3.3192 (18)	168.9 (19)
O1 <i>W</i> —H1 <i>W</i> ...C11 <sup>i</sup>	0.92 (3)	2.17 (3)	3.0513 (16)	159 (2)
O1 <i>W</i> —H2 <i>W</i> ...C11 <sup>ii</sup>	0.86 (3)	2.29 (3)	3.1084 (16)	159 (2)

Symmetry codes: (i)  $-x, -y+1, -z+1$ ; (ii)  $-x+1, -y+1, -z+1$ .**Table 6**

Selected geometric parameters (Å, °) for (III)

O1—C15	1.299 (3)	N1—C1	1.454 (3)
N1—C15	1.333 (3)	N2—C15	1.314 (3)
N1—C6	1.443 (3)		
C15—N1—C6	122.1 (2)	O1—C15—N2	122.0 (2)
C15—N1—C1	120.6 (2)	O1—C15—N1	116.7 (2)
C6—N1—C1	116.5 (2)	N1—C15—N2	121.3 (2)

**Table 7**

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

<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>
O1—H1...O1 <i>W</i>	0.84 (3)	1.67 (4)	2.510 (3)	175 (3)
N2—H1 <i>N</i> ...Br1 <sup>i</sup>	0.86 (2)	2.58 (2)	3.431 (2)	172 (3)
N2—H2 <i>N</i> ...Br1 <sup>ii</sup>	0.86 (2)	2.58 (2)	3.355 (2)	149 (3)
O1 <i>W</i> —H1 <i>W</i> ...Br1	0.87 (2)	2.45 (2)	3.2381 (19)	152 (3)
O1 <i>W</i> —H2 <i>W</i> ...Br1 <sup>i</sup>	0.86 (2)	2.40 (2)	3.1960 (19)	154 (3)

Symmetry codes: (i)  $x+1, y, z$ ; (ii)  $-x+1, -y+1, -z+1$ .**Table 8**

Amide Group C-O And C-N Bond Distances (Å) In DCBZ And DCBZ(H) Containing Structures.

Compound	CO	CNH <sub>2</sub>	CN <sub>ring</sub>	conformation
Cl salt ion A	1.300 (3)	1.323 (3)	1.331 (3)	<i>syn</i>
Cl salt ion B	1.309 (3)	1.318 (3)	1.333 (3)	<i>syn</i>
Cl hydrate salt	1.297 (2)	1.314 (2)	1.339 (2)	<i>anti</i>
Br hydrate salt	1.299 (3)	1.314 (2)	1.333 (3)	<i>anti</i>
MeSO <sub>3</sub> salt	1.3005 (17)	1.3101 (19)	1.3390 (19)	<i>anti</i>
DCBZ polymorph I	1.219	1.338	1.377	<i>anti</i>
DCBZ polymorph II	1.234	1.349	1.384	<i>anti</i>
DCBZ polymorph III	1.233	1.337	1.392	<i>anti</i>
DCBZ polymorph IV	1.252	1.333	1.380	<i>syn</i>
acetic acid solvate	1.247	1.343	1.366	<i>anti</i>

formic acid solvate	1.248	1.341	1.370	anti
formamide solvate	1.245	1.345	1.366	anti
DMSO solvate	1.236	1.339	1.382	mixed
saccharin cocrystal	1.253	1.340	1.369	anti

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**Figure 1**

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

**Figure 2**

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

**Figure 3**

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

**Figure 4**

Hydrogen bonding results in dimers of cation-anion pairs in the structure of (II). (III) is isostructural.

**Figure 5**

1 Dimensional hydrogen bonded polymer extending parallel to  $a$  in the structure of (II).

**Figure 6**

1 Dimensional hydrogen bonded polymer extending parallel to  $a$  in the structure of (I).



## supporting information

## Salt forms of the amide dihydrocarbamazepine.

## Computing details

For all compounds, data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) for (I); *SHELXS* (Sheldrick, 2015) for (II), (III). For all compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2015). Molecular graphics: *Mercury* (Macrae *et al.*, 2008) & *ORTEP-3* (Farrugia, 2012) for (I), (II); *ORTEP-3* (Farrugia, 2012) for (III). Software used to prepare material for publication: *SHELXL* for (I), (III); *SHELXL97* for (II).

## (I)

## Crystal data

$C_{15}H_{15}N_2O \cdot Cl$

$M_r = 274.74$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.4867$  (17) Å

$b = 9.8381$  (3) Å

$c = 50.3061$  (17) Å

$V = 2715.5$  (9) Å<sup>3</sup>

$Z = 8$

$F(000) = 1152$

$D_x = 1.344$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 10284 reflections

$\theta = 3.2$ – $28.1^\circ$

$\mu = 0.27$  mm<sup>-1</sup>

$T = 123$  K

Fragment, colourless

$0.28 \times 0.20 \times 0.18$  mm

## Data collection

Oxford Diffraction Xcalibur E  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

*CrysAlis PRO*, Oxford Diffraction Ltd., Version

1.171.34.40 (release 27-08-2010 CrysAlis171 .NET)

(compiled Aug 27 2010, 11:50:40) Empirical

absorption correction using spherical harmonics,

implemented in SCALE3 ABSPACK scaling

algorithm.

$T_{\min} = 0.907$ ,  $T_{\max} = 1.000$

28541 measured reflections

6173 independent reflections

5189 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\max} = 28.2^\circ$ ,  $\theta_{\min} = 3.2^\circ$

$h = -7 \rightarrow 7$

$k = -12 \rightarrow 12$

$l = -64 \rightarrow 64$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.093$

$S = 1.06$

6173 reflections

367 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 atoms treated by a mixture of independent and  
constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 1.1761P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack H D (1983), Acta Cryst.  
 A39, 876-881  
 Absolute structure parameter: 0.00 (5)

*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 ( $\text{\AA}^2$ ) for (I)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	-0.40173 (13)	-0.32252 (6)	0.093469 (12)	0.02391 (15)
C12	0.11444 (13)	1.04391 (6)	0.157770 (13)	0.02736 (16)
O1	-0.0122 (4)	-0.21374 (17)	0.06205 (3)	0.0228 (4)
O2	0.4882 (3)	0.92086 (17)	0.19029 (3)	0.0235 (4)
N1	0.2174 (4)	-0.02588 (19)	0.06253 (4)	0.0157 (4)
N2	0.0385 (4)	-0.1048 (2)	0.10162 (4)	0.0183 (5)
N3	0.7142 (4)	0.7310 (2)	0.18699 (4)	0.0175 (5)
N4	0.5366 (4)	0.8250 (2)	0.14929 (4)	0.0187 (5)
C1	0.2361 (5)	-0.0348 (2)	0.03397 (5)	0.0170 (5)
C2	0.0785 (5)	0.0467 (2)	0.01936 (5)	0.0185 (5)
C3	-0.0934 (5)	0.1391 (3)	0.03395 (5)	0.0230 (6)
H3A	-0.1861	0.0851	0.0471	0.028*
H3B	-0.2116	0.1777	0.0211	0.028*
C4	0.0371 (5)	0.2557 (2)	0.04833 (5)	0.0208 (6)
H4A	0.1075	0.3161	0.0346	0.025*
H4B	-0.0883	0.3091	0.0579	0.025*
C5	0.2375 (5)	0.2227 (2)	0.06800 (5)	0.0172 (5)
C6	0.3180 (4)	0.0931 (2)	0.07535 (5)	0.0148 (5)
C7	0.5036 (4)	0.0739 (2)	0.09362 (5)	0.0180 (5)
H7	0.5562	-0.0156	0.0978	0.022*
C8	0.6135 (5)	0.1846 (2)	0.10587 (5)	0.0212 (5)
H8	0.7379	0.1717	0.1187	0.025*
C9	0.5387 (5)	0.3135 (3)	0.09899 (5)	0.0232 (6)
H9	0.6134	0.3903	0.1071	0.028*
C10	0.3561 (5)	0.3322 (2)	0.08045 (5)	0.0221 (6)
H10	0.3089	0.4222	0.0760	0.027*
C11	0.0932 (5)	0.0388 (3)	-0.00838 (5)	0.0241 (6)
H11	-0.0130	0.0920	-0.0191	0.029*
C12	0.2621 (5)	-0.0464 (3)	-0.02035 (5)	0.0254 (6)
H12	0.2703	-0.0510	-0.0392	0.030*
C13	0.4188 (5)	-0.1248 (3)	-0.00521 (5)	0.0259 (6)
H13	0.5342	-0.1826	-0.0136	0.031*
C14	0.4068 (5)	-0.1188 (2)	0.02225 (5)	0.0217 (5)
H14	0.5143	-0.1715	0.0329	0.026*
C15	0.0810 (5)	-0.1148 (2)	0.07582 (4)	0.0160 (5)
C16	0.8125 (4)	0.6166 (2)	0.17232 (5)	0.0163 (5)
C17	0.7296 (5)	0.4849 (2)	0.17727 (5)	0.0184 (5)
C18	0.5266 (5)	0.4449 (3)	0.19626 (5)	0.0231 (6)

H18A	0.5903	0.3724	0.2080	0.028*
H18B	0.3937	0.4044	0.1856	0.028*
C19	0.4133 (5)	0.5552 (3)	0.21409 (5)	0.0258 (6)
H19A	0.3170	0.6183	0.2029	0.031*
H19B	0.3004	0.5117	0.2269	0.031*
C20	0.7449 (5)	0.7268 (2)	0.21544 (5)	0.0190 (6)
C21	0.6011 (5)	0.6350 (2)	0.22922 (5)	0.0232 (6)
C22	0.6423 (6)	0.6201 (3)	0.25637 (5)	0.0331 (7)
H22	0.5460	0.5584	0.2664	0.040*
C23	0.8233 (6)	0.6951 (3)	0.26887 (5)	0.0382 (8)
H23	0.8527	0.6828	0.2873	0.046*
C24	0.9615 (6)	0.7878 (3)	0.25459 (6)	0.0347 (7)
H24	1.0827	0.8402	0.2633	0.042*
C25	0.9232 (5)	0.8040 (3)	0.22762 (5)	0.0254 (6)
H25	1.0175	0.8669	0.2177	0.030*
C26	0.8478 (5)	0.3804 (3)	0.16360 (5)	0.0222 (6)
H26	0.7993	0.2891	0.1668	0.027*
C27	1.0327 (5)	0.4055 (3)	0.14566 (5)	0.0239 (6)
H27	1.1077	0.3319	0.1366	0.029*
C28	1.1100 (5)	0.5378 (2)	0.14079 (5)	0.0216 (5)
H28	1.2353	0.5556	0.1282	0.026*
C29	1.0009 (5)	0.6431 (2)	0.15459 (5)	0.0195 (5)
H29	1.0549	0.7338	0.1519	0.023*
C30	0.5795 (5)	0.8258 (2)	0.17506 (4)	0.0173 (5)
H1	-0.128 (6)	-0.252 (3)	0.0726 (6)	0.046 (10)*
H1N	-0.066 (5)	-0.170 (3)	0.1087 (5)	0.027 (7)*
H2N	0.086 (5)	-0.037 (3)	0.1121 (6)	0.031 (8)*
H2	0.351 (7)	0.969 (3)	0.1799 (7)	0.068 (11)*
H3N	0.432 (5)	0.890 (3)	0.1436 (5)	0.023 (7)*
H4N	0.579 (6)	0.754 (3)	0.1374 (6)	0.039 (8)*

Atomic displacement parameters ( $\text{\AA}^2$ ) for (I)

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0308 (4)	0.0228 (3)	0.0181 (3)	-0.0075 (3)	0.0056 (3)	-0.0031 (2)
Cl2	0.0361 (4)	0.0263 (3)	0.0197 (3)	0.0120 (3)	-0.0069 (3)	-0.0054 (3)
O1	0.0298 (10)	0.0231 (9)	0.0154 (9)	-0.0111 (8)	0.0050 (8)	-0.0033 (7)
O2	0.0310 (11)	0.0244 (9)	0.0152 (9)	0.0084 (8)	-0.0016 (8)	-0.0039 (7)
N1	0.0216 (11)	0.0161 (10)	0.0094 (10)	-0.0019 (9)	0.0005 (8)	-0.0013 (8)
N2	0.0231 (13)	0.0197 (11)	0.0120 (10)	-0.0054 (10)	0.0025 (9)	-0.0012 (9)
N3	0.0227 (11)	0.0192 (10)	0.0106 (10)	0.0032 (9)	0.0014 (9)	0.0015 (8)
N4	0.0252 (12)	0.0198 (11)	0.0110 (10)	0.0053 (10)	-0.0005 (8)	0.0018 (9)
C1	0.0207 (13)	0.0196 (13)	0.0107 (12)	-0.0045 (11)	0.0006 (10)	-0.0006 (10)
C2	0.0184 (13)	0.0215 (12)	0.0157 (12)	-0.0031 (12)	-0.0008 (11)	0.0004 (10)
C3	0.0191 (13)	0.0324 (14)	0.0175 (12)	0.0034 (13)	-0.0028 (12)	0.0003 (10)
C4	0.0213 (14)	0.0230 (13)	0.0182 (13)	0.0049 (11)	0.0032 (10)	0.0028 (10)
C5	0.0182 (13)	0.0205 (13)	0.0127 (12)	-0.0017 (11)	0.0014 (10)	-0.0010 (10)
C6	0.0189 (13)	0.0155 (11)	0.0101 (11)	-0.0013 (10)	0.0037 (10)	-0.0015 (9)
C7	0.0193 (12)	0.0196 (12)	0.0150 (12)	0.0016 (10)	0.0011 (11)	-0.0015 (10)
C8	0.0174 (13)	0.0291 (13)	0.0171 (12)	-0.0028 (13)	0.0000 (11)	-0.0036 (11)
C9	0.0267 (15)	0.0216 (13)	0.0213 (14)	-0.0055 (12)	0.0034 (11)	-0.0077 (11)
C10	0.0280 (15)	0.0154 (12)	0.0229 (13)	0.0039 (11)	0.0044 (11)	-0.0015 (10)

C11	0.0296 (14)	0.0283 (13)	0.0144 (12)	-0.0022 (14)	-0.0024 (12)	0.0034 (11)
C12	0.0387 (17)	0.0235 (14)	0.0139 (13)	-0.0063 (13)	0.0008 (12)	-0.0026 (11)
C13	0.0315 (15)	0.0241 (13)	0.0223 (13)	-0.0001 (13)	0.0107 (13)	-0.0065 (11)
C14	0.0233 (13)	0.0207 (12)	0.0210 (13)	-0.0015 (12)	-0.0012 (12)	-0.0039 (10)
C15	0.0192 (13)	0.0172 (11)	0.0116 (11)	-0.0002 (11)	-0.0018 (11)	-0.0010 (9)
C16	0.0172 (13)	0.0202 (13)	0.0114 (12)	0.0021 (10)	-0.0024 (10)	-0.0019 (10)
C17	0.0188 (13)	0.0224 (13)	0.0141 (13)	0.0013 (11)	-0.0047 (10)	0.0013 (10)
C18	0.0226 (14)	0.0263 (14)	0.0204 (14)	-0.0018 (12)	-0.0020 (11)	0.0027 (11)
C19	0.0221 (14)	0.0339 (14)	0.0214 (13)	-0.0019 (14)	0.0064 (12)	0.0052 (11)
C20	0.0227 (14)	0.0221 (13)	0.0122 (12)	0.0063 (12)	0.0006 (10)	-0.0007 (10)
C21	0.0281 (14)	0.0260 (13)	0.0156 (12)	0.0077 (13)	0.0016 (12)	-0.0008 (10)
C22	0.050 (2)	0.0356 (15)	0.0139 (13)	0.0120 (15)	0.0049 (14)	0.0062 (12)
C23	0.060 (2)	0.0421 (18)	0.0120 (13)	0.0217 (17)	-0.0097 (13)	-0.0042 (13)
C24	0.0375 (18)	0.0390 (16)	0.0278 (16)	0.0128 (14)	-0.0142 (14)	-0.0104 (13)
C25	0.0249 (14)	0.0289 (14)	0.0224 (13)	0.0055 (13)	-0.0004 (12)	-0.0046 (11)
C26	0.0252 (15)	0.0168 (12)	0.0244 (14)	-0.0003 (11)	-0.0036 (11)	-0.0029 (10)
C27	0.0214 (14)	0.0249 (13)	0.0255 (14)	0.0075 (12)	-0.0028 (11)	-0.0075 (11)
C28	0.0185 (13)	0.0297 (13)	0.0167 (12)	0.0018 (13)	0.0020 (11)	-0.0012 (10)
C29	0.0186 (13)	0.0202 (13)	0.0195 (13)	0.0000 (11)	-0.0018 (11)	0.0007 (10)
C30	0.0192 (13)	0.0194 (12)	0.0134 (11)	-0.0011 (12)	0.0010 (10)	-0.0006 (10)

*Geometric parameters (Å, °) for (I)*

O1—C15	1.300 (3)	C10—H10	0.9500
O1—H1	0.91 (3)	C11—C12	1.387 (4)
O2—C30	1.309 (3)	C11—H11	0.9500
O2—H2	1.03 (4)	C12—C13	1.383 (4)
N1—C15	1.331 (3)	C12—H12	0.9500
N1—C1	1.443 (3)	C13—C14	1.384 (3)
N1—C6	1.446 (3)	C13—H13	0.9500
N2—C15	1.323 (3)	C14—H14	0.9500
N2—H1N	0.93 (3)	C16—C29	1.390 (3)
N2—H2N	0.89 (3)	C16—C17	1.396 (3)
N3—C30	1.333 (3)	C17—C26	1.397 (3)
N3—C20	1.442 (3)	C17—C18	1.519 (3)
N3—C16	1.450 (3)	C18—C19	1.539 (4)
N4—C30	1.318 (3)	C18—H18A	0.9900
N4—H3N	0.90 (3)	C18—H18B	0.9900
N4—H4N	0.95 (3)	C19—C21	1.503 (4)
C1—C14	1.381 (4)	C19—H19A	0.9900
C1—C2	1.389 (3)	C19—H19B	0.9900
C2—C11	1.400 (3)	C20—C25	1.381 (4)
C2—C3	1.502 (3)	C20—C21	1.386 (4)
C3—C4	1.534 (3)	C21—C22	1.392 (3)
C3—H3A	0.9900	C22—C23	1.387 (4)
C3—H3B	0.9900	C22—H22	0.9500
C4—C5	1.514 (3)	C23—C24	1.387 (4)
C4—H4A	0.9900	C23—H23	0.9500
C4—H4B	0.9900	C24—C25	1.382 (4)
C5—C6	1.399 (3)	C24—H24	0.9500
C5—C10	1.406 (3)	C25—H25	0.9500
C6—C7	1.385 (3)	C26—C27	1.380 (4)

C7—C8	1.389 (3)	C26—H26	0.9500
C7—H7	0.9500	C27—C28	1.391 (4)
C8—C9	1.377 (4)	C27—H27	0.9500
C8—H8	0.9500	C28—C29	1.383 (3)
C9—C10	1.381 (4)	C28—H28	0.9500
C9—H9	0.9500	C29—H29	0.9500
C15—O1—H1	106 (2)	C14—C13—H13	120.1
C30—O2—H2	108.2 (19)	C1—C14—C13	118.9 (3)
C15—N1—C1	120.0 (2)	C1—C14—H14	120.5
C15—N1—C6	121.51 (19)	C13—C14—H14	120.5
C1—N1—C6	117.80 (19)	O1—C15—N2	120.6 (2)
C15—N2—H1N	115.6 (16)	O1—C15—N1	116.5 (2)
C15—N2—H2N	125.8 (18)	N2—C15—N1	122.9 (2)
H1N—N2—H2N	118 (2)	C29—C16—C17	122.0 (2)
C30—N3—C20	122.1 (2)	C29—C16—N3	117.3 (2)
C30—N3—C16	121.4 (2)	C17—C16—N3	120.6 (2)
C20—N3—C16	116.08 (19)	C16—C17—C26	116.4 (2)
C30—N4—H3N	115.0 (17)	C16—C17—C18	126.3 (2)
C30—N4—H4N	125.7 (18)	C26—C17—C18	117.3 (2)
H3N—N4—H4N	118 (2)	C17—C18—C19	118.7 (2)
C14—C1—C2	122.8 (2)	C17—C18—H18A	107.6
C14—C1—N1	120.6 (2)	C19—C18—H18A	107.6
C2—C1—N1	116.6 (2)	C17—C18—H18B	107.6
C1—C2—C11	117.4 (2)	C19—C18—H18B	107.6
C1—C2—C3	118.8 (2)	H18A—C18—H18B	107.1
C11—C2—C3	123.8 (2)	C21—C19—C18	112.8 (2)
C2—C3—C4	113.0 (2)	C21—C19—H19A	109.0
C2—C3—H3A	109.0	C18—C19—H19A	109.0
C4—C3—H3A	109.0	C21—C19—H19B	109.0
C2—C3—H3B	109.0	C18—C19—H19B	109.0
C4—C3—H3B	109.0	H19A—C19—H19B	107.8
H3A—C3—H3B	107.8	C25—C20—C21	122.7 (2)
C5—C4—C3	119.1 (2)	C25—C20—N3	120.5 (2)
C5—C4—H4A	107.5	C21—C20—N3	116.7 (2)
C3—C4—H4A	107.5	C20—C21—C22	117.8 (3)
C5—C4—H4B	107.5	C20—C21—C19	118.5 (2)
C3—C4—H4B	107.5	C22—C21—C19	123.6 (3)
H4A—C4—H4B	107.0	C23—C22—C21	120.4 (3)
C6—C5—C10	115.7 (2)	C23—C22—H22	119.8
C6—C5—C4	126.7 (2)	C21—C22—H22	119.8
C10—C5—C4	117.6 (2)	C24—C23—C22	120.4 (3)
C7—C6—C5	122.2 (2)	C24—C23—H23	119.8
C7—C6—N1	117.8 (2)	C22—C23—H23	119.8
C5—C6—N1	120.0 (2)	C25—C24—C23	120.1 (3)
C6—C7—C8	120.4 (2)	C25—C24—H24	120.0
C6—C7—H7	119.8	C23—C24—H24	120.0
C8—C7—H7	119.8	C20—C25—C24	118.7 (3)
C9—C8—C7	118.8 (2)	C20—C25—H25	120.7
C9—C8—H8	120.6	C24—C25—H25	120.7
C7—C8—H8	120.6	C27—C26—C17	122.1 (2)
C8—C9—C10	120.5 (2)	C27—C26—H26	118.9

C8—C9—H9	119.7	C17—C26—H26	118.9
C10—C9—H9	119.7	C26—C27—C28	120.4 (2)
C9—C10—C5	122.3 (2)	C26—C27—H27	119.8
C9—C10—H10	118.8	C28—C27—H27	119.8
C5—C10—H10	118.8	C29—C28—C27	118.7 (2)
C12—C11—C2	120.3 (2)	C29—C28—H28	120.6
C12—C11—H11	119.9	C27—C28—H28	120.6
C2—C11—H11	119.9	C28—C29—C16	120.3 (2)
C13—C12—C11	120.9 (2)	C28—C29—H29	119.9
C13—C12—H12	119.6	C16—C29—H29	119.9
C11—C12—H12	119.6	O2—C30—N4	120.8 (2)
C12—C13—C14	119.7 (3)	O2—C30—N3	116.7 (2)
C12—C13—H13	120.1	N4—C30—N3	122.5 (2)
C15—N1—C1—C14	-86.0 (3)	C30—N3—C16—C29	71.1 (3)
C6—N1—C1—C14	103.5 (3)	C20—N3—C16—C29	-116.4 (2)
C15—N1—C1—C2	95.3 (3)	C30—N3—C16—C17	-112.8 (3)
C6—N1—C1—C2	-75.2 (3)	C20—N3—C16—C17	59.8 (3)
C14—C1—C2—C11	1.6 (4)	C29—C16—C17—C26	0.6 (4)
N1—C1—C2—C11	-179.7 (2)	N3—C16—C17—C26	-175.4 (2)
C14—C1—C2—C3	-177.4 (2)	C29—C16—C17—C18	179.7 (2)
N1—C1—C2—C3	1.3 (3)	N3—C16—C17—C18	3.8 (4)
C1—C2—C3—C4	68.5 (3)	C16—C17—C18—C19	-6.3 (4)
C11—C2—C3—C4	-110.5 (3)	C26—C17—C18—C19	172.8 (2)
C2—C3—C4—C5	-55.4 (3)	C17—C18—C19—C21	-51.4 (3)
C3—C4—C5—C6	-1.5 (4)	C30—N3—C20—C25	-85.2 (3)
C3—C4—C5—C10	178.9 (2)	C16—N3—C20—C25	102.4 (3)
C10—C5—C6—C7	-0.4 (4)	C30—N3—C20—C21	99.7 (3)
C4—C5—C6—C7	180.0 (2)	C16—N3—C20—C21	-72.8 (3)
C10—C5—C6—N1	-176.4 (2)	C25—C20—C21—C22	-0.7 (4)
C4—C5—C6—N1	3.9 (4)	N3—C20—C21—C22	174.3 (2)
C15—N1—C6—C7	70.4 (3)	C25—C20—C21—C19	-179.5 (2)
C1—N1—C6—C7	-119.3 (2)	N3—C20—C21—C19	-4.5 (3)
C15—N1—C6—C5	-113.4 (3)	C18—C19—C21—C20	72.3 (3)
C1—N1—C6—C5	56.9 (3)	C18—C19—C21—C22	-106.5 (3)
C5—C6—C7—C8	1.5 (4)	C20—C21—C22—C23	-0.4 (4)
N1—C6—C7—C8	177.7 (2)	C19—C21—C22—C23	178.4 (3)
C6—C7—C8—C9	-1.7 (4)	C21—C22—C23—C24	1.4 (4)
C7—C8—C9—C10	0.7 (4)	C22—C23—C24—C25	-1.4 (4)
C8—C9—C10—C5	0.5 (4)	C21—C20—C25—C24	0.7 (4)
C6—C5—C10—C9	-0.7 (4)	N3—C20—C25—C24	-174.1 (2)
C4—C5—C10—C9	179.0 (2)	C23—C24—C25—C20	0.3 (4)
C1—C2—C11—C12	-0.8 (4)	C16—C17—C26—C27	-1.5 (4)
C3—C2—C11—C12	178.1 (2)	C18—C17—C26—C27	179.2 (2)
C2—C11—C12—C13	-0.1 (4)	C17—C26—C27—C28	0.7 (4)
C11—C12—C13—C14	0.2 (4)	C26—C27—C28—C29	1.1 (4)
C2—C1—C14—C13	-1.5 (4)	C27—C28—C29—C16	-2.0 (4)
N1—C1—C14—C13	179.9 (2)	C17—C16—C29—C28	1.2 (4)
C12—C13—C14—C1	0.5 (4)	N3—C16—C29—C28	177.3 (2)
C1—N1—C15—O1	5.9 (3)	C20—N3—C30—O2	4.3 (3)
C6—N1—C15—O1	176.0 (2)	C16—N3—C30—O2	176.4 (2)
C1—N1—C15—N2	-173.7 (2)	C20—N3—C30—N4	-175.2 (2)

C6—N1—C15—N2

−3.6 (4)

C16—N3—C30—N4

−3.1 (4)

*Hydrogen-bond geometry (Å, °) for (I)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ Cl1	0.91 (3)	1.96 (3)	2.865 (2)	174 (3)
N2—H1 <i>N</i> $\cdots$ Cl1	0.93 (3)	2.49 (3)	3.254 (2)	139 (2)
N2—H2 <i>N</i> $\cdots$ Cl2 <sup>i</sup>	0.89 (3)	2.44 (3)	3.208 (2)	145 (2)
O2—H2 $\cdots$ Cl2	1.03 (4)	1.86 (4)	2.889 (2)	173 (3)
N4—H3 <i>N</i> $\cdots$ Cl2	0.90 (3)	2.42 (3)	3.192 (2)	144 (2)
N4—H4 <i>N</i> $\cdots$ Cl1 <sup>ii</sup>	0.95 (3)	2.34 (3)	3.179 (2)	148 (2)

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*+1, *y*+1, *z*.**(II)***Crystal data*C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O·Cl·H<sub>2</sub>O*M<sub>r</sub>* = 292.76Monoclinic, *P*2<sub>1</sub>/*c*Hall symbol: −*P* 2ybc*a* = 5.3048 (3) Å*b* = 24.4966 (14) Å*c* = 11.0163 (6) Å $\beta$  = 96.731 (5)°*V* = 1421.70 (14) Å<sup>3</sup>*Z* = 4*F*(000) = 616*D<sub>x</sub>* = 1.368 Mg m<sup>−3</sup>Mo *K*α radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 2171 reflections

 $\theta$  = 3.1–29.8° $\mu$  = 0.27 mm<sup>−1</sup>*T* = 123 K

Block, colourless

0.25 × 0.22 × 0.18 mm

*Data collection*Oxford Diffraction Xcalibur E  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 $\omega$  scans

Absorption correction: multi-scan

*CrysAlis PRO*, Oxford Diffraction Ltd., Version1.171.34.40 (release 27-08-2010 *CrysAlis171 .NET*)

(compiled Aug 27 2010, 11:50:40) Empirical

absorption correction using spherical harmonics,

implemented in *SCALE3 ABSPACK* scaling

algorithm.

*T<sub>min</sub>* = 0.967, *T<sub>max</sub>* = 1.000

7044 measured reflections

3507 independent reflections

2477 reflections with *I* > 2σ(*I*)*R<sub>int</sub>* = 0.032 $\theta_{\max}$  = 29.0°,  $\theta_{\min}$  = 3.1°*h* = −7→6*k* = −29→31*l* = −15→14*Refinement*Refinement on *F*<sup>2</sup>

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.044$  $wR(F^2) = 0.099$ *S* = 1.03

3507 reflections

201 parameters

0 restraints

Primary atom site location: structure-invariant direct  
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring  
sitesH atoms treated by a mixture of independent and  
constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 0.1996P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.27 \text{ e } \text{Å}^{-3}$  $\Delta\rho_{\min} = -0.27 \text{ e } \text{Å}^{-3}$

*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 ( $\text{\AA}^2$ ) for (II)*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.22098 (8)	0.54240 (2)	0.68704 (4)	0.02364 (13)
O1	0.3193 (2)	0.35371 (5)	0.42865 (12)	0.0195 (3)
O1W	0.2533 (3)	0.40465 (6)	0.23288 (12)	0.0221 (3)
N1	0.5160 (3)	0.36537 (6)	0.61893 (13)	0.0153 (3)
N2	0.2632 (3)	0.43409 (7)	0.52585 (16)	0.0206 (4)
C1	0.5617 (3)	0.39448 (7)	0.73387 (16)	0.0153 (4)
C2	0.4221 (3)	0.37804 (8)	0.82641 (16)	0.0174 (4)
C3	0.2334 (3)	0.33258 (8)	0.80044 (17)	0.0197 (4)
H3A	0.1249	0.3403	0.7230	0.024*
H3B	0.1226	0.3309	0.8667	0.024*
C4	0.3647 (4)	0.27728 (8)	0.79053 (17)	0.0204 (4)
H4A	0.4579	0.2688	0.8715	0.025*
H4B	0.2307	0.2492	0.7738	0.025*
C5	0.5485 (3)	0.27070 (8)	0.69585 (16)	0.0178 (4)
C6	0.6178 (3)	0.31080 (8)	0.61605 (16)	0.0164 (4)
C7	0.6633 (4)	0.21941 (8)	0.68785 (19)	0.0252 (5)
H7	0.6189	0.1908	0.7396	0.030*
C8	0.8387 (4)	0.20906 (9)	0.60743 (19)	0.0283 (5)
H8	0.9121	0.1738	0.6041	0.034*
C9	0.9075 (4)	0.25027 (9)	0.53148 (19)	0.0270 (5)
H9	1.0302	0.2436	0.4770	0.032*
C10	0.7963 (3)	0.30103 (8)	0.53575 (17)	0.0201 (4)
H10	0.8419	0.3294	0.4837	0.024*
C11	0.4745 (4)	0.40282 (8)	0.94024 (17)	0.0227 (4)
H11	0.3804	0.3928	1.0050	0.027*
C12	0.6633 (4)	0.44207 (8)	0.95966 (18)	0.0246 (5)
H12	0.6994	0.4583	1.0381	0.030*
C13	0.7997 (4)	0.45781 (8)	0.86587 (17)	0.0231 (4)
H13	0.9279	0.4849	0.8799	0.028*
C14	0.7491 (3)	0.43393 (8)	0.75109 (17)	0.0188 (4)
H14	0.8412	0.4445	0.6859	0.023*
C15	0.3652 (3)	0.38528 (7)	0.52315 (16)	0.0156 (4)
H1	0.284 (5)	0.3755 (11)	0.355 (2)	0.059 (8)*
H1N	0.288 (4)	0.4565 (10)	0.586 (2)	0.036 (7)*
H1W	0.112 (5)	0.4259 (11)	0.239 (2)	0.055 (8)*
H2N	0.150 (4)	0.4426 (9)	0.463 (2)	0.033 (6)*
H2W	0.381 (5)	0.4265 (11)	0.244 (2)	0.058 (9)*

*Atomic displacement parameters ( $\text{\AA}^2$ ) for (II)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0191 (2)	0.0264 (3)	0.0251 (3)	0.0011 (2)	0.00162 (18)	-0.0048 (2)



O1	0.0249 (7)	0.0190 (7)	0.0142 (7)	-0.0008 (6)	0.0009 (6)	-0.0010 (5)
O1W	0.0223 (7)	0.0255 (8)	0.0185 (7)	0.0008 (7)	0.0023 (6)	0.0008 (6)
N1	0.0181 (7)	0.0154 (8)	0.0128 (7)	0.0002 (6)	0.0031 (6)	-0.0004 (6)
N2	0.0251 (9)	0.0214 (9)	0.0147 (8)	0.0042 (7)	0.0001 (7)	-0.0008 (7)
C1	0.0168 (8)	0.0157 (9)	0.0130 (9)	0.0032 (7)	0.0003 (7)	-0.0015 (7)
C2	0.0169 (9)	0.0181 (10)	0.0168 (9)	0.0019 (8)	0.0005 (7)	0.0008 (7)
C3	0.0175 (9)	0.0237 (10)	0.0187 (10)	-0.0019 (8)	0.0056 (8)	0.0020 (8)
C4	0.0212 (9)	0.0195 (10)	0.0204 (10)	-0.0040 (8)	0.0011 (8)	0.0025 (8)
C5	0.0167 (9)	0.0185 (10)	0.0172 (9)	-0.0024 (8)	-0.0025 (8)	-0.0017 (8)
C6	0.0153 (8)	0.0152 (9)	0.0176 (9)	0.0009 (7)	-0.0026 (7)	-0.0032 (7)
C7	0.0270 (10)	0.0194 (10)	0.0275 (11)	0.0001 (9)	-0.0036 (9)	0.0012 (9)
C8	0.0278 (10)	0.0220 (11)	0.0329 (12)	0.0070 (9)	-0.0055 (10)	-0.0075 (9)
C9	0.0225 (9)	0.0322 (12)	0.0259 (11)	0.0041 (9)	0.0012 (9)	-0.0100 (9)
C10	0.0186 (9)	0.0235 (10)	0.0179 (9)	-0.0022 (8)	0.0006 (8)	-0.0043 (8)
C11	0.0258 (10)	0.0263 (11)	0.0164 (9)	0.0024 (9)	0.0045 (8)	-0.0007 (8)
C12	0.0307 (10)	0.0254 (11)	0.0165 (10)	0.0021 (9)	-0.0020 (8)	-0.0042 (8)
C13	0.0238 (10)	0.0184 (10)	0.0256 (11)	-0.0018 (9)	-0.0039 (8)	-0.0011 (8)
C14	0.0193 (9)	0.0177 (10)	0.0197 (10)	0.0013 (8)	0.0033 (7)	0.0025 (8)
C15	0.0157 (8)	0.0165 (9)	0.0153 (9)	-0.0024 (7)	0.0051 (7)	0.0006 (7)

*Geometric parameters (Å, °) for (II)*

O1—C15	1.297 (2)	C4—H4B	0.9900
O1—H1	0.97 (3)	C5—C6	1.396 (3)
O1W—H1W	0.92 (3)	C5—C7	1.404 (3)
O1W—H2W	0.86 (3)	C6—C10	1.390 (3)
N1—C15	1.339 (2)	C7—C8	1.381 (3)
N1—C6	1.444 (2)	C7—H7	0.9500
N1—C1	1.449 (2)	C8—C9	1.387 (3)
N2—C15	1.314 (2)	C8—H8	0.9500
N2—H1N	0.86 (2)	C9—C10	1.379 (3)
N2—H2N	0.89 (2)	C9—H9	0.9500
C1—C14	1.384 (3)	C10—H10	0.9500
C1—C2	1.388 (2)	C11—C12	1.387 (3)
C2—C11	1.392 (3)	C11—H11	0.9500
C2—C3	1.502 (3)	C12—C13	1.384 (3)
C3—C4	1.533 (3)	C12—H12	0.9500
C3—H3A	0.9900	C13—C14	1.390 (3)
C3—H3B	0.9900	C13—H13	0.9500
C4—C5	1.518 (3)	C14—H14	0.9500
C4—H4A	0.9900		
C15—O1—H1	110.2 (16)	C10—C6—N1	117.25 (17)
H1W—O1W—H2W	106 (2)	C5—C6—N1	120.72 (16)
C15—N1—C6	120.69 (14)	C8—C7—C5	122.31 (19)
C15—N1—C1	122.19 (15)	C8—C7—H7	118.8
C6—N1—C1	116.77 (14)	C5—C7—H7	118.8
C15—N2—H1N	124.8 (15)	C7—C8—C9	119.86 (19)
C15—N2—H2N	116.1 (15)	C7—C8—H8	120.1
H1N—N2—H2N	119 (2)	C9—C8—H8	120.1
C14—C1—C2	122.59 (16)	C10—C9—C8	119.46 (19)
C14—C1—N1	120.50 (16)	C10—C9—H9	120.3

C2—C1—N1	116.75 (16)	C8—C9—H9	120.3
C1—C2—C11	117.89 (17)	C9—C10—C6	120.18 (19)
C1—C2—C3	118.43 (16)	C9—C10—H10	119.9
C11—C2—C3	123.59 (17)	C6—C10—H10	119.9
C2—C3—C4	111.75 (15)	C12—C11—C2	120.39 (18)
C2—C3—H3A	109.3	C12—C11—H11	119.8
C4—C3—H3A	109.3	C2—C11—H11	119.8
C2—C3—H3B	109.3	C13—C12—C11	120.62 (18)
C4—C3—H3B	109.3	C13—C12—H12	119.7
H3A—C3—H3B	107.9	C11—C12—H12	119.7
C5—C4—C3	118.47 (16)	C12—C13—C14	119.98 (18)
C5—C4—H4A	107.7	C12—C13—H13	120.0
C3—C4—H4A	107.7	C14—C13—H13	120.0
C5—C4—H4B	107.7	C1—C14—C13	118.52 (18)
C3—C4—H4B	107.7	C1—C14—H14	120.7
H4A—C4—H4B	107.1	C13—C14—H14	120.7
C6—C5—C7	116.23 (17)	O1—C15—N2	121.44 (17)
C6—C5—C4	126.58 (17)	O1—C15—N1	117.00 (16)
C7—C5—C4	117.18 (17)	N2—C15—N1	121.53 (17)
C10—C6—C5	121.94 (18)		
C15—N1—C1—C14	-85.0 (2)	C1—N1—C6—C5	58.2 (2)
C6—N1—C1—C14	101.7 (2)	C6—C5—C7—C8	1.1 (3)
C15—N1—C1—C2	99.4 (2)	C4—C5—C7—C8	-178.24 (17)
C6—N1—C1—C2	-73.8 (2)	C5—C7—C8—C9	0.3 (3)
C14—C1—C2—C11	0.3 (3)	C7—C8—C9—C10	-1.1 (3)
N1—C1—C2—C11	175.75 (16)	C8—C9—C10—C6	0.3 (3)
C14—C1—C2—C3	-176.46 (17)	C5—C6—C10—C9	1.2 (3)
N1—C1—C2—C3	-1.0 (2)	N1—C6—C10—C9	177.79 (16)
C1—C2—C3—C4	71.6 (2)	C1—C2—C11—C12	-0.9 (3)
C11—C2—C3—C4	-105.0 (2)	C3—C2—C11—C12	175.67 (18)
C2—C3—C4—C5	-57.9 (2)	C2—C11—C12—C13	1.0 (3)
C3—C4—C5—C6	1.5 (3)	C11—C12—C13—C14	-0.4 (3)
C3—C4—C5—C7	-179.22 (16)	C2—C1—C14—C13	0.2 (3)
C7—C5—C6—C10	-1.9 (2)	N1—C1—C14—C13	-175.05 (16)
C4—C5—C6—C10	177.41 (16)	C12—C13—C14—C1	-0.2 (3)
C7—C5—C6—N1	-178.36 (15)	C6—N1—C15—O1	-0.9 (2)
C4—C5—C6—N1	0.9 (3)	C1—N1—C15—O1	-173.93 (15)
C15—N1—C6—C10	68.2 (2)	C6—N1—C15—N2	177.44 (17)
C1—N1—C6—C10	-118.44 (17)	C1—N1—C15—N2	4.5 (3)
C15—N1—C6—C5	-115.18 (19)		

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

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ O1 <i>W</i>	0.97 (3)	1.51 (3)	2.4807 (18)	173 (3)
N2—H1 <i>N</i> $\cdots$ Cl1	0.86 (2)	2.42 (3)	3.2151 (19)	153 (2)
N2—H2 <i>N</i> $\cdots$ Cl1 <sup>i</sup>	0.89 (2)	2.45 (2)	3.3192 (18)	168.9 (19)
O1 <i>W</i> —H1 <i>W</i> $\cdots$ Cl1 <sup>i</sup>	0.92 (3)	2.17 (3)	3.0513 (16)	159 (2)
O1 <i>W</i> —H2 <i>W</i> $\cdots$ Cl1 <sup>ii</sup>	0.86 (3)	2.29 (3)	3.1084 (16)	159 (2)

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

**(III)***Crystal data*

$C_{15}H_{15}N_2O \cdot Br \cdot H_2O$

$M_r = 337.22$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 5.4857(2)\ \text{\AA}$

$b = 24.5526(9)\ \text{\AA}$

$c = 10.9796(4)\ \text{\AA}$

$\beta = 96.931(3)^\circ$

$V = 1468.02(9)\ \text{\AA}^3$

$Z = 4$

$F(000) = 688$

$D_x = 1.526\ \text{Mg m}^{-3}$

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

Cell parameters from 2990 reflections

$\theta = 3.1\text{--}29.2^\circ$

$\mu = 2.80\ \text{mm}^{-1}$

$T = 123\ \text{K}$

Prism, colourless

$0.25 \times 0.20 \times 0.15\ \text{mm}$

*Data collection*

Oxford Diffraction Xcalibur E  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

*CrysAlis PRO*, Oxford Diffraction Ltd., Version

1.171.34.40 (release 27-08-2010 CrysAlis171 .NET)

(compiled Aug 27 2010,11:50:40) Empirical

absorption correction using spherical harmonics,  
implemented in SCALE3 ABSPACK scaling  
algorithm.

$T_{\min} = 0.794, T_{\max} = 1.000$

6786 measured reflections

3324 independent reflections

2687 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 27.5^\circ, \theta_{\min} = 3.1^\circ$

$h = -7 \rightarrow 4$

$k = -27 \rightarrow 31$

$l = -13 \rightarrow 14$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.078$

$S = 1.02$

3324 reflections

201 parameters

4 restraints

Primary atom site location: structure-invariant direct  
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring  
sites

H atoms treated by a mixture of independent and  
constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.7435P]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.67\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.39\ \text{e \AA}^{-3}$

*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 ( $\text{\AA}^2$ ) for (III)*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.23260 (4)	0.545139 (11)	0.68613 (2)	0.02088 (9)
O1	0.6696 (3)	0.64943 (8)	0.57548 (17)	0.0178 (4)

O1W	0.7590 (3)	0.60056 (8)	0.77670 (17)	0.0209 (4)
N1	0.4675 (3)	0.63562 (9)	0.38819 (18)	0.0139 (4)
N2	0.7246 (4)	0.56885 (10)	0.4784 (2)	0.0194 (5)
C1	0.3659 (4)	0.69024 (10)	0.3908 (2)	0.0152 (5)
C2	0.4346 (4)	0.73025 (11)	0.3119 (2)	0.0177 (6)
C3	0.6149 (5)	0.72373 (11)	0.2181 (3)	0.0224 (6)
H3A	0.7445	0.7516	0.2362	0.027*
H3B	0.5263	0.7325	0.1365	0.027*
C4	0.7425 (5)	0.66865 (11)	0.2077 (2)	0.0208 (6)
H4A	0.8500	0.6706	0.1416	0.025*
H4B	0.8473	0.6609	0.2856	0.025*
C5	0.5615 (4)	0.62304 (11)	0.1805 (2)	0.0159 (5)
C6	0.4244 (4)	0.60684 (10)	0.2730 (2)	0.0144 (5)
C7	0.5138 (5)	0.59752 (12)	0.0668 (2)	0.0238 (6)
H7	0.6057	0.6073	0.0021	0.029*
C8	0.3328 (5)	0.55798 (12)	0.0476 (3)	0.0255 (7)
H8	0.3017	0.5410	-0.0304	0.031*
C9	0.1970 (5)	0.54294 (11)	0.1402 (3)	0.0230 (6)
H9	0.0724	0.5160	0.1255	0.028*
C10	0.2431 (5)	0.56730 (11)	0.2551 (2)	0.0186 (6)
H10	0.1524	0.5571	0.3199	0.022*
C11	0.3226 (5)	0.78114 (12)	0.3188 (3)	0.0270 (7)
H11	0.3655	0.8097	0.2671	0.032*
C12	0.1501 (5)	0.79107 (12)	0.3992 (3)	0.0306 (7)
H12	0.0781	0.8261	0.4025	0.037*
C13	0.0837 (5)	0.74979 (12)	0.4743 (3)	0.0272 (7)
H13	-0.0360	0.7563	0.5283	0.033*
C14	0.1917 (5)	0.69905 (12)	0.4707 (2)	0.0199 (6)
H14	0.1474	0.6705	0.5222	0.024*
C15	0.6217 (4)	0.61702 (10)	0.4822 (2)	0.0146 (5)
H1N	0.844 (4)	0.5600 (13)	0.532 (2)	0.037 (10)*
H1W	0.639 (5)	0.5774 (12)	0.773 (3)	0.051 (11)*
H1	0.708 (6)	0.6333 (15)	0.642 (3)	0.041 (10)*
H2N	0.698 (6)	0.5474 (11)	0.416 (2)	0.034 (9)*
H2W	0.894 (5)	0.5824 (14)	0.777 (3)	0.057 (12)*

Atomic displacement parameters ( $\text{\AA}^2$ ) for (III)

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.01676 (14)	0.02352 (16)	0.02204 (15)	0.00066 (11)	0.00097 (10)	-0.00367 (12)
O1	0.0246 (10)	0.0175 (10)	0.0105 (9)	-0.0003 (8)	-0.0007 (8)	-0.0022 (8)
O1W	0.0215 (10)	0.0240 (11)	0.0172 (10)	-0.0010 (9)	0.0025 (8)	-0.0015 (8)
N1	0.0163 (10)	0.0135 (11)	0.0120 (10)	0.0004 (8)	0.0022 (8)	-0.0011 (9)
N2	0.0245 (12)	0.0185 (13)	0.0144 (12)	0.0052 (10)	-0.0012 (10)	-0.0024 (10)
C1	0.0145 (12)	0.0148 (13)	0.0150 (12)	0.0009 (10)	-0.0040 (10)	-0.0027 (11)
C2	0.0155 (12)	0.0159 (14)	0.0200 (13)	-0.0023 (10)	-0.0047 (11)	-0.0012 (11)
C3	0.0238 (14)	0.0197 (15)	0.0229 (14)	-0.0049 (12)	0.0002 (12)	0.0064 (12)
C4	0.0198 (13)	0.0250 (16)	0.0182 (14)	-0.0047 (11)	0.0052 (11)	0.0032 (12)
C5	0.0168 (12)	0.0167 (14)	0.0145 (13)	0.0010 (10)	0.0026 (10)	0.0021 (11)
C6	0.0160 (12)	0.0152 (13)	0.0112 (12)	0.0034 (10)	-0.0011 (10)	-0.0013 (10)
C7	0.0307 (15)	0.0285 (16)	0.0132 (13)	0.0046 (12)	0.0066 (12)	0.0027 (12)
C8	0.0340 (16)	0.0257 (17)	0.0152 (14)	0.0026 (12)	-0.0037 (12)	-0.0053 (12)

C9	0.0235 (14)	0.0187 (14)	0.0248 (14)	-0.0021 (11)	-0.0047 (11)	-0.0024 (13)
C10	0.0199 (13)	0.0164 (14)	0.0197 (14)	0.0009 (11)	0.0036 (11)	0.0023 (12)
C11	0.0309 (16)	0.0179 (15)	0.0293 (16)	0.0002 (12)	-0.0085 (13)	0.0026 (13)
C12	0.0308 (16)	0.0217 (16)	0.0363 (18)	0.0105 (13)	-0.0080 (14)	-0.0098 (14)
C13	0.0223 (14)	0.0317 (17)	0.0267 (16)	0.0070 (12)	-0.0007 (12)	-0.0104 (14)
C14	0.0185 (13)	0.0234 (15)	0.0175 (13)	-0.0002 (11)	0.0001 (11)	-0.0050 (12)
C15	0.0142 (12)	0.0174 (14)	0.0130 (12)	-0.0025 (10)	0.0051 (10)	0.0006 (11)

*Geometric parameters (Å, °) for (III)*

O1—C15	1.299 (3)	C4—H4B	0.9900
O1—H1	0.84 (3)	C5—C6	1.392 (3)
O1W—H1W	0.868 (18)	C5—C7	1.393 (4)
O1W—H2W	0.861 (18)	C6—C10	1.387 (4)
N1—C15	1.333 (3)	C7—C8	1.386 (4)
N1—C6	1.443 (3)	C7—H7	0.9500
N1—C1	1.454 (3)	C8—C9	1.381 (4)
N2—C15	1.314 (3)	C8—H8	0.9500
N2—H1N	0.855 (18)	C9—C10	1.392 (4)
N2—H2N	0.863 (18)	C9—H9	0.9500
C1—C14	1.390 (4)	C10—H10	0.9500
C1—C2	1.392 (4)	C11—C12	1.391 (4)
C2—C11	1.399 (4)	C11—H11	0.9500
C2—C3	1.519 (4)	C12—C13	1.383 (4)
C3—C4	1.533 (4)	C12—H12	0.9500
C3—H3A	0.9900	C13—C14	1.382 (4)
C3—H3B	0.9900	C13—H13	0.9500
C4—C5	1.502 (4)	C14—H14	0.9500
C4—H4A	0.9900		
C15—O1—H1	114 (2)	C10—C6—N1	120.4 (2)
H1W—O1W—H2W	108 (4)	C5—C6—N1	117.0 (2)
C15—N2—H1N	120 (2)	C8—C7—C5	120.3 (2)
C15—N2—H2N	123 (2)	C8—C7—H7	119.8
H1N—N2—H2N	116 (3)	C5—C7—H7	119.8
C15—N1—C6	122.1 (2)	C9—C8—C7	121.0 (3)
C15—N1—C1	120.6 (2)	C9—C8—H8	119.5
C6—N1—C1	116.5 (2)	C7—C8—H8	119.5
C14—C1—C2	122.8 (2)	C8—C9—C10	119.8 (3)
C14—C1—N1	116.8 (2)	C8—C9—H9	120.1
C2—C1—N1	120.4 (2)	C10—C9—H9	120.1
C1—C2—C11	116.3 (2)	C6—C10—C9	118.6 (3)
C1—C2—C3	126.5 (2)	C6—C10—H10	120.7
C11—C2—C3	117.2 (2)	C9—C10—H10	120.7
C2—C3—C4	118.9 (2)	C12—C11—C2	121.9 (3)
C2—C3—H3A	107.6	C12—C11—H11	119.1
C4—C3—H3A	107.6	C2—C11—H11	119.1
C2—C3—H3B	107.6	C13—C12—C11	119.9 (3)
C4—C3—H3B	107.6	C13—C12—H12	120.1
H3A—C3—H3B	107.0	C11—C12—H12	120.1
C5—C4—C3	112.1 (2)	C14—C13—C12	119.9 (3)
C5—C4—H4A	109.2	C14—C13—H13	120.0

C3—C4—H4A	109.2	C12—C13—H13	120.0
C5—C4—H4B	109.2	C13—C14—C1	119.2 (3)
C3—C4—H4B	109.2	C13—C14—H14	120.4
H4A—C4—H4B	107.9	C1—C14—H14	120.4
C6—C5—C7	117.7 (2)	O1—C15—N2	122.0 (2)
C6—C5—C4	118.0 (2)	O1—C15—N1	116.7 (2)
C7—C5—C4	124.2 (2)	N1—C15—N2	121.3 (2)
C10—C6—C5	122.6 (2)		
C15—N1—C1—C14	-71.5 (3)	C1—N1—C6—C5	74.8 (3)
C6—N1—C1—C14	118.1 (2)	C6—C5—C7—C8	0.9 (4)
C15—N1—C1—C2	111.5 (3)	C4—C5—C7—C8	-176.0 (3)
C6—N1—C1—C2	-59.0 (3)	C5—C7—C8—C9	-0.2 (4)
C14—C1—C2—C11	1.5 (4)	C7—C8—C9—C10	-0.6 (4)
N1—C1—C2—C11	178.4 (2)	C5—C6—C10—C9	0.0 (4)
C14—C1—C2—C3	-177.4 (2)	N1—C6—C10—C9	176.0 (2)
N1—C1—C2—C3	-0.5 (4)	C8—C9—C10—C6	0.7 (4)
C1—C2—C3—C4	-1.3 (4)	C1—C2—C11—C12	-0.7 (4)
C11—C2—C3—C4	179.8 (2)	C3—C2—C11—C12	178.3 (2)
C2—C3—C4—C5	57.4 (3)	C2—C11—C12—C13	-0.6 (4)
C3—C4—C5—C6	-70.7 (3)	C11—C12—C13—C14	1.0 (4)
C3—C4—C5—C7	106.2 (3)	C12—C13—C14—C1	-0.2 (4)
C7—C5—C6—C10	-0.8 (4)	C2—C1—C14—C13	-1.1 (4)
C4—C5—C6—C10	176.3 (2)	N1—C1—C14—C13	-178.1 (2)
C7—C5—C6—N1	-176.9 (2)	C6—N1—C15—O1	171.6 (2)
C4—C5—C6—N1	0.2 (3)	C1—N1—C15—O1	1.7 (3)
C15—N1—C6—C10	88.3 (3)	C6—N1—C15—N2	-6.6 (4)
C1—N1—C6—C10	-101.4 (3)	C1—N1—C15—N2	-176.5 (2)
C15—N1—C6—C5	-95.5 (3)		

*Hydrogen-bond geometry (Å, °) for (III)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ O1 <i>W</i>	0.84 (3)	1.67 (4)	2.510 (3)	175 (3)
N2—H1 <i>N</i> $\cdots$ Br1 <sup>i</sup>	0.86 (2)	2.58 (2)	3.431 (2)	172 (3)
N2—H2 <i>N</i> $\cdots$ Br1 <sup>ii</sup>	0.86 (2)	2.58 (2)	3.355 (2)	149 (3)
O1 <i>W</i> —H1 <i>W</i> $\cdots$ Br1	0.87 (2)	2.45 (2)	3.2381 (19)	152 (3)
O1 <i>W</i> —H2 <i>W</i> $\cdots$ Br1 <sup>i</sup>	0.86 (2)	2.40 (2)	3.1960 (19)	154 (3)

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