Salt forms of amides: protonation of acetanilide

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Treating the amide acetanilide (N-phenylacetamide, C_8H_9NO) with aqueous strong acids allowed the structures of five hemi-protonated salt forms of acetanilide to be elucidated. N-(1-Hydroxyethylidene)anilinium chloride–N-phenylacetamide (1/1), $[(C_8H_9NO)_2H][Cl]$, and the bromide, $[(C_8H_9NO)_2H][Br]$, triiodide, $[(C_8H_9NO)_2H][I_3]$, tetrafluoroborate, $[(C_8H_9NO)_2H][BF_4]$, and diiodobromide hemi(diiodine), $[(C_8H_9NO)_2H][I_2Br]\cdot0.5I_2$, analogues all feature centrosymmetric dimeric units linked by O—H$\cdots$O hydrogen bonds that extend into one-dimensional hydrogen-bonded chains through N—H$\cdots X$ interactions, where X is the halide atom of the anion. Protonation occurs at the amide O atom and results in systematic lengthening of the C=O bond and a corresponding shortening of the C—N bond. The size of these geometric changes is similar to those found for hemi-protonated paracetamol structures, but less than those in fully protonated paracetamol structures. The bond angles of the amide fragments are also found to change on protonation, but these angular changes are also influenced by conformation, namely, whether the amide group is coplanar with the phenyl ring or twisted out of plane.

1. Introduction

The formation of salt phases of Active Pharmaceutical Ingredients (APIs) is a simple technique used by the pharmaceutical industry to enhance desirable materials properties of an acidic or basic API, whilst retaining the essential functional groups of the organic compound. Often the targeted property is enhanced aqueous solubility (Stahl & Wermuth, 2008). Salt screening is unlikely to be performed if the API contains only traditionally neutral functional groups, such as amides. All chemists learn at an early stage that amides are much less basic than amines, and it is perhaps this seed that leads to the misidentification or misnaming of amides as 'non-ionizable' (Manallack, 2007; Bethune *et al.*, 2009). Just because a compound is not normally ionized, or not protonated under normal physiological conditions, does not of course mean that it cannot be protonated given the right conditions. Protonation of amides is common in acidic solution and protonated forms of amides may even be isolated in the solid state to allow characterization by diffraction. In 2012, Nanubolu *et al.* (2012) surveyed known crystal structures of protonated amides. Since then, much API relevant work on the crystal structures of protonated amides has concentrated on carbamazepine and its relatives (Perumalla & Sun, 2012, 2013; Buist *et al.*, 2013, 2015; Buist & Kennedy, 2016; Eberlin *et al.*, 2013) and, most importantly to the current work, on paracetamol (Perumalla & Sun, 2012; Perumalla *et al.*, 2012; Trzybiński *et al.*, 2016; Kennedy *et al.*, 2018; Suzuki *et al.*, 2020). Protonated amide cations are of course themselves strong acids and thus highly unlikely drug candidates. The interest in their isolation and characterization is thus driven by academic
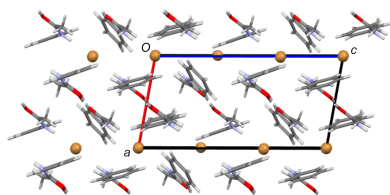
Table 1
Experimental details.

Experiments were carried out at 100 K with Cu $K\alpha$ radiation using a Rigaku Synergy-i diffractometer. H atoms were treated by a mixture of independent and constrained refinement.

	$[(ACT)_2H][Cl]$	$[(ACT)_2H][Br]$	$[(ACT)_2H][I_3]$
Crystal data			
Chemical formula	$C_8H_{10}NO^+ \cdot Cl^- \cdot C_8H_9NO$	$C_8H_{10}NO^+ \cdot Br^- \cdot C_8H_9NO$	$C_8H_{10}NO^+ \cdot I_3^- \cdot C_8H_9NO$
M_r	306.78	351.24	652.03
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a, b, c (Å)	7.7936 (1), 18.3639 (2), 16.3922 (1)	7.8794 (2), 9.7748 (3), 16.2720 (4)	7.3766 (2), 8.8131 (3), 9.3226 (2)
α, β, γ (°)	90, 102.245 (1), 90	104.385 (3), 98.342 (2), 96.386 (2)	113.612 (2), 103.144 (2), 104.263 (3)
V (Å^3)	2292.69 (4)	1186.86 (6)	500.61 (3)
Z	6	3	1
μ (mm^{-1})	2.26	3.59	36.86
Crystal size (mm)	$0.20 \times 0.15 \times 0.12$	$0.18 \times 0.04 \times 0.04$	$0.32 \times 0.08 \times 0.05$
Data collection			
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2023)	Analytical [*CrysAlis PRO* (Rigaku OD, 2023), based on expressions derived by Clark & Reid (1995)]	Gaussian (*CrysAlis PRO*; Rigaku OD, 2023)
T_{min}, T_{max}	0.725, 1.000	0.668, 0.890	0.034, 0.480
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23203, 4444, 4113	8381, 8381, 7175	7238, 1900, 1846
R_{int}	0.033	Not applicable	0.054
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.615	0.615	0.615
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.088, 1.04	0.054, 0.164, 1.11	0.038, 0.107, 1.10
No. of reflections	4444	8381	1900
No. of parameters	309	310	115
No. of restraints	2	5	2
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.26, −0.30	0.73, −0.90	1.24, −1.79

	$[(ACT)_2H][BF_4]$	$[(ACT)_2H][I_2Br] \cdot 0.5I_2$
Crystal data		
Chemical formula	$C_8H_{10}NO^+ \cdot BF_4^- \cdot C_8H_9NO$	$C_8H_{10}NO^+ \cdot I_2Br^- \cdot C_8H_9NO \cdot 0.5I_2$
M_r	358.14	735.18
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/m$
a, b, c (Å)	7.1070 (1), 9.5381 (1), 13.3592 (1)	5.8956 (1), 18.6224 (4), 19.9632 (4)
α, β, γ (°)	98.765 (1), 98.034 (1), 105.977 (1)	90, 91.970 (2), 90
V (Å^3)	844.56 (2)	2190.47 (7)
Z	2	4
μ (mm^{-1})	1.05	36.46
Crystal size (mm)	$0.15 \times 0.15 \times 0.10$	$0.24 \times 0.08 \times 0.06$
Data collection		
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2023)	Analytical [*CrysAlis PRO* (Rigaku OD, 2023), based on expressions derived by Clark & Reid (1995)]
T_{min}, T_{max}	0.816, 1.000	0.014, 0.164
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16151, 3261, 3204	21645, 4338, 3762
R_{int}	0.026	0.096
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.615	0.615
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.099, 1.04	0.052, 0.151, 1.08
No. of reflections	3261	4338
No. of parameters	241	245
No. of restraints	1	2
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.50, −0.29	1.50, −1.86

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *SHELXL2018* in *WinGX* (Farrugia, 2012).

interest and by manufacturing considerations, such as utilizing their mechanical properties to change compaction and tableting properties prior to final formulation (Perumalla *et al.*, 2012). Herein we report five crystal structures of hemiprotonated salt forms of the paracetamol congener acetanilide (ACT). Despite its historical use as a pharmaceutical and its structural similarity to paracetamol, ACT is no longer used as an API (Brodie & Axelrod, 1948). However, as a fundamental simple amide, it has multiple industrial uses, including as a synthetic precursor in the pharmaceutical industry (Singh *et*

al., 2019; Li *et al.*, 2024). The structures presented herein are [(ACT)$_2$H][Cl], [(ACT)$_2$H][Br], [(ACT)$_2$H][I$_3$], [(ACT)$_2$H]-[BF$_4$] and [(ACT)$_2$H][I$_2$Br]·0.5I$_2$. Previous solid-state phase work on such a fundamental compound as ACT has been surprisingly limited. Structures previously reported include that of the compound itself (Wasserman *et al.*, 1985), those of a small number of cocrystal forms (*e.g.* Megumi *et al.*, 2013; Oliveira *et al.*, 2013), and a few structures where ACT acts as a ligand (*e.g.* Buchner & Müller,, 2023; Marchetti *et al.*, 2008).

Scheme 1
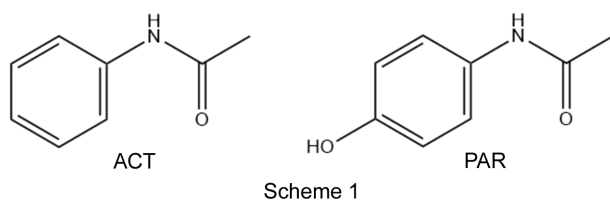
2. Experimental

### 2.1. Synthesis and crystallization

The I$_3$, BF$_4$ and mixed Br/I samples were obtained by dissolving ACT (0.21 g, 1.6 mmol) in methanol (1 ml). Approximately 1 ml of the appropriate concentrated aqueous acid was then added. For the mixed Br/I species, this acid was a 5:1 mixture of HI and HBr. In each case, after 3–7 d of slow evaporation, crystals were deposited. In the case of the mixed Br/I species, orange crystals of the ACT salt form were mixed with colourless crystals of the decomposition product [PhNH$_3$]-[Br]. Crystals of the Cl salt were prepared in a similar way, but here ACT (0.40 g, 3 mmol) was dissolved in methanol (4 ml) and concentrated HCl (2 ml) added. Using similar techniques
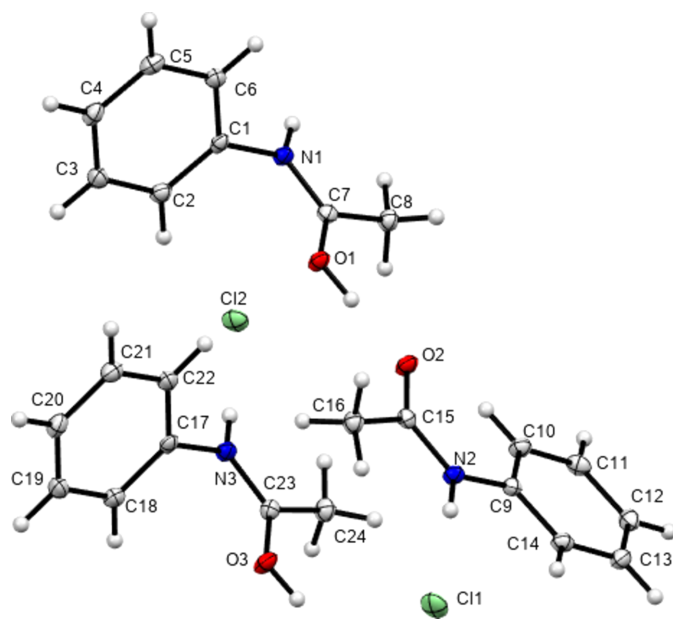
Figure 1
Contents of the asymmetric unit of [(ACT)$_2$H][Cl]. Note that atom Cl1 sits on a crystallographic centre of symmetry. Here and elsewhere, displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary size.
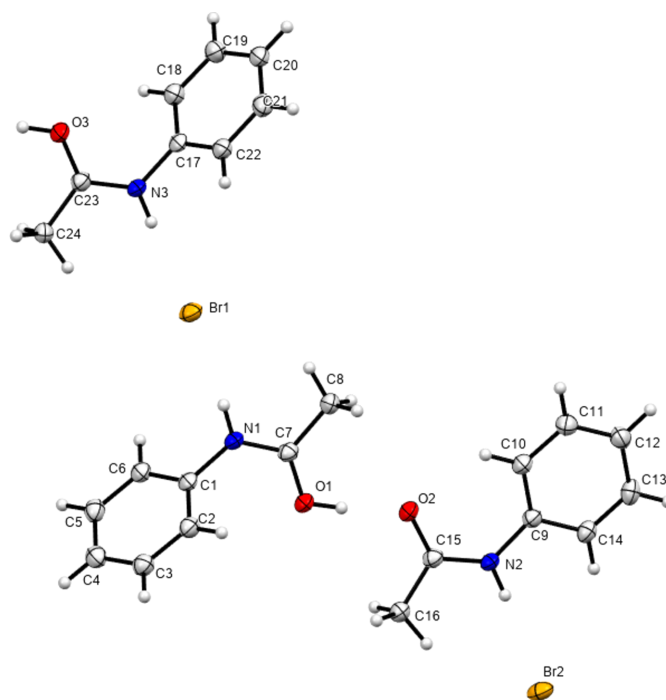
Figure 2
Contents of the asymmetric unit of [(ACT)$_2$H][Br].

with concentrated HBr gave only crystals of [PhNH$_3$][Br]. Crystals of the required Br salt form were thus prepared by dissolving ACT (0.25 g) in concentrated aqueous HBr (2 ml). Crystals of the Br salt were deposited within 3 d.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Data measured for [(ACT)$_2$H][Br] were treated as twinned by a 180° rotation about [0, 0.71, −0.71] to give a HKLF 5 formatted reflection file. The BASF parameter refined to 0.3996 (13). The structure of the mixed I/Br species was originally refined as [(ACT)$_2$H][I$_2$Br]·0.5I$_2$, with all halide sites ordered. However, residual electron density and displacement parameters suggested that this treatment was not idealized. Individual trial calculations treating each halide site as a mixture of I and Br suggested that a mixed model was appropriate for two of the halide sites. Thus, the I5/Br3 and Br1/I7 sites were modelled as mixed occupancy, each with a total halide occupancy of one. See Section 3 (*Results and discussion*) for further comment. All H atoms bound to C atoms were placed in idealized positions and refined in riding modes, with C—H = 0.95 and 0.98 Å for CH and CH$_3$ groups, respectively. U_{iso} values were set at 1.2U_{eq} or 1.5U_{eq} of the parent atom for CH and CH$_3$ groups, respectively. H atoms bound to N or to O atoms were refined isotropically, but with the X—H distances restrained to 0.88 (1) Å. The exceptions to this latter statement were [(ACT)$_2$H][Cl], where H atoms bound to N atoms were refined freely and isotropically, and [(ACT)$_2$H][I$_2$Br]·0.5I$_2$, where the half-occupancy H atoms of the OH groups were placed in idealized positions.

3. Results and discussion

In 2012, Perumalla & Sun (2012) reported that non-aqueous sources of HCl were capable of protonating amides that concentrated aqueous hydrochloric acid could not, and that non-aqueous sources of HCl could give anhydrous versions of salt forms of amides where aqueous acid could not. It has been shown since that salt forms of amides (including anhydrous salts) are accessible by either simply dissolving the amide in the concentrated aqueous acid or by adding concentrated aqueous acid to alcohol solutions of the amide (Buist *et al.*, 2015; Kennedy *et al.*, 2018). The latter aqueous methods were adopted here using the strong acids HX (X = Cl, Br and I) and HBF$_4$. All isolated crystals containing ACT were found to be anhydrous hemi-protonated salt forms. The asymmetric unit contents of the five structures [(ACT)$_2$H][Cl], [(ACT)$_2$H][Br], [(ACT)$_2$H][I$_3$], [(ACT)$_2$H][BF$_4$] and [(ACT)$_2$H][I$_2$Br]·0.5I$_2$ are presented in Figs. 1–5, with selected crystallographic and refinement parameters given in Table 1. Note that for the mixed I/Br species, the formula used herein, [(ACT)$_2$H]-[I$_2$Br]·0.5I$_2$, is a simplified approximation. Two of the halide atom sites were modelled as mixed I/Br sites, see Section 2.2 (*Refinement*). A small excess of I in the refined model implies the existence of some I$_3^-$ anions, as well as the majority I$_2$Br$^-$, and gives an overall formula of [(ACT)$_2$H][I$_2$Br]$_{0.93}$[I$_3$]$_{0.07}$·0.5I$_2$. All the halide atoms of this structure lie on the mirror plane of the space group $P2_1/m$. Well-ordered organic structures containing mixed-halide anions such as I$_2$Br are known (Buist & Kennedy, 2014), but, as here, structures with mixed I/Br polyhalides are often found to be disordered (*e.g.* Kobra *et al.*, 2019; Laukhina *et al.*, 1997). A recent article describes how the structures of polyiodide and related salt forms can be treated as being formed from X^-, X_3^- and X_2 building blocks (Blake *et al.*, 2024).

All five structures are protonated at the amide O atom and all form O—H···O hydrogen-bonded dimers between what have been modelled as protonated ACT(H) cations and neutral ACT molecules. Note that, in all cases, free refinement of the H-atom position resulted in the H atom moving towards
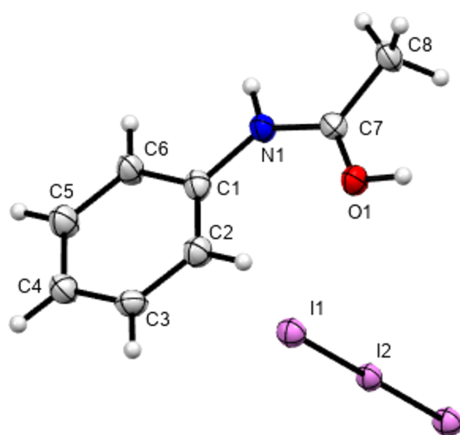
Figure 3
Contents of the asymmetric unit of [(ACT)$_2$H][I$_3$], expanded to show the complete triiodide anion.
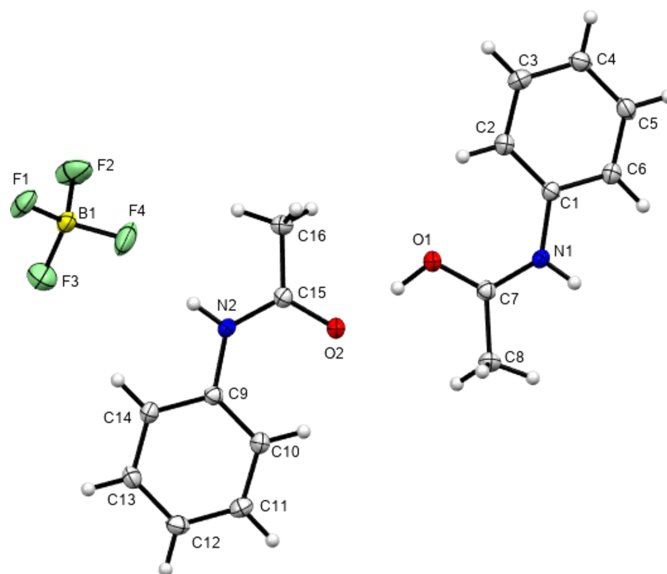
Figure 4
Contents of the asymmetric unit of [(ACT)$_2$H][BF$_4$].

the centre of the O···O separation and that in the given models the acidic H atom has been restrained to sit 0.88 (1) Å from the O atom to which it was found to be closest. The very short O···O distances of 2.422 (10)–2.4650 (12) Å indicate strong interactions and it should be borne in mind that the models with distinct ACT(H) and ACT units may in fact represent cases where the H atom is intermediate between the two O-atom positions. A relevant precedent for such an intermediate behaviour is given by Eberlin *et al.* (2013). An obvious difference between paracetamol (PAR) and ACT is that, under a wide variety of aqueous, non-aqueous and even solid-grinding preparation methods, PAR tends to give fully protonated [PAR(H)][X] species, where X is Cl, Br, I or a variety of RSO$_3$ anions (Perumalla *et al.*, 2012; Suzuki *et al.*, 2020; Trzybiński *et al.*, 2016; Kennedy *et al.*, 2018). In contrast, the only structures of PAR hemi-protonated forms reported are with Cl$^-$ and I$_3^-$ anions (Perumalla & Sun, 2012; Kennedy *et al.*, 2018). That ACT was only found to form hemi-protonated salts may be due to a lower basicity of the amide caused by it lacking the electron-donating *para*-OH group of PAR. This conjecture is supported by the only other structure available with a protonated (Ar)NHC(O)Me fragment. Reaction of *o*-tolylNHC(O)Me, which has no strong electron-donating substituent, with nitric acid was found to give a hemi-protonated salt form (Gubin *et al.*, 1989). All hemi-protonated forms of PAR and of *o*-tolylNHC(O)Me feature the same dimer motif linked by O—H···O hydrogen bonding between protonated and neutral amide functions, as is seen in the five ACT structures.

Protonation of the amide in carbamazepine has been shown to lengthen the amide C—O bond and shorten the amide C—N bond, as would be expected for a structure showing resonance of the N-atom lone pair through to the O atom (Buist *et al.*, 2013; Eberlin *et al.*, 2013). Similar geometric changes can be seen in the amide groups of the five protonated

ACT structures (see Fig. 6). The C=O bond distances lengthen from 1.238 Å in ACT to a range of 1.257 (5)–1.2843 (15) Å for the ACT(H) species. This is accompanied by a corresponding decrease in the C—N distance from 1.356 Å in ACT to 1.3114 (16)–1.336 (10) Å for ACT(H). That all crystallographically independent ACT fragments show changes in bond lengths indicate that all are affected to some degree by protonation – despite the structural models formally containing both ACT and ACT(H) fragments. Comparison of Fig. 6 with Fig. 7 shows that these changes are comparable with those found in the structures of hemi-protonated PAR salt forms (Perumalla & Sun, 2012; Kennedy et al., 2018). They are also similar to the geometric changes caused by coordination of ACT to main group or transition metals (Megumi et al., 2013; Oliveira et al., 2013). Fig. 7 also shows a cluster of points below and to the right of the hemi-protonated species, these are the fully-protonated PAR salt forms which can be seen to show larger deviations from the geometries of the parent APIs than do the hemi-protonated salt forms (Perumalla et al., 2012; Suzuki et al., 2020; Trzybiński et al., 2016; Kennedy et al., 2018).

The bond angles of the amide group can also be seen to change upon protonation. The N—C—CH$_3$ angle widens from 115.4° in ACT to between 116.1 (1) and 118.4 (1)° in the ACT(H) fragments. Correspondingly, the O—C—N angle decreases from 123.4° in ACT to between 120.1 (1) and 121.9 (1)° for ACT(H). Plotting N—C—CH$_3$ against the N—C bond length (Fig. 6) shows that the values for two of the ACT(H) fragments are displaced somewhat towards the values for ACT. Interestingly, these displaced values are for the single crystallographically independent ACT moiety in the Cl and Br structures that are modelled as being nonprotonated. Thus, despite undoubtably having an intermediate-type geometry, these moieties modelled as ACT are truly more ACT-like than are those modelled as ACT(H). The same is not true of the fragment modelled as ACT in the BF$_4$ structure, and careful examination of the residual electron density suggests that the ACT/ACT(H) model adopted here is indeed less suitable and that both fragments should perhaps bear a partial H atom.

A final interesting feature shown in Fig. 6 is that, on protonation of the amide, the C—N—C angles do not either uniformly widen or narrow. Instead, both behaviours are

observed [C—N—C for ACT of 127.4° versus the range 124.8 (3)–130.4 (6)° for the ACT(H) salt forms]. This causes the ACT(H) structures to split into two separate clusters when, for instance, the C—N—C angle is plotted against the

(a)

(b)

(c)
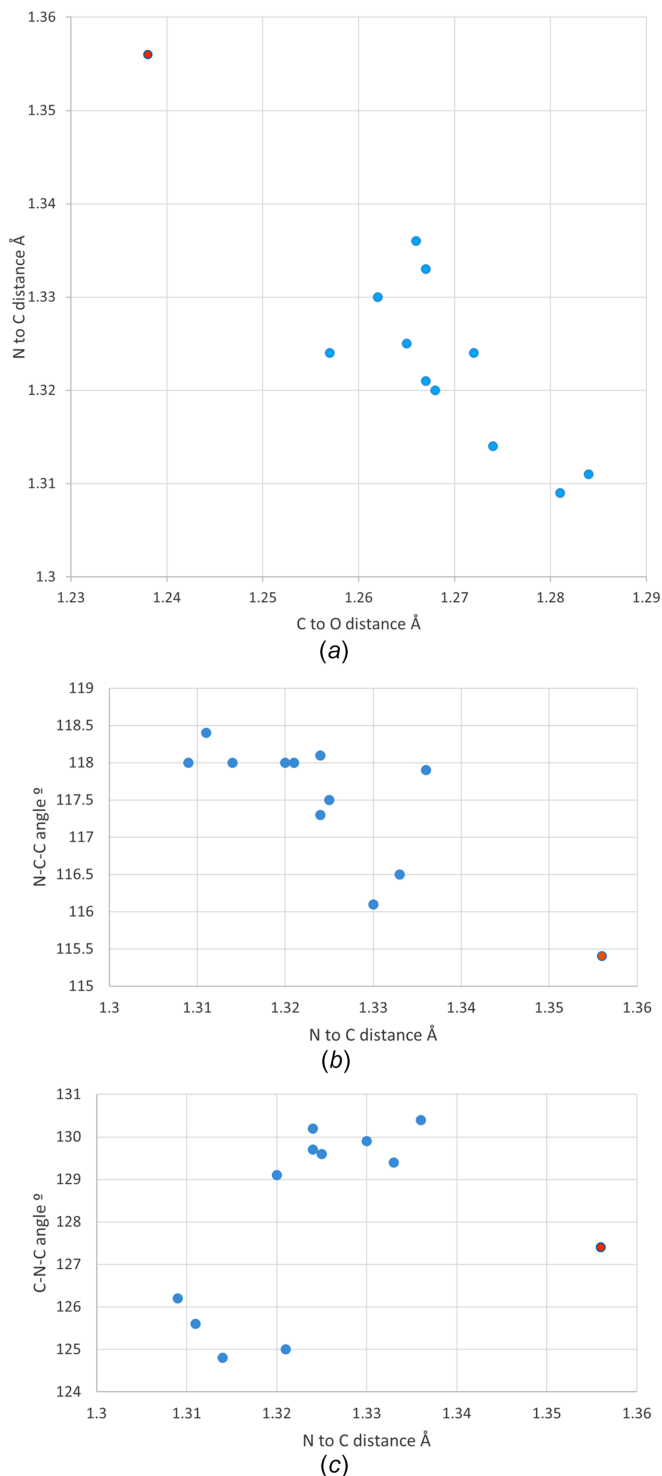
Figure 6
(a) Amide C—O and N—C distances in hemi-protonated ACT(H) structures. Amide N—C distances plotted against (b) N—C—C and (c) C—N—C angles. Blue dots = hemi-protonated ACT species from this article and orange dots = neutral ACT from the high-resolution charge–density data set of Hathwar et al. (2011).

Figure 5
Contents of the asymmetric unit of [(ACT)$_2$H][I$_2$Br]·0.5I$_2$, with atoms of the minor disorder positions omitted for clarity.

Table 2
Hydrogen-bond geometry (Å, °) for [(ACT)₂H][Cl].

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
N1—H1N⋯Cl2[i]	0.854 (18)	2.237 (19)	3.0899 (11)	176.6 (16)
N2—H2N⋯Cl1	0.851 (18)	2.297 (18)	3.1464 (10)	177.0 (16)
N3—H3N⋯Cl2	0.844 (18)	2.275 (18)	3.1189 (11)	177.6 (16)
O1—H1*H*⋯O2	0.90 (1)	1.57 (1)	2.4650 (12)	175 (3)
O3—H2*H*⋯O3[ii]	0.88 (1)	1.56 (1)	2.4370 (16)	176 (7)

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

Table 3
Hydrogen-bond geometry (Å, °) for [(ACT)₂H][Br].

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
N1—H1N⋯Br1	0.88 (1)	2.35 (1)	3.228 (3)	176 (4)
N2—H2N⋯Br2	0.88 (1)	2.44 (1)	3.316 (3)	176 (4)
N3—H3N⋯Br1	0.88 (1)	2.39 (2)	3.256 (3)	174 (4)
O1—H1*H*⋯O2	0.89 (1)	1.57 (2)	2.454 (4)	172 (6)
O3—H2*H*⋯O3[i]	0.88 (1)	1.55 (2)	2.428 (5)	173 (16)

Symmetry code: (i) $-x - 1, -y, -z$.

Table 4
Hydrogen-bond geometry (Å, °) for [(ACT)₂H][I₃].

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
N1—H1N⋯I1[i]	0.88 (1)	2.82 (1)	3.700 (3)	178 (5)
O1—H1*H*⋯O1[ii]	0.88 (1)	1.55 (2)	2.430 (6)	175 (15)

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

Table 5
Hydrogen-bond geometry (Å, °) for [(ACT)₂H][BF₄].

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
N1—H1N⋯F1[i]	0.854 (18)	2.007 (19)	2.8606 (13)	177.6 (16)
N2—H2N⋯F4	0.859 (17)	2.033 (18)	2.8744 (14)	166.0 (15)
O1—H1*H*⋯O2	0.91 (1)	1.53 (1)	2.4333 (12)	174 (3)

Symmetry code: (i) $x, y, z + 1$.

Table 6
Hydrogen-bond geometry (Å, °) for [(ACT)₂H][I₂Br]·0.5I₂.

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
N1—H1N⋯Br2	0.88 (1)	2.49 (1)	3.367 (5)	175 (7)
N2—H2N⋯Br1	0.88 (1)	2.69 (2)	3.546 (10)	164 (7)
O1—H1*H*⋯O1[i]	0.88	1.62	2.442 (10)	155
O2—H2*H*⋯O2[ii]	0.88	1.58	2.434 (10)	164

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

N—C distance. The four points where the angle has narrowed correspond to the four fragments with nonplanar conformations, whilst the larger group all have the amide group approximately coplanar with the aromatic ring (compare twist angles of 49.1–57.5 ° for the nonplanar group to twist angles of 2.0–13.6° for the planar group). A similar effect can be seen in the protonated PAR structures from the literature. Of 14 crystallographically independent PAR units, ten are planar and th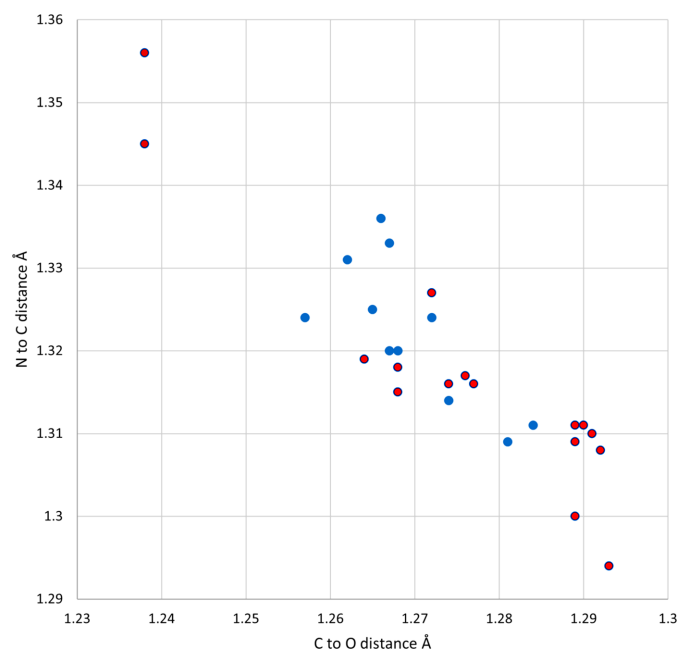ese all show an increase in the C—N—C angle upon protonation. Four structures of protonated PAR structures, those with sulfonate anions, adopt twisted conformations and

Figure 7
Amide C—O and N—C distances in ACT and PAR structures. Blue dots = hemi-protonated ACT species from this article, orange dots = neutral ACT and PAR (Nichols & Frampton, 1998), and red dots = hemi- and fully-protonated PAR species.

for these the C—N—C angle remains constant or decreases upon protonation. Presumably an out-of-plane twist reduces steric contacts between the amide fragments and the rings, allowing the angles about the N atom to narrow.

As described above, the main intermolecular feature of each hemi-protonated ACT structure is the strong centro-symmetric O—H⋯O hydrogen-bond contact that forms dimers between ACT molecules and ACT(H) cations. This dimer is also seen in the structures of other hemi-protonated amides. Another intermolecular contact common to all five ACT species herein is that the N—H group always acts as a hydrogen-bond donor to the anion (see Tables 2–6 for details). In the Cl, Br and mixed I/Br salt forms, the N—H to anion interactions link the dimers described above to give $C_3^2(10)$ one-dimensional hydrogen-bonded chains (see Fig. 8 for an example). In the Cl and Br salts, each chain involves all crystallographically unique molecules and ions, whilst in the mixed I/Br structure, it is only the Br site of each I₂Br⁻ anion that accepts hydrogen bonds from N—H and each crystallographically unique ACT fragment propagates a separate hydrogen-bonded chain. The I₃ and BF₄ salt forms display equivalent chain motifs, but, in these cases, a three-atom link through the body of the anion replaces the single halide atom link above (see Fig. 9). Thus, these are formally $C_3^3(12)$ motifs.

Other intermolecular contacts of around the sum of the van der Waals radii or less are more variable. The I₃, BF₄ and mixed I/Br salt forms all feature π–π interactions between ACT fragments [minimum C⋯C distances of 3.330 (7), 3.355 (2) and 3.348 (11) Å for the I₃, BF₄ and mixed I/Br salts, respectively]. For the latter species, this is between offset parallel ACT units, and for the I₃ and BF₄ salt forms, this is between antiparallel units. Fig. 10 shows the π–π interactions of [(ACT)₂H][I₃] and also illustrates the last type of inter-
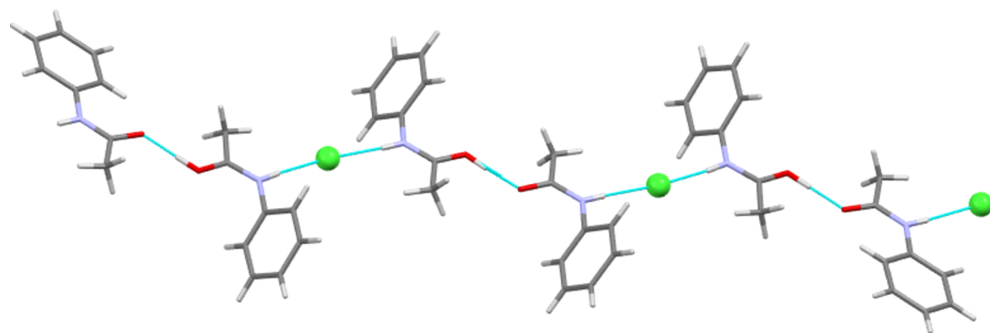
Figure 8
The one-dimensional hydrogen-bonded chain formed by O—H···O and N—H···Cl contacts in [(ACT)$_2$H][Cl]. Similar chains are present in the Br and I/Br salt structures.
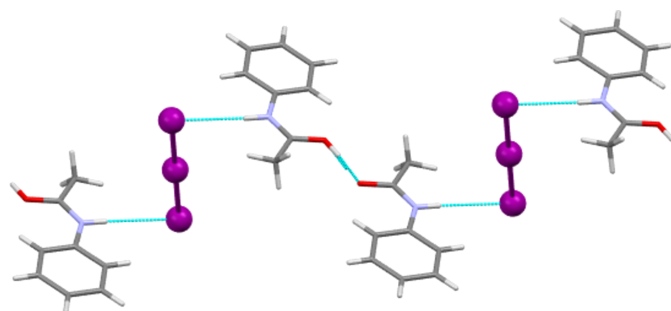
Figure 9
The stepped one-dimensional hydrogen-bonded chain formed by O—H···O and N—H···I contacts in [(ACT)$_2$H][I$_3$]. A similar chain motif is present in [(ACT)$_2$H][BF$_4$], but here the steps caused by the linear I$_3^-$ anion are absent.

Figure 11
The packing structure of [(ACT)$_2$H][Cl], viewed along the *b* axis.

molecular contact to be highlighted here. The Cl, Br and I$_3$ salt forms all feature short π-geometry contacts between halide atoms and C atoms adjacent to the N atom of the formally positively charged amide group. The C···X distances are 3.3286 (12), 3.469 (4) and 3.677 (4) Å for the Cl, Br and I$_3$ salts, respectively. For Cl and Br, these distances are to the carbonyl C atom, but for I$_3$, the closest contact is to atom C1 of the phenyl ring.

In many ways, the structures of the Cl and Br salt forms are very similar. Both contain three crystallographically independent ACT fragments, two of which have twisted conformations, and two halide sites, one of which is a crystallographic centre of symmetry. As Table 7 shows, they also feature the same types of intermolecular interactions. Despite this, the

Table 7
Intermolecular interactions found in hemi-protonated ACT structures.

Anion	O—H···O dimer	Hydrogen-bonded chain	π-anion	π–π	Layering
Cl	Yes	Yes	Yes	No	No
Br	Yes	Yes	Yes	No	Yes
I$_3$	Yes	Yes	Yes	Yes	Yes
BF$_4$	Yes	Yes	No	Yes	No
I$_2$Br	Yes	Yes	No	Yes	Yes

two salt forms have different packing structures. Comparing Figs. 11 and 12 shows that the Br salt forms a layered structure with alternating layers of anions and bilayers of ACT species, whilst in the Cl salt structure, there are no complete anion

Figure 10
Section of the structure of [(ACT)$_2$H][I$_3$], showing both antiparallel π–π contacts between ACT fragments and π-geometry C···I contacts between the amide and the anion.
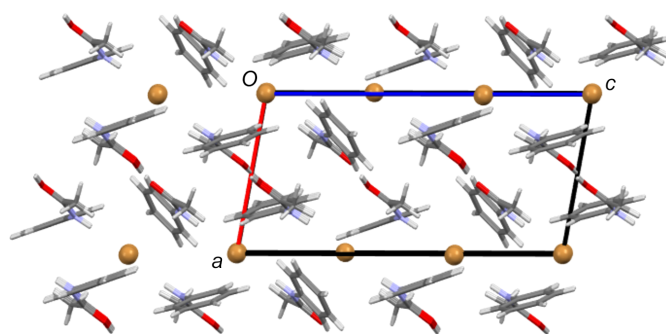
Figure 12
The packing structure of [(ACT)$_2$H][Br], viewed along the *b* axis. Note the layers of halide ions and bilayers of ACT fragments that alternate along the *a* direction.

layers due to their interruption by amide fragments. Of the other structures, the I_3 and mixed I/Br salt forms give structures with alternate monolayers of anions and organic species (see Fig. 13), whilst the BF_4 salt does not form layers.

4. Summary

The structures of five anhydrous hemi-protonated salt forms of the simple amide ACT are presented. That no fully protonated forms were isolated is a fundamental difference from ACT's close congener PAR. All five structures are based around O—H···O-contacted ACT(H)–ACT dimers that further link into one-dimensional hydrogen-bonded chains through N—H···anion hydrogen bonds. Both amide bond lengths and bond angles change upon protonation. As expected from resonance considerations, the C=O bond lengthens and the C—N bond shortens. The magnitude of these deviations from the geometry of neutral ACT are in line with similar changes seen in hemi-protonated PAR but less than those seen in fully protonated PAR salts. That care should be taken in ascribing all observed changes to protonation is shown by the C—N—C angle. Here large changes seem to be associated more with a change in conformation between planar and twisted units than they are with protonation of the amide.

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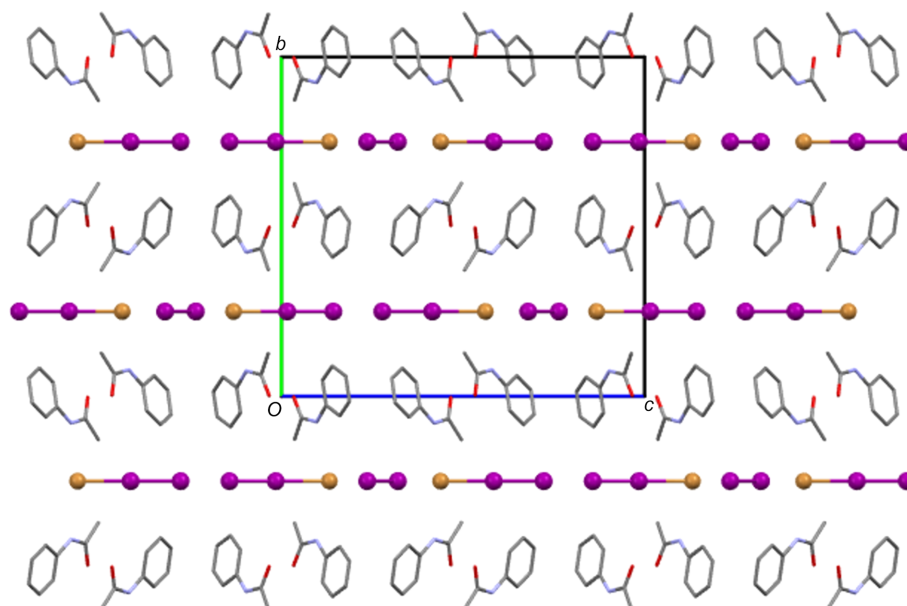
Figure 13
The packing structure of $[(ACT)_2H][I_2Br]\cdot0.5I_2$, with H atoms and minor disorder components omitted for clarity. The view is down the *a* axis. Note the layers of halide atoms and ACT fragments that alternate along the *b* direction.

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supporting information

Salt forms of amides: protonation of acetanilide

Harry S. Jaconelli and Alan R. Kennedy

Computing details

N-(1-Hydroxyethylidene)anilinium chloride–*N*-phenylacetamide (1/1) (ACTHCl)

Crystal data

$C_8H_{10}NO^+\cdot Cl^-\cdot C_8H_9NO$	$F(000) = 972$
$M_r = 306.78$	$D_x = 1.333$ Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$a = 7.7936$ (1) Å	Cell parameters from 17138 reflections
$b = 18.3639$ (2) Å	$\theta = 3.6$–71.5°
$c = 16.3922$ (1) Å	$\mu = 2.26$ mm^{-1}
$\beta = 102.245$ (1)°	$T = 100$ K
$V = 2292.69$ (4) Å^3	Fragment, colourless
$Z = 6$	$0.20 \times 0.15 \times 0.12$ mm

Data collection

Rigaku Synergy-i diffractometer	4444 independent reflections
Radiation source: microsource tube	4113 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.033$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2023)	$\theta_{max} = 71.6°$, $\theta_{min} = 3.7°$
$T_{min} = 0.725$, $T_{max} = 1.000$	$h = -9 \rightarrow 9$
23203 measured reflections	$k = -22 \rightarrow 22$
	$l = -20 \rightarrow 19$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.031$	
$wR(F^2) = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.7515P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
4444 reflections	$(\Delta/\sigma)_{max} = 0.002$
309 parameters	$\Delta\rho_{max} = 0.26$ e Å^{-3}
2 restraints	$\Delta\rho_{min} = -0.30$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	−0.500000	0.500000	0.500000	0.02398 (12)	
Cl2	0.48309 (4)	0.51388 (2)	0.83954 (2)	0.01975 (10)	
O1	0.06759 (11)	0.55205 (5)	0.89225 (5)	0.01583 (19)	
O2	−0.07277 (11)	0.46451 (5)	0.78459 (5)	0.01730 (19)	
O3	0.05548 (12)	0.54574 (5)	0.55287 (5)	0.0184 (2)	
N1	0.26521 (14)	0.56132 (6)	1.01360 (6)	0.0138 (2)	
N2	−0.25432 (13)	0.43603 (6)	0.66144 (6)	0.0141 (2)	
N3	0.22695 (14)	0.56869 (6)	0.67856 (6)	0.0152 (2)	
C1	0.26759 (15)	0.63949 (6)	1.01664 (7)	0.0132 (2)	
C2	0.32839 (16)	0.67877 (7)	0.95615 (7)	0.0155 (2)	
H2	0.363096	0.654464	0.911101	0.019*	
C3	0.33770 (16)	0.75415 (7)	0.96250 (7)	0.0176 (3)	
H3	0.378720	0.781593	0.921355	0.021*	
C4	0.28744 (16)	0.78985 (7)	1.02862 (8)	0.0175 (3)	
H4	0.293194	0.841450	1.032342	0.021*	
C5	0.22884 (16)	0.74965 (7)	1.08915 (7)	0.0171 (3)	
H5	0.194935	0.773926	1.134420	0.021*	
C6	0.21946 (15)	0.67413 (7)	1.08391 (7)	0.0154 (2)	
H6	0.180757	0.646587	1.125651	0.018*	
C7	0.17577 (15)	0.52162 (7)	0.95266 (7)	0.0138 (2)	
C8	0.19861 (16)	0.44101 (7)	0.95723 (8)	0.0163 (3)	
H8A	0.087714	0.418050	0.962105	0.024*	
H8B	0.290077	0.428440	1.006073	0.024*	
H8C	0.233041	0.423554	0.906519	0.024*	
C9	−0.23672 (15)	0.35903 (7)	0.65964 (7)	0.0131 (2)	
C10	−0.10451 (16)	0.31976 (7)	0.71214 (7)	0.0154 (2)	
H10	−0.019600	0.344153	0.753194	0.019*	
C11	−0.09841 (16)	0.24457 (7)	0.70370 (7)	0.0173 (3)	
H11	−0.008348	0.217709	0.739280	0.021*	
C12	−0.22177 (16)	0.20794 (7)	0.64410 (7)	0.0172 (3)	
H12	−0.216216	0.156513	0.638978	0.021*	
C13	−0.35313 (16)	0.24732 (7)	0.59217 (7)	0.0171 (3)	
H13	−0.438269	0.222712	0.551424	0.021*	
C14	−0.36067 (16)	0.32241 (7)	0.59948 (7)	0.0154 (2)	
H14	−0.450426	0.349080	0.563465	0.018*	
C15	−0.18110 (15)	0.48381 (7)	0.71954 (7)	0.0138 (2)	
C16	−0.23444 (17)	0.56161 (7)	0.70313 (8)	0.0174 (3)	
H16A	−0.291679	0.579119	0.747181	0.026*	
H16B	−0.316379	0.565393	0.648967	0.026*	
H16C	−0.130206	0.591275	0.702497	0.026*	
C17	0.20133 (15)	0.64599 (7)	0.67550 (7)	0.0139 (2)	
C18	0.23953 (16)	0.68648 (7)	0.60997 (7)	0.0162 (3)	
H18	0.280695	0.663189	0.566039	0.019*	
C19	0.21668 (16)	0.76145 (7)	0.60961 (8)	0.0181 (3)	
H19	0.242217	0.789559	0.565000	0.022*	

C20	0.15684 (16)	0.79586 (7)	0.67383 (8)	0.0176 (3)	
H20	0.140390	0.847137	0.672841	0.021*	
C21	0.12123 (16)	0.75474 (7)	0.73948 (8)	0.0176 (3)	
H21	0.081215	0.778060	0.783725	0.021*	
C22	0.14391 (16)	0.67973 (7)	0.74066 (7)	0.0160 (3)	
H22	0.120315	0.651685	0.785735	0.019*	
C23	0.15859 (15)	0.52293 (7)	0.61828 (7)	0.0145 (2)	
C24	0.20486 (17)	0.44421 (7)	0.63026 (8)	0.0179 (3)	
H24A	0.097099	0.415107	0.621524	0.027*	
H24B	0.272889	0.436418	0.687104	0.027*	
H24C	0.274947	0.429423	0.590004	0.027*	
H1N	0.331 (2)	0.5392 (10)	1.0543 (11)	0.030 (5)*	
H2N	−0.324 (2)	0.4522 (10)	0.6180 (11)	0.028 (4)*	
H3N	0.294 (2)	0.5535 (9)	0.7228 (11)	0.027 (4)*	
H1H	0.011 (4)	0.5215 (13)	0.8525 (14)	0.113 (11)*	
H2H	0.011 (8)	0.513 (3)	0.516 (3)	0.066 (14)*	0.5

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0214 (2)	0.0286 (2)	0.0187 (2)	0.00005 (18)	−0.00286 (17)	0.01083 (18)
Cl2	0.01927 (16)	0.02283 (18)	0.01485 (16)	0.00253 (12)	−0.00154 (11)	0.00524 (11)
O1	0.0179 (4)	0.0131 (4)	0.0135 (4)	−0.0002 (3)	−0.0032 (3)	−0.0005 (3)
O2	0.0189 (4)	0.0157 (4)	0.0140 (4)	−0.0013 (4)	−0.0037 (3)	−0.0015 (3)
O3	0.0209 (4)	0.0145 (5)	0.0158 (4)	−0.0002 (4)	−0.0050 (3)	−0.0029 (4)
N1	0.0159 (5)	0.0116 (5)	0.0119 (5)	0.0005 (4)	−0.0015 (4)	0.0010 (4)
N2	0.0148 (5)	0.0133 (5)	0.0122 (5)	0.0011 (4)	−0.0013 (4)	0.0009 (4)
N3	0.0177 (5)	0.0129 (5)	0.0125 (5)	−0.0007 (4)	−0.0021 (4)	0.0014 (4)
C1	0.0131 (5)	0.0108 (6)	0.0132 (5)	−0.0004 (4)	−0.0030 (4)	−0.0007 (4)
C2	0.0166 (6)	0.0159 (6)	0.0126 (5)	−0.0002 (5)	−0.0003 (4)	−0.0009 (5)
C3	0.0197 (6)	0.0162 (6)	0.0154 (6)	−0.0023 (5)	0.0008 (5)	0.0029 (5)
C4	0.0186 (6)	0.0119 (6)	0.0198 (6)	−0.0008 (5)	−0.0013 (5)	−0.0011 (5)
C5	0.0178 (6)	0.0168 (6)	0.0156 (6)	0.0004 (5)	0.0006 (5)	−0.0042 (5)
C6	0.0159 (6)	0.0160 (6)	0.0132 (5)	−0.0020 (5)	0.0005 (4)	0.0002 (5)
C7	0.0142 (6)	0.0145 (6)	0.0134 (5)	−0.0003 (5)	0.0042 (4)	−0.0002 (4)
C8	0.0187 (6)	0.0128 (6)	0.0166 (6)	−0.0003 (5)	0.0020 (5)	−0.0005 (5)
C9	0.0149 (5)	0.0138 (6)	0.0110 (5)	−0.0001 (5)	0.0032 (4)	0.0002 (4)
C10	0.0149 (6)	0.0172 (6)	0.0129 (5)	0.0004 (5)	0.0001 (4)	0.0001 (5)
C11	0.0182 (6)	0.0182 (6)	0.0153 (6)	0.0043 (5)	0.0027 (5)	0.0030 (5)
C12	0.0225 (6)	0.0127 (6)	0.0178 (6)	−0.0002 (5)	0.0077 (5)	−0.0008 (5)
C13	0.0177 (6)	0.0180 (6)	0.0152 (6)	−0.0031 (5)	0.0027 (5)	−0.0033 (5)
C14	0.0146 (5)	0.0180 (6)	0.0126 (5)	0.0005 (5)	0.0004 (4)	0.0009 (5)
C15	0.0134 (5)	0.0146 (6)	0.0142 (6)	−0.0020 (5)	0.0045 (4)	0.0000 (4)
C16	0.0199 (6)	0.0137 (6)	0.0180 (6)	−0.0005 (5)	0.0026 (5)	−0.0002 (5)
C17	0.0134 (5)	0.0129 (6)	0.0124 (5)	−0.0024 (5)	−0.0037 (4)	−0.0002 (4)
C18	0.0170 (6)	0.0174 (6)	0.0132 (5)	−0.0028 (5)	0.0006 (4)	−0.0015 (5)
C19	0.0208 (6)	0.0171 (6)	0.0152 (6)	−0.0043 (5)	0.0009 (5)	0.0031 (5)
C20	0.0175 (6)	0.0124 (6)	0.0209 (6)	−0.0016 (5)	−0.0004 (5)	−0.0007 (5)

C21	0.0171 (6)	0.0188 (6)	0.0163 (6)	−0.0015 (5)	0.0022 (5)	−0.0034 (5)
C22	0.0161 (6)	0.0175 (6)	0.0131 (5)	−0.0038 (5)	0.0000 (4)	0.0006 (5)
C23	0.0141 (6)	0.0143 (6)	0.0148 (6)	−0.0018 (5)	0.0026 (4)	−0.0002 (5)
C24	0.0215 (6)	0.0130 (6)	0.0187 (6)	0.0003 (5)	0.0030 (5)	0.0001 (5)

Geometric parameters (Å, º)

O1—C7	1.2843 (15)	C9—C14	1.3978 (16)
O1—H1H	0.901 (10)	C10—C11	1.3897 (18)
O2—C15	1.2624 (15)	C10—H10	0.9500
O3—C23	1.2670 (15)	C11—C12	1.3902 (17)
O3—H2H	0.879 (10)	C11—H11	0.9500
N1—C7	1.3114 (16)	C12—C13	1.3878 (18)
N1—C1	1.4363 (15)	C12—H12	0.9500
N1—H1N	0.854 (18)	C13—C14	1.3865 (18)
N2—C15	1.3312 (16)	C13—H13	0.9500
N2—C9	1.4215 (16)	C14—H14	0.9500
N2—H2N	0.851 (18)	C15—C16	1.4964 (17)
N3—C23	1.3202 (16)	C16—H16A	0.9800
N3—C17	1.4329 (16)	C16—H16B	0.9800
N3—H3N	0.844 (18)	C16—H16C	0.9800
C1—C2	1.3883 (17)	C17—C22	1.3885 (17)
C1—C6	1.3918 (17)	C17—C18	1.3897 (17)
C2—C3	1.3889 (18)	C18—C19	1.3880 (18)
C2—H2	0.9500	C18—H18	0.9500
C3—C4	1.3922 (18)	C19—C20	1.3904 (18)
C3—H3	0.9500	C19—H19	0.9500
C4—C5	1.3893 (18)	C20—C21	1.3900 (18)
C4—H4	0.9500	C20—H20	0.9500
C5—C6	1.3904 (17)	C21—C22	1.3885 (18)
C5—H5	0.9500	C21—H21	0.9500
C6—H6	0.9500	C22—H22	0.9500
C7—C8	1.4910 (17)	C23—C24	1.4928 (17)
C8—H8A	0.9800	C24—H24A	0.9800
C8—H8B	0.9800	C24—H24B	0.9800
C8—H8C	0.9800	C24—H24C	0.9800
C9—C10	1.3950 (16)		
C7—O1—H1H	115 (2)	C12—C11—H11	119.4
C23—O3—H2H	116 (4)	C13—C12—C11	119.29 (12)
C7—N1—C1	125.65 (10)	C13—C12—H12	120.4
C7—N1—H1N	117.7 (12)	C11—C12—H12	120.4
C1—N1—H1N	116.6 (12)	C14—C13—C12	120.29 (11)
C15—N2—C9	129.93 (10)	C14—C13—H13	119.9
C15—N2—H2N	117.9 (12)	C12—C13—H13	119.9
C9—N2—H2N	112.1 (12)	C13—C14—C9	120.26 (11)
C23—N3—C17	124.98 (10)	C13—C14—H14	119.9
C23—N3—H3N	120.7 (12)	C9—C14—H14	119.9

C17—N3—H3N	114.3 (12)	O2—C15—N2	121.86 (11)
C2—C1—C6	121.23 (11)	O2—C15—C16	122.03 (11)
C2—C1—N1	119.89 (11)	N2—C15—C16	116.11 (11)
C6—C1—N1	118.73 (11)	C15—C16—H16A	109.5
C1—C2—C3	118.99 (11)	C15—C16—H16B	109.5
C1—C2—H2	120.5	H16A—C16—H16B	109.5
C3—C2—H2	120.5	C15—C16—H16C	109.5
C2—C3—C4	120.58 (12)	H16A—C16—H16C	109.5
C2—C3—H3	119.7	H16B—C16—H16C	109.5
C4—C3—H3	119.7	C22—C17—C18	120.84 (12)
C5—C4—C3	119.68 (12)	C22—C17—N3	118.71 (11)
C5—C4—H4	120.2	C18—C17—N3	120.41 (11)
C3—C4—H4	120.2	C19—C18—C17	119.06 (11)
C4—C5—C6	120.46 (11)	C19—C18—H18	120.5
C4—C5—H5	119.8	C17—C18—H18	120.5
C6—C5—H5	119.8	C18—C19—C20	120.72 (12)
C5—C6—C1	119.04 (11)	C18—C19—H19	119.6
C5—C6—H6	120.5	C20—C19—H19	119.6
C1—C6—H6	120.5	C21—C20—C19	119.57 (12)
O1—C7—N1	120.10 (11)	C21—C20—H20	120.2
O1—C7—C8	121.50 (11)	C19—C20—H20	120.2
N1—C7—C8	118.37 (11)	C22—C21—C20	120.27 (12)
C7—C8—H8A	109.5	C22—C21—H21	119.9
C7—C8—H8B	109.5	C20—C21—H21	119.9
H8A—C8—H8B	109.5	C21—C22—C17	119.53 (11)
C7—C8—H8C	109.5	C21—C22—H22	120.2
H8A—C8—H8C	109.5	C17—C22—H22	120.2
H8B—C8—H8C	109.5	O3—C23—N3	120.38 (11)
C10—C9—C14	119.74 (11)	O3—C23—C24	121.57 (11)
C10—C9—N2	124.28 (11)	N3—C23—C24	118.04 (11)
C14—C9—N2	115.97 (10)	C23—C24—H24A	109.5
C11—C10—C9	119.25 (11)	C23—C24—H24B	109.5
C11—C10—H10	120.4	H24A—C24—H24B	109.5
C9—C10—H10	120.4	C23—C24—H24C	109.5
C10—C11—C12	121.17 (11)	H24A—C24—H24C	109.5
C10—C11—H11	119.4	H24B—C24—H24C	109.5
C7—N1—C1—C2	−61.24 (17)	C11—C12—C13—C14	0.26 (18)
C7—N1—C1—C6	123.03 (13)	C12—C13—C14—C9	−0.46 (18)
C6—C1—C2—C3	−1.26 (18)	C10—C9—C14—C13	0.34 (18)
N1—C1—C2—C3	−176.88 (11)	N2—C9—C14—C13	179.22 (11)
C1—C2—C3—C4	0.21 (18)	C9—N2—C15—O2	2.7 (2)
C2—C3—C4—C5	0.53 (18)	C9—N2—C15—C16	−177.45 (11)
C3—C4—C5—C6	−0.24 (18)	C23—N3—C17—C22	127.72 (13)
C4—C5—C6—C1	−0.77 (17)	C23—N3—C17—C18	−54.59 (17)
C2—C1—C6—C5	1.54 (17)	C22—C17—C18—C19	−1.09 (18)
N1—C1—C6—C5	177.21 (11)	N3—C17—C18—C19	−178.72 (11)
C1—N1—C7—O1	−6.34 (18)	C17—C18—C19—C20	0.14 (18)

C1—N1—C7—C8	175.79 (11)	C18—C19—C20—C21	0.65 (18)
C15—N2—C9—C10	−15.5 (2)	C19—C20—C21—C22	−0.50 (18)
C15—N2—C9—C14	165.71 (12)	C20—C21—C22—C17	−0.42 (18)
C14—C9—C10—C11	−0.04 (17)	C18—C17—C22—C21	1.23 (18)
N2—C9—C10—C11	−178.82 (11)	N3—C17—C22—C21	178.90 (10)
C9—C10—C11—C12	−0.15 (18)	C17—N3—C23—O3	−3.28 (19)
C10—C11—C12—C13	0.04 (18)	C17—N3—C23—C24	177.45 (11)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1N⋯Cl2[i]	0.854 (18)	2.237 (19)	3.0899 (11)	176.6 (16)
N2—H2N⋯Cl1	0.851 (18)	2.297 (18)	3.1464 (10)	177.0 (16)
N3—H3N⋯Cl2	0.844 (18)	2.275 (18)	3.1189 (11)	177.6 (16)
O1—H1H⋯O2	0.90 (1)	1.57 (1)	2.4650 (12)	175 (3)
O3—H2H⋯O3[ii]	0.88 (1)	1.56 (1)	2.4370 (16)	176 (7)

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

N-(1-Hydroxyethylidene)anilinium bromide–N-phenylacetamide (1/1) (ACTHBr)

Crystal data

$C_8H_{10}NO^+ \cdot Br^- \cdot C_8H_9NO$
$M_r = 351.24$
Triclinic, $P\overline{1}$
$a = 7.8794$ (2) Å
$b = 9.7748$ (3) Å
$c = 16.2720$ (4) Å
$\alpha = 104.385$ (3)°
$\beta = 98.342$ (2)°
$\gamma = 96.386$ (2)°
$V = 1186.86$ (6) Å³

$Z = 3$
$F(000) = 540$
$D_x = 1.474$ Mg m⁻³
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 12581 reflections
$\theta = 4.7$–71.0°
$\mu = 3.59$ mm⁻¹
$T = 100$ K
Brick, colourless
$0.18 \times 0.04 \times 0.04$ mm

Data collection

Rigaku Synergy-i
  diffractometer
Radiation source: microsource tube
ω scans
Absorption correction: analytical
  [CrysAlis PRO (Rigaku OD, 2023), based on
  expressions derived by Clark & Reid (1995)]
$T_{min} = 0.668$, $T_{max} = 0.890$

8381 measured reflections
8381 independent reflections
7175 reflections with $I > 2\sigma(I)$
$\theta_{max} = 71.5°$, $\theta_{min} = 2.9°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 12$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.164$
$S = 1.11$
8381 reflections
310 parameters
5 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent
  and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1085P)^2 + 0.3679P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.73$ e Å⁻³
$\Delta\rho_{min} = -0.89$ e Å⁻³

Special details

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

Refinement. Refined as a 2-component twin.
Refined against a hklf 5 formatted reflection file created by CrysalisPro. Twinned by 180 degree rotation about direct [0, 0.71, -0.71].
BASF refined to 0.3996 (13)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Br1	−0.00602 (5)	0.34965 (4)	0.33170 (2)	0.02865 (17)	
Br2	1.000000	1.000000	1.000000	0.03169 (19)	
O1	0.4235 (4)	0.5268 (3)	0.63295 (18)	0.0260 (6)	
O2	0.5665 (4)	0.7734 (3)	0.70166 (18)	0.0273 (6)	
O3	−0.4387 (4)	0.1245 (3)	0.03333 (19)	0.0274 (6)	
N1	0.2337 (4)	0.3905 (3)	0.5172 (2)	0.0237 (7)	
N2	0.7472 (4)	0.9426 (3)	0.8094 (2)	0.0226 (6)	
N3	−0.2650 (4)	0.2824 (3)	0.1466 (2)	0.0243 (7)	
C1	0.2182 (5)	0.2625 (4)	0.5456 (2)	0.0253 (8)	
C2	0.1581 (5)	0.2622 (4)	0.6219 (2)	0.0264 (8)	
H2	0.131148	0.347421	0.656919	0.032*	
C3	0.1380 (5)	0.1356 (4)	0.6461 (2)	0.0285 (8)	
H3	0.098346	0.134591	0.698376	0.034*	
C4	0.1755 (5)	0.0103 (4)	0.5944 (3)	0.0294 (8)	
H4	0.161757	−0.075893	0.611414	0.035*	
C5	0.2331 (5)	0.0119 (4)	0.5178 (3)	0.0292 (8)	
H5	0.258480	−0.073577	0.482297	0.035*	
C6	0.2538 (5)	0.1387 (4)	0.4926 (2)	0.0259 (8)	
H6	0.291790	0.139731	0.439966	0.031*	
C7	0.3253 (5)	0.5140 (4)	0.5606 (3)	0.0236 (8)	
C8	0.3163 (5)	0.6366 (4)	0.5217 (3)	0.0264 (8)	
H8A	0.267078	0.711502	0.558722	0.040*	
H8B	0.242638	0.603984	0.464497	0.040*	
H8C	0.433324	0.674983	0.516404	0.040*	
C9	0.7386 (5)	1.0653 (4)	0.7777 (2)	0.0228 (7)	
C10	0.6149 (5)	1.0724 (4)	0.7087 (2)	0.0268 (8)	
H10	0.528277	0.992407	0.679939	0.032*	
C11	0.6198 (5)	1.1976 (4)	0.6827 (2)	0.0293 (8)	
H11	0.534882	1.203047	0.636223	0.035*	
C12	0.7464 (5)	1.3147 (4)	0.7233 (3)	0.0289 (8)	
H12	0.750615	1.398643	0.703798	0.035*	
C13	0.8678 (5)	1.3079 (4)	0.7932 (3)	0.0297 (8)	
H13	0.953099	1.388521	0.822479	0.036*	
C14	0.8640 (5)	1.1844 (4)	0.8198 (2)	0.0262 (8)	
H14	0.947293	1.180257	0.867250	0.031*	

C15	0.6709 (5)	0.8079 (4)	0.7731 (3)	0.0237 (8)	
C16	0.7114 (5)	0.7016 (4)	0.8219 (3)	0.0265 (8)	
H16A	0.603436	0.654437	0.832463	0.040*	
H16B	0.787250	0.750527	0.877147	0.040*	
H16C	0.770231	0.629968	0.788241	0.040*	
C17	−0.2776 (5)	0.4036 (4)	0.1122 (2)	0.0232 (8)	
C18	−0.2323 (5)	0.4012 (4)	0.0326 (2)	0.0283 (8)	
H18	−0.194259	0.319168	−0.000052	0.034*	
C19	−0.2434 (5)	0.5206 (4)	0.0015 (3)	0.0306 (8)	
H19	−0.212383	0.520087	−0.052886	0.037*	
C20	−0.2990 (5)	0.6402 (4)	0.0486 (3)	0.0304 (8)	
H20	−0.307166	0.721000	0.026550	0.036*	
C21	−0.3428 (5)	0.6414 (4)	0.1284 (3)	0.0303 (8)	
H21	−0.381078	0.723343	0.160965	0.036*	
C22	−0.3310 (5)	0.5231 (4)	0.1610 (2)	0.0269 (8)	
H22	−0.359168	0.524403	0.215935	0.032*	
C23	−0.3404 (5)	0.1512 (4)	0.1066 (3)	0.0242 (8)	
C24	−0.3097 (5)	0.0363 (4)	0.1504 (3)	0.0254 (8)	
H24A	−0.421197	−0.019420	0.150223	0.038*	
H24B	−0.250319	0.079760	0.210067	0.038*	
H24C	−0.237484	−0.026649	0.119696	0.038*	
H1N	0.172 (5)	0.383 (4)	0.4663 (14)	0.020 (10)*	
H2N	0.818 (5)	0.962 (5)	0.8591 (16)	0.027 (12)*	
H3N	−0.202 (5)	0.301 (5)	0.1981 (15)	0.029 (12)*	
H1H	0.483 (7)	0.613 (3)	0.659 (3)	0.07 (2)*	
H2H	−0.486 (19)	0.037 (6)	0.005 (9)	0.06 (3)*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0268 (3)	0.0342 (3)	0.0211 (3)	0.00078 (17)	−0.00316 (17)	0.00647 (17)
Br2	0.0268 (3)	0.0441 (4)	0.0207 (3)	0.0008 (2)	−0.0027 (2)	0.0083 (2)
O1	0.0268 (14)	0.0233 (13)	0.0233 (14)	−0.0018 (10)	−0.0044 (11)	0.0051 (10)
O2	0.0279 (14)	0.0237 (13)	0.0247 (15)	−0.0017 (10)	−0.0043 (11)	0.0040 (11)
O3	0.0275 (14)	0.0226 (13)	0.0266 (15)	−0.0015 (11)	−0.0063 (12)	0.0052 (11)
N1	0.0251 (16)	0.0245 (15)	0.0180 (16)	−0.0010 (12)	−0.0030 (13)	0.0050 (12)
N2	0.0227 (16)	0.0237 (15)	0.0180 (16)	−0.0012 (12)	−0.0031 (12)	0.0053 (12)
N3	0.0266 (16)	0.0234 (15)	0.0190 (16)	−0.0017 (12)	−0.0040 (13)	0.0056 (13)
C1	0.0225 (18)	0.0246 (18)	0.0241 (19)	−0.0025 (14)	−0.0064 (15)	0.0065 (15)
C2	0.0261 (18)	0.0262 (18)	0.0243 (19)	0.0037 (14)	0.0012 (15)	0.0039 (14)
C3	0.0273 (19)	0.0295 (19)	0.027 (2)	0.0009 (15)	0.0022 (15)	0.0072 (15)
C4	0.0252 (19)	0.0273 (18)	0.034 (2)	0.0004 (14)	−0.0014 (16)	0.0103 (16)
C5	0.0262 (19)	0.0246 (18)	0.033 (2)	0.0019 (14)	−0.0010 (16)	0.0047 (15)
C6	0.0238 (18)	0.0250 (18)	0.0257 (19)	0.0001 (14)	−0.0014 (15)	0.0059 (14)
C7	0.0202 (18)	0.0264 (18)	0.0228 (19)	0.0026 (14)	0.0000 (15)	0.0070 (15)
C8	0.028 (2)	0.0234 (18)	0.025 (2)	−0.0004 (14)	0.0003 (16)	0.0063 (15)
C9	0.0223 (17)	0.0237 (17)	0.0205 (19)	0.0019 (14)	0.0018 (14)	0.0045 (14)
C10	0.0266 (18)	0.0258 (18)	0.0251 (19)	0.0003 (14)	−0.0014 (15)	0.0063 (14)

C11	0.031 (2)	0.0273 (19)	0.029 (2)	0.0050 (15)	0.0011 (16)	0.0074 (15)
C12	0.033 (2)	0.0250 (18)	0.030 (2)	0.0037 (15)	0.0068 (16)	0.0085 (15)
C13	0.0256 (19)	0.0246 (18)	0.034 (2)	−0.0008 (14)	0.0034 (16)	0.0016 (15)
C14	0.0235 (18)	0.0261 (18)	0.0248 (19)	0.0009 (14)	0.0001 (14)	0.0029 (14)
C15	0.0212 (18)	0.0261 (18)	0.0217 (19)	0.0021 (14)	0.0004 (15)	0.0057 (15)
C16	0.0278 (19)	0.0259 (18)	0.023 (2)	0.0008 (15)	0.0001 (15)	0.0063 (15)
C17	0.0186 (17)	0.0229 (17)	0.0234 (19)	−0.0026 (13)	−0.0049 (14)	0.0055 (14)
C18	0.029 (2)	0.0264 (18)	0.027 (2)	0.0005 (15)	0.0012 (15)	0.0068 (15)
C19	0.032 (2)	0.0294 (19)	0.029 (2)	−0.0009 (15)	0.0038 (16)	0.0096 (15)
C20	0.033 (2)	0.0248 (18)	0.029 (2)	−0.0018 (15)	−0.0049 (16)	0.0087 (15)
C21	0.029 (2)	0.0247 (18)	0.033 (2)	0.0007 (15)	−0.0007 (16)	0.0056 (15)
C22	0.0273 (19)	0.0262 (18)	0.0242 (19)	−0.0015 (14)	−0.0003 (15)	0.0063 (14)
C23	0.0236 (19)	0.0243 (18)	0.023 (2)	0.0027 (14)	0.0014 (15)	0.0047 (15)
C24	0.0277 (19)	0.0217 (17)	0.025 (2)	0.0010 (14)	0.0003 (16)	0.0066 (15)

Geometric parameters (Å, º)

O1—C7	1.281 (5)	C9—C14	1.397 (5)
O1—H1H	0.887 (14)	C10—C11	1.390 (5)
O2—C15	1.267 (5)	C10—H10	0.9500
O3—C23	1.274 (5)	C11—C12	1.386 (5)
O3—H2H	0.878 (14)	C11—H11	0.9500
N1—C7	1.309 (5)	C12—C13	1.395 (6)
N1—C1	1.436 (5)	C12—H12	0.9500
N1—H1N	0.880 (13)	C13—C14	1.379 (5)
N2—C15	1.333 (5)	C13—H13	0.9500
N2—C9	1.424 (4)	C14—H14	0.9500
N2—H2N	0.876 (14)	C15—C16	1.492 (5)
N3—C23	1.314 (5)	C16—H16A	0.9800
N3—C17	1.437 (4)	C16—H16B	0.9800
N3—H3N	0.875 (13)	C16—H16C	0.9800
C1—C6	1.384 (5)	C17—C22	1.384 (5)
C1—C2	1.392 (5)	C17—C18	1.388 (5)
C2—C3	1.388 (5)	C18—C19	1.390 (5)
C2—H2	0.9500	C18—H18	0.9500
C3—C4	1.391 (5)	C19—C20	1.383 (6)
C3—H3	0.9500	C19—H19	0.9500
C4—C5	1.391 (6)	C20—C21	1.389 (6)
C4—H4	0.9500	C20—H20	0.9500
C5—C6	1.398 (5)	C21—C22	1.393 (5)
C5—H5	0.9500	C21—H21	0.9500
C6—H6	0.9500	C22—H22	0.9500
C7—C8	1.492 (5)	C23—C24	1.495 (5)
C8—H8A	0.9800	C24—H24A	0.9800
C8—H8B	0.9800	C24—H24B	0.9800
C8—H8C	0.9800	C24—H24C	0.9800
C9—C10	1.396 (5)		

C7—O1—H1H	116 (4)	C10—C11—H11	119.5
C23—O3—H2H	121 (10)	C11—C12—C13	119.3 (3)
C7—N1—C1	126.2 (3)	C11—C12—H12	120.3
C7—N1—H1N	119 (3)	C13—C12—H12	120.3
C1—N1—H1N	115 (3)	C14—C13—C12	120.1 (3)
C15—N2—C9	129.4 (3)	C14—C13—H13	120.0
C15—N2—H2N	118 (3)	C12—C13—H13	120.0
C9—N2—H2N	112 (3)	C13—C14—C9	120.6 (3)
C23—N3—C17	124.8 (3)	C13—C14—H14	119.7
C23—N3—H3N	120 (3)	C9—C14—H14	119.7
C17—N3—H3N	115 (3)	O2—C15—N2	121.5 (3)
C6—C1—C2	121.3 (3)	O2—C15—C16	122.0 (3)
C6—C1—N1	118.3 (3)	N2—C15—C16	116.5 (3)
C2—C1—N1	120.3 (3)	C15—C16—H16A	109.5
C3—C2—C1	119.1 (3)	C15—C16—H16B	109.5
C3—C2—H2	120.4	H16A—C16—H16B	109.5
C1—C2—H2	120.4	C15—C16—H16C	109.5
C2—C3—C4	120.6 (4)	H16A—C16—H16C	109.5
C2—C3—H3	119.7	H16B—C16—H16C	109.5
C4—C3—H3	119.7	C22—C17—C18	121.1 (3)
C5—C4—C3	119.7 (4)	C22—C17—N3	118.8 (3)
C5—C4—H4	120.2	C18—C17—N3	120.1 (3)
C3—C4—H4	120.2	C17—C18—C19	118.9 (4)
C4—C5—C6	120.3 (4)	C17—C18—H18	120.5
C4—C5—H5	119.8	C19—C18—H18	120.5
C6—C5—H5	119.8	C20—C19—C18	120.8 (4)
C1—C6—C5	119.0 (4)	C20—C19—H19	119.6
C1—C6—H6	120.5	C18—C19—H19	119.6
C5—C6—H6	120.5	C19—C20—C21	119.6 (4)
O1—C7—N1	120.4 (3)	C19—C20—H20	120.2
O1—C7—C8	121.6 (3)	C21—C20—H20	120.2
N1—C7—C8	118.0 (3)	C20—C21—C22	120.4 (4)
C7—C8—H8A	109.5	C20—C21—H21	119.8
C7—C8—H8B	109.5	C22—C21—H21	119.8
H8A—C8—H8B	109.5	C17—C22—C21	119.2 (4)
C7—C8—H8C	109.5	C17—C22—H22	120.4
H8A—C8—H8C	109.5	C21—C22—H22	120.4
H8B—C8—H8C	109.5	O3—C23—N3	120.3 (3)
C10—C9—C14	119.6 (3)	O3—C23—C24	121.6 (3)
C10—C9—N2	124.2 (3)	N3—C23—C24	118.0 (3)
C14—C9—N2	116.2 (3)	C23—C24—H24A	109.5
C11—C10—C9	119.3 (3)	C23—C24—H24B	109.5
C11—C10—H10	120.4	H24A—C24—H24B	109.5
C9—C10—H10	120.4	C23—C24—H24C	109.5
C12—C11—C10	121.1 (4)	H24A—C24—H24C	109.5
C12—C11—H11	119.5	H24B—C24—H24C	109.5
C7—N1—C1—C6	−126.7 (4)	C11—C12—C13—C14	1.7 (6)

C7—N1—C1—C2	57.3 (5)	C12—C13—C14—C9	−0.4 (6)
C6—C1—C2—C3	1.7 (6)	C10—C9—C14—C13	−0.8 (6)
N1—C1—C2—C3	177.5 (3)	N2—C9—C14—C13	179.2 (3)
C1—C2—C3—C4	−0.7 (6)	C9—N2—C15—O2	−3.7 (6)
C2—C3—C4—C5	−0.2 (6)	C9—N2—C15—C16	177.8 (4)
C3—C4—C5—C6	0.2 (6)	C23—N3—C17—C22	126.4 (4)
C2—C1—C6—C5	−1.7 (5)	C23—N3—C17—C18	−55.3 (5)
N1—C1—C6—C5	−177.6 (3)	C22—C17—C18—C19	−0.9 (6)
C4—C5—C6—C1	0.8 (5)	N3—C17—C18—C19	−179.1 (3)
C1—N1—C7—O1	5.7 (6)	C17—C18—C19—C20	−0.2 (6)
C1—N1—C7—C8	−176.5 (4)	C18—C19—C20—C21	0.6 (6)
C15—N2—C9—C10	15.0 (6)	C19—C20—C21—C22	0.0 (6)
C15—N2—C9—C14	−165.0 (4)	C18—C17—C22—C21	1.4 (6)
C14—C9—C10—C11	0.6 (6)	N3—C17—C22—C21	179.7 (3)
N2—C9—C10—C11	−179.4 (3)	C20—C21—C22—C17	−1.0 (6)
C9—C10—C11—C12	0.8 (6)	C17—N3—C23—O3	−2.9 (6)
C10—C11—C12—C13	−1.9 (6)	C17—N3—C23—C24	178.2 (3)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···Br1	0.88 (1)	2.35 (1)	3.228 (3)	176 (4)
N2—H2N···Br2	0.88 (1)	2.44 (1)	3.316 (3)	176 (4)
N3—H3N···Br1	0.88 (1)	2.38 (2)	3.256 (3)	174 (4)
O1—H1H···O2	0.89 (1)	1.57 (2)	2.454 (4)	172 (6)
O3—H2H···O3^i	0.88 (1)	1.55 (2)	2.428 (5)	173 (16)

Symmetry code: (i) −x−1, −y, −z.

N-(1-Hydroxyethylidene)anilinium triiodide–N-phenylacetamide (1/1) (ACTHI3)

Crystal data

$C_8H_{10}NO^+ \cdot I_3^- \cdot C_8H_9NO$

$M_r = 652.03$

Triclinic, $P\bar{1}$

$a = 7.3766$ (2) Å

$b = 8.8131$ (3) Å

$c = 9.3226$ (2) Å

$\alpha = 113.612$ (2)°

$\beta = 103.144$ (2)°

$\gamma = 104.263$ (3)°

$V = 500.61$ (3) Å³

$Z = 1$

$F(000) = 304$

$D_x = 2.163$ Mg m^{-3}

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 6490 reflections

$\theta = 5.5$–71.1°

$\mu = 36.86$ mm^{-1}

$T = 100$ K

Needle, red

0.32 × 0.08 × 0.05 mm

Data collection

Rigaku Synergy-i diffractometer

Radiation source: microsource tube

ω scans

Absorption correction: gaussian (CrysAlis PRO; Rigaku OD, 2023)

$T_{min} = 0.034$, $T_{max} = 0.480$

7238 measured reflections

1900 independent reflections

1846 reflections with $I > 2\sigma(I)$

$R_{int} = 0.054$

$\theta_{max} = 71.4°$, $\theta_{min} = 5.6°$

$h = -6 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.038$	and constrained refinement
$wR(F^2) = 0.107$	$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2 + 0.0507P]$
$S = 1.10$	where $P = (F_o^2 + 2F_c^2)/3$
1900 reflections	$(\Delta/\sigma)_{max} = 0.001$
115 parameters	$\Delta\rho_{max} = 1.24$ e Å^{-3}
2 restraints	$\Delta\rho_{min} = -1.79$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
I1	0.55941 (4)	0.66145 (3)	0.88696 (3)	0.02516 (16)	
I2	0.500000	1.000000	1.000000	0.02257 (17)	
O1	0.1752 (4)	0.0806 (4)	0.5302 (4)	0.0272 (6)	
N1	0.3915 (5)	0.2177 (5)	0.4434 (4)	0.0241 (7)	
C1	0.5812 (6)	0.2611 (5)	0.5644 (5)	0.0246 (8)	
C2	0.6054 (7)	0.2189 (6)	0.6934 (6)	0.0276 (9)	
H2	0.491090	0.154855	0.705554	0.033*	
C3	0.7970 (7)	0.2704 (6)	0.8050 (5)	0.0271 (9)	
H3	0.812915	0.242810	0.894584	0.033*	
C4	0.9670 (7)	0.3625 (6)	0.7877 (5)	0.0283 (9)	
H4	1.098103	0.395625	0.863205	0.034*	
C5	0.9405 (8)	0.4045 (7)	0.6575 (6)	0.0325 (10)	
H5	1.054485	0.468933	0.645208	0.039*	
C6	0.7492 (7)	0.3533 (6)	0.5454 (6)	0.0282 (9)	
H6	0.732544	0.381001	0.455922	0.034*	
C7	0.2071 (6)	0.1329 (5)	0.4278 (5)	0.0239 (8)	
C8	0.0359 (6)	0.1033 (6)	0.2834 (5)	0.0289 (9)	
H8A	−0.040316	−0.025349	0.209444	0.043*	
H8B	0.089110	0.156041	0.219639	0.043*	
H8C	−0.052750	0.159959	0.326851	0.043*	
H1N	0.401 (9)	0.244 (7)	0.363 (5)	0.035 (14)*	
H1H	0.049 (7)	0.027 (17)	0.514 (18)	0.03 (3)*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0246 (2)	0.0289 (2)	0.0257 (2)	0.01119 (15)	0.00874 (15)	0.01610 (17)
I2	0.0190 (3)	0.0293 (3)	0.0231 (3)	0.00887 (19)	0.00770 (18)	0.0162 (2)
O1	0.0199 (16)	0.0354 (15)	0.0274 (15)	0.0057 (13)	0.0100 (13)	0.0184 (13)
N1	0.0168 (17)	0.0313 (17)	0.0244 (17)	0.0056 (14)	0.0069 (14)	0.0160 (14)

C1	0.020 (2)	0.0243 (19)	0.027 (2)	0.0070 (17)	0.0077 (17)	0.0110 (16)
C2	0.024 (2)	0.032 (2)	0.029 (2)	0.0087 (18)	0.0106 (17)	0.0169 (18)
C3	0.030 (2)	0.032 (2)	0.0204 (19)	0.0102 (18)	0.0088 (18)	0.0140 (16)
C4	0.023 (2)	0.032 (2)	0.026 (2)	0.0073 (18)	0.0061 (17)	0.0139 (16)
C5	0.024 (2)	0.040 (2)	0.033 (2)	0.0071 (18)	0.0098 (19)	0.022 (2)
C6	0.021 (2)	0.039 (2)	0.030 (2)	0.0091 (18)	0.0095 (17)	0.0232 (18)
C7	0.020 (2)	0.0265 (19)	0.0210 (19)	0.0081 (16)	0.0054 (16)	0.0089 (15)
C8	0.018 (2)	0.038 (2)	0.029 (2)	0.0076 (18)	0.0046 (17)	0.0186 (18)

Geometric parameters (Å, º)

I1—I2	2.9224 (3)	C3—H3	0.9500
O1—C7	1.257 (5)	C4—C5	1.392 (6)
O1—H1H	0.880 (10)	C4—H4	0.9500
N1—C7	1.324 (6)	C5—C6	1.387 (6)
N1—C1	1.432 (5)	C5—H5	0.9500
N1—H1N	0.877 (10)	C6—H6	0.9500
C1—C2	1.381 (6)	C7—C8	1.503 (6)
C1—C6	1.395 (6)	C8—H8A	0.9800
C2—C3	1.387 (6)	C8—H8B	0.9800
C2—H2	0.9500	C8—H8C	0.9800
C3—C4	1.398 (6)		
I1—I2—I1[i]	180.0	C3—C4—H4	120.7
C7—O1—H1H	117 (9)	C6—C5—C4	120.6 (4)
C7—N1—C1	129.7 (4)	C6—C5—H5	119.7
C7—N1—H1N	116 (4)	C4—C5—H5	119.7
C1—N1—H1N	114 (4)	C5—C6—C1	119.9 (4)
C2—C1—C6	120.1 (4)	C5—C6—H6	120.0
C2—C1—N1	124.9 (4)	C1—C6—H6	120.0
C6—C1—N1	115.1 (4)	O1—C7—N1	121.7 (4)
C1—C2—C3	119.8 (4)	O1—C7—C8	121.0 (4)
C1—C2—H2	120.1	N1—C7—C8	117.3 (4)
C3—C2—H2	120.1	C7—C8—H8A	109.5
C2—C3—C4	120.9 (4)	C7—C8—H8B	109.5
C2—C3—H3	119.5	H8A—C8—H8B	109.5
C4—C3—H3	119.5	C7—C8—H8C	109.5
C5—C4—C3	118.7 (4)	H8A—C8—H8C	109.5
C5—C4—H4	120.7	H8B—C8—H8C	109.5
C7—N1—C1—C2	0.1 (7)	C3—C4—C5—C6	−1.1 (7)
C7—N1—C1—C6	−179.7 (4)	C4—C5—C6—C1	1.0 (7)
C6—C1—C2—C3	0.8 (6)	C2—C1—C6—C5	−0.8 (7)
N1—C1—C2—C3	−179.0 (4)	N1—C1—C6—C5	179.0 (4)
C1—C2—C3—C4	−1.0 (7)	C1—N1—C7—O1	2.3 (7)
C2—C3—C4—C5	1.1 (7)	C1—N1—C7—C8	−178.5 (4)

Symmetry code: (i) −x+1, −y+2, −z+2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···I1^{ii}	0.88 (1)	2.82 (1)	3.700 (3)	178 (5)
O1—H1H···O1^{iii}	0.88 (1)	1.55 (2)	2.430 (6)	175 (15)

Symmetry codes: (ii) −x+1, −y+1, −z+1; (iii) −x, −y, −z+1.

N-(1-Hydroxyethylidene)anilinium tetrafluoroborate–*N*-phenylacetamide (1/1) (ACTHBF4)

Crystal data

$C_8H_{10}NO^+ \cdot BF_4^- \cdot C_8H_9NO$	$Z = 2$
$M_r = 358.14$	$F(000) = 372$
Triclinic, $P\bar{1}$	$D_x = 1.408$ Mg m^{-3}
$a = 7.1070$ (1) Å	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$b = 9.5381$ (1) Å	Cell parameters from 15273 reflections
$c = 13.3592$ (1) Å	$\theta = 3.4–71.3°$
$\alpha = 98.765$ (1)°	$\mu = 1.05$ mm^{-1}
$\beta = 98.034$ (1)°	$T = 100$ K
$\gamma = 105.977$ (1)°	Fragment, colourless
$V = 844.56$ (2) Å^3	0.15 × 0.15 × 0.10 mm

Data collection

Rigaku SYnergy-i diffractometer	3261 independent reflections
Radiation source: microsource tube	3204 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.026$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2023)	$\theta_{max} = 71.5°$, $\theta_{min} = 3.4°$
$T_{min} = 0.816$, $T_{max} = 1.000$	$h = -8 \rightarrow 8$
16151 measured reflections	$k = -11 \rightarrow 11$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.418P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.099$	
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
3261 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
241 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
1 restraint	Extinction correction: SHELXL2018 (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Hydrogen site location: mixed	
	Extinction coefficient: 0.0029 (5)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
F1	0.17479 (13)	0.72969 (10)	0.15243 (6)	0.0363 (2)
F2	0.45003 (17)	0.87053 (10)	0.26709 (8)	0.0523 (3)
F3	0.39396 (17)	0.62099 (11)	0.22065 (8)	0.0468 (3)
F4	0.20689 (16)	0.70838 (12)	0.32094 (7)	0.0468 (3)
O1	0.20732 (14)	0.80521 (9)	0.80500 (6)	0.0217 (2)
O2	0.23624 (14)	0.62120 (9)	0.66512 (6)	0.0219 (2)
N1	0.20551 (16)	0.86193 (11)	0.97469 (8)	0.0180 (2)
N2	0.26024 (15)	0.57454 (11)	0.49737 (8)	0.0173 (2)
C1	0.24994 (17)	1.01975 (13)	0.98913 (9)	0.0178 (3)
C2	0.2341 (2)	1.09537 (14)	0.90877 (10)	0.0236 (3)
H2	0.195142	1.042722	0.839170	0.028*
C3	0.2760 (2)	1.24928 (15)	0.93179 (11)	0.0267 (3)
H3	0.266060	1.301806	0.877286	0.032*
C4	0.3320 (2)	1.32715 (14)	1.03304 (10)	0.0237 (3)
H4	0.359178	1.432192	1.047840	0.028*
C5	0.34800 (19)	1.25081 (14)	1.11246 (10)	0.0230 (3)
H5	0.386573	1.303734	1.181995	0.028*
C6	0.30789 (19)	1.09700 (14)	1.09096 (9)	0.0203 (3)
H6	0.320031	1.044962	1.145575	0.024*
C7	0.18644 (18)	0.76409 (13)	0.88973 (9)	0.0179 (3)
C8	0.1340 (2)	0.60302 (14)	0.89584 (10)	0.0232 (3)
H8A	−0.006812	0.553716	0.864800	0.035*
H8B	0.157393	0.593867	0.968273	0.035*
H8C	0.217160	0.555952	0.858443	0.035*
C9	0.24731 (17)	0.42074 (13)	0.48218 (9)	0.0170 (2)
C10	0.25925 (19)	0.34282 (14)	0.56188 (10)	0.0208 (3)
H10	0.275176	0.391188	0.631532	0.025*
C11	0.2475 (2)	0.19309 (14)	0.53781 (10)	0.0233 (3)
H11	0.256422	0.139456	0.591755	0.028*
C12	0.22300 (19)	0.12099 (14)	0.43664 (10)	0.0225 (3)
H12	0.213171	0.018354	0.421188	0.027*
C13	0.21292 (19)	0.19988 (14)	0.35790 (10)	0.0224 (3)
H13	0.196856	0.151079	0.288343	0.027*
C14	0.22618 (18)	0.34966 (14)	0.38024 (9)	0.0196 (3)
H14	0.220859	0.403536	0.326216	0.024*
C15	0.25639 (17)	0.66609 (13)	0.58175 (9)	0.0172 (3)
C16	0.27463 (19)	0.82377 (13)	0.57439 (10)	0.0211 (3)
H16A	0.145435	0.841245	0.576130	0.032*
H16B	0.316262	0.842749	0.509563	0.032*
H16C	0.374149	0.890788	0.632662	0.032*
B1	0.3084 (2)	0.73385 (16)	0.24067 (11)	0.0250 (3)
H1N	0.198 (2)	0.8250 (19)	1.0289 (14)	0.028 (4)*
H2N	0.263 (2)	0.6114 (18)	0.4426 (13)	0.024 (4)*
H1H	0.211 (4)	0.732 (2)	0.7540 (16)	0.100 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0403 (5)	0.0370 (5)	0.0223 (4)	−0.0034 (4)	−0.0040 (3)	0.0153 (3)
F2	0.0645 (7)	0.0252 (5)	0.0435 (6)	−0.0108 (4)	−0.0187 (5)	0.0074 (4)
F3	0.0661 (7)	0.0406 (5)	0.0433 (6)	0.0272 (5)	0.0181 (5)	0.0094 (4)
F4	0.0645 (7)	0.0642 (7)	0.0284 (5)	0.0313 (5)	0.0211 (4)	0.0265 (4)
O1	0.0330 (5)	0.0191 (4)	0.0141 (4)	0.0089 (4)	0.0058 (4)	0.0030 (3)
O2	0.0332 (5)	0.0199 (4)	0.0147 (4)	0.0101 (4)	0.0068 (4)	0.0038 (3)
N1	0.0242 (5)	0.0164 (5)	0.0137 (5)	0.0049 (4)	0.0047 (4)	0.0050 (4)
N2	0.0229 (5)	0.0163 (5)	0.0143 (5)	0.0063 (4)	0.0052 (4)	0.0056 (4)
C1	0.0186 (6)	0.0165 (6)	0.0187 (6)	0.0047 (4)	0.0059 (5)	0.0035 (5)
C2	0.0333 (7)	0.0206 (6)	0.0172 (6)	0.0083 (5)	0.0046 (5)	0.0040 (5)
C3	0.0374 (8)	0.0210 (6)	0.0250 (7)	0.0102 (6)	0.0089 (6)	0.0093 (5)
C4	0.0266 (7)	0.0167 (6)	0.0285 (7)	0.0058 (5)	0.0099 (5)	0.0036 (5)
C5	0.0261 (6)	0.0209 (6)	0.0200 (6)	0.0052 (5)	0.0068 (5)	−0.0008 (5)
C6	0.0238 (6)	0.0207 (6)	0.0168 (6)	0.0062 (5)	0.0058 (5)	0.0045 (5)
C7	0.0182 (6)	0.0183 (6)	0.0164 (6)	0.0046 (5)	0.0026 (4)	0.0033 (4)
C8	0.0300 (7)	0.0167 (6)	0.0216 (6)	0.0049 (5)	0.0053 (5)	0.0041 (5)
C9	0.0170 (6)	0.0162 (6)	0.0184 (6)	0.0051 (4)	0.0047 (4)	0.0040 (5)
C10	0.0259 (6)	0.0199 (6)	0.0167 (6)	0.0075 (5)	0.0038 (5)	0.0038 (5)
C11	0.0278 (7)	0.0211 (6)	0.0236 (6)	0.0093 (5)	0.0050 (5)	0.0092 (5)
C12	0.0244 (6)	0.0174 (6)	0.0273 (7)	0.0082 (5)	0.0069 (5)	0.0043 (5)
C13	0.0263 (6)	0.0217 (6)	0.0196 (6)	0.0084 (5)	0.0071 (5)	0.0007 (5)
C14	0.0228 (6)	0.0210 (6)	0.0170 (6)	0.0071 (5)	0.0063 (5)	0.0059 (5)
C15	0.0164 (5)	0.0179 (6)	0.0168 (6)	0.0044 (4)	0.0026 (4)	0.0036 (4)
C16	0.0249 (6)	0.0166 (6)	0.0225 (6)	0.0065 (5)	0.0058 (5)	0.0044 (5)
B1	0.0362 (8)	0.0196 (7)	0.0152 (7)	0.0028 (6)	0.0015 (6)	0.0052 (5)

Geometric parameters (Å, º)

F1—B1	1.3946 (17)	C5—H5	0.9500
F2—B1	1.3693 (17)	C6—H6	0.9500
F3—B1	1.3849 (18)	C7—C8	1.4958 (17)
F4—B1	1.3889 (18)	C8—H8A	0.9800
O1—C7	1.2679 (15)	C8—H8B	0.9800
O1—H1H	0.906 (10)	C8—H8C	0.9800
O2—C15	1.2651 (15)	C9—C14	1.3936 (17)
N1—C7	1.3199 (16)	C9—C10	1.3941 (17)
N1—C1	1.4268 (15)	C10—C11	1.3917 (17)
N1—H1N	0.854 (18)	C10—H10	0.9500
N2—C15	1.3251 (16)	C11—C12	1.3838 (19)
N2—C9	1.4253 (15)	C11—H11	0.9500
N2—H2N	0.859 (17)	C12—C13	1.3884 (18)
C1—C2	1.3901 (17)	C12—H12	0.9500
C1—C6	1.3907 (17)	C13—C14	1.3882 (17)
C2—C3	1.3908 (18)	C13—H13	0.9500
C2—H2	0.9500	C14—H14	0.9500

C3—C4	1.3857 (19)	C15—C16	1.4931 (16)
C3—H3	0.9500	C16—H16A	0.9800
C4—C5	1.3843 (19)	C16—H16B	0.9800
C4—H4	0.9500	C16—H16C	0.9800
C5—C6	1.3909 (18)		
C7—O1—H1H	114.0 (19)	C14—C9—C10	120.27 (11)
C7—N1—C1	129.10 (11)	C14—C9—N2	115.64 (10)
C7—N1—H1N	114.4 (11)	C10—C9—N2	124.07 (11)
C1—N1—H1N	116.3 (11)	C11—C10—C9	118.97 (11)
C15—N2—C9	129.59 (10)	C11—C10—H10	120.5
C15—N2—H2N	115.5 (11)	C9—C10—H10	120.5
C9—N2—H2N	114.8 (11)	C12—C11—C10	121.13 (12)
C2—C1—C6	120.46 (11)	C12—C11—H11	119.4
C2—C1—N1	123.78 (11)	C10—C11—H11	119.4
C6—C1—N1	115.75 (11)	C11—C12—C13	119.45 (11)
C1—C2—C3	119.00 (12)	C11—C12—H12	120.3
C1—C2—H2	120.5	C13—C12—H12	120.3
C3—C2—H2	120.5	C14—C13—C12	120.38 (12)
C4—C3—C2	121.00 (12)	C14—C13—H13	119.8
C4—C3—H3	119.5	C12—C13—H13	119.8
C2—C3—H3	119.5	C13—C14—C9	119.78 (11)
C5—C4—C3	119.53 (12)	C13—C14—H14	120.1
C5—C4—H4	120.2	C9—C14—H14	120.1
C3—C4—H4	120.2	O2—C15—N2	121.22 (11)
C4—C5—C6	120.32 (12)	O2—C15—C16	121.29 (11)
C4—C5—H5	119.8	N2—C15—C16	117.48 (10)
C6—C5—H5	119.8	C15—C16—H16A	109.5
C1—C6—C5	119.69 (11)	C15—C16—H16B	109.5
C1—C6—H6	120.2	H16A—C16—H16B	109.5
C5—C6—H6	120.2	C15—C16—H16C	109.5
O1—C7—N1	120.94 (11)	H16A—C16—H16C	109.5
O1—C7—C8	121.04 (11)	H16B—C16—H16C	109.5
N1—C7—C8	118.00 (11)	F2—B1—F3	111.25 (14)
C7—C8—H8A	109.5	F2—B1—F4	110.09 (12)
C7—C8—H8B	109.5	F3—B1—F4	107.84 (11)
H8A—C8—H8B	109.5	F2—B1—F1	109.04 (11)
C7—C8—H8C	109.5	F3—B1—F1	108.86 (12)
H8A—C8—H8C	109.5	F4—B1—F1	109.74 (13)
H8B—C8—H8C	109.5		
C7—N1—C1—C2	16.3 (2)	C15—N2—C9—C14	170.86 (12)
C7—N1—C1—C6	−165.00 (12)	C15—N2—C9—C10	−10.7 (2)
C6—C1—C2—C3	−0.3 (2)	C14—C9—C10—C11	−0.71 (18)
N1—C1—C2—C3	178.26 (12)	N2—C9—C10—C11	−179.10 (11)
C1—C2—C3—C4	−0.3 (2)	C9—C10—C11—C12	−0.42 (19)
C2—C3—C4—C5	0.5 (2)	C10—C11—C12—C13	1.0 (2)
C3—C4—C5—C6	−0.1 (2)	C11—C12—C13—C14	−0.35 (19)

C2—C1—C6—C5	0.73 (19)	C12—C13—C14—C9	−0.78 (19)
N1—C1—C6—C5	−177.98 (11)	C10—C9—C14—C13	1.31 (19)
C4—C5—C6—C1	−0.50 (19)	N2—C9—C14—C13	179.82 (11)
C1—N1—C7—O1	−0.2 (2)	C9—N2—C15—O2	−1.05 (19)
C1—N1—C7—C8	−178.57 (11)	C9—N2—C15—C16	179.57 (11)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1N⋯F1[i]	0.854 (18)	2.007 (19)	2.8606 (13)	177.6 (16)
N2—H2N⋯F4	0.859 (17)	2.033 (18)	2.8744 (14)	166.0 (15)
O1—H1H⋯O2	0.91 (1)	1.53 (1)	2.4333 (12)	174 (3)

Symmetry code: (i) $x, y, z+1$.

N-(1-Hydroxyethylidene)anilinium diiodobromide–\ N-phenylacetamide–diiodine (2/2/1) (ACTHI2Br)

Crystal data

$C_8H_{10}NO^+ \cdot I_2Br^- \cdot C_8H_9NO \cdot 0.5I_2$	$F(000) = 1361$
$M_r = 735.18$	$D_x = 2.229$ Mg m^{-3}
Monoclinic, $P2_1/m$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$a = 5.8956$ (1) Å	Cell parameters from 13599 reflections
$b = 18.6224$ (4) Å	$\theta = 2.4–71.5°$
$c = 19.9632$ (4) Å	$\mu = 36.46$ mm^{-1}
$\beta = 91.970$ (2)°	$T = 100$ K
$V = 2190.47$ (7) Å^3	Broken needle, yellow
$Z = 4$	0.24 × 0.08 × 0.06 mm

Data collection

Rigaku Synergy-i diffractometer	21645 measured reflections
Radiation source: microsource tube	4338 independent reflections
ω scans	3762 reflections with $I > 2\sigma(I)$
Absorption correction: analytical [CrysAlis PRO (Rigaku OD, 2023), based on expressions derived by Clark & Reid (1995)]	$R_{int} = 0.096$
	$\theta_{max} = 71.5°$, $\theta_{min} = 3.3°$
	$h = -6 \rightarrow 7$
	$k = -22 \rightarrow 22$
$T_{min} = 0.014$, $T_{max} = 0.164$	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.052$	
$wR(F^2) = 0.151$	$w = 1/[\sigma^2(F_o^2) + (0.1066P)^2]$
$S = 1.08$	where $P = (F_o^2 + 2F_c^2)/3$
4338 reflections	$(\Delta/\sigma)_{max} = 0.001$
245 parameters	$\Delta\rho_{max} = 1.50$ e Å^{-3}
2 restraints	$\Delta\rho_{min} = -1.86$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
I1	−0.35472 (12)	0.250000	0.67963 (3)	0.0560 (2)	
I2	0.01890 (11)	0.250000	0.76417 (3)	0.05183 (19)	
I3	0.79982 (13)	0.250000	1.14308 (3)	0.0586 (2)	
I4	0.60633 (11)	0.250000	1.01597 (3)	0.04923 (19)	
I5	0.2583 (5)	0.250000	0.27778 (5)	0.0741 (7)	0.872 (9)
I6	0.21383 (12)	0.250000	0.41535 (3)	0.0539 (2)	
Br1	0.187 (3)	0.250000	0.5623 (9)	0.0472 (13)	0.734 (9)
Br2	0.45302 (18)	0.250000	0.86816 (5)	0.0466 (2)	
Br3	0.377 (5)	0.250000	0.2786 (6)	0.0741 (7)	0.128 (9)
I7	0.163 (5)	0.250000	0.5672 (16)	0.0472 (13)	0.266 (9)
O1	0.1683 (9)	0.4984 (2)	0.9661 (2)	0.0505 (10)	
H1H	0.076093	0.499548	0.999810	0.061*	0.5
O2	−0.3239 (9)	0.4969 (3)	0.5335 (3)	0.0586 (12)	
H2H	−0.446965	0.490872	0.508030	0.070*	0.5
N1	0.3798 (10)	0.4251 (3)	0.9033 (3)	0.0484 (12)	
N2	−0.0642 (11)	0.4216 (3)	0.5801 (3)	0.0552 (14)	
C1	0.0715 (12)	0.3731 (3)	0.9637 (4)	0.0501 (14)	
H1A	0.098353	0.362739	1.011495	0.075*	
H1B	0.113691	0.331174	0.937228	0.075*	
H1C	−0.089496	0.384005	0.955193	0.075*	
C2	0.2127 (12)	0.4365 (3)	0.9443 (3)	0.0456 (13)	
C3	0.5419 (12)	0.4735 (3)	0.8774 (3)	0.0473 (14)	
C4	0.5362 (13)	0.5478 (4)	0.8870 (4)	0.0520 (16)	
H4	0.419452	0.569179	0.911890	0.062*	
C5	0.7052 (13)	0.5903 (4)	0.8594 (4)	0.0527 (15)	
H5	0.702697	0.640867	0.865450	0.063*	
C6	0.8759 (14)	0.5591 (4)	0.8234 (4)	0.0548 (16)	
H6	0.991771	0.588384	0.805864	0.066*	
C7	0.8792 (13)	0.4857 (4)	0.8128 (4)	0.0530 (15)	
H7	0.994642	0.464790	0.787078	0.064*	
C8	0.7116 (13)	0.4424 (4)	0.8400 (3)	0.0501 (15)	
H8	0.713507	0.391949	0.833071	0.060*	
C9	−0.3515 (13)	0.3723 (4)	0.5042 (4)	0.0606 (18)	
H9A	−0.498372	0.362062	0.523622	0.091*	
H9B	−0.253279	0.329991	0.508838	0.091*	
H9C	−0.374370	0.384069	0.456578	0.091*	
C10	−0.2426 (14)	0.4342 (4)	0.5399 (4)	0.0539 (16)	
C11	0.0751 (14)	0.4693 (4)	0.6187 (4)	0.0548 (16)	
C12	0.0262 (15)	0.5416 (4)	0.6283 (4)	0.0616 (19)	
H12	−0.107929	0.562506	0.609158	0.074*	
C13	0.1803 (17)	0.5823 (5)	0.6669 (4)	0.069 (2)	
H13	0.150763	0.631944	0.673515	0.082*	
C14	0.3728 (16)	0.5528 (6)	0.6956 (4)	0.071 (2)	
H14	0.475421	0.581829	0.721396	0.085*	
C15	0.4175 (16)	0.4804 (5)	0.6869 (4)	0.071 (2)	

H15	0.550402	0.459333	0.706665	0.085*
C16	0.2661 (14)	0.4392 (5)	0.6490 (4)	0.0617 (19)
H16	0.294132	0.389301	0.643721	0.074*
H1N	0.408 (13)	0.3798 (12)	0.895 (3)	0.047 (19)*
H2N	−0.009 (13)	0.3780 (18)	0.584 (4)	0.05 (2)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0409 (4)	0.0747 (4)	0.0524 (4)	0.000	0.0011 (3)	0.000
I2	0.0408 (4)	0.0622 (3)	0.0525 (4)	0.000	0.0015 (3)	0.000
I3	0.0608 (5)	0.0568 (3)	0.0573 (4)	0.000	−0.0090 (3)	0.000
I4	0.0426 (4)	0.0480 (3)	0.0567 (4)	0.000	−0.0034 (3)	0.000
I5	0.1209 (18)	0.0587 (4)	0.0424 (4)	0.000	−0.0016 (6)	0.000
I6	0.0648 (5)	0.0505 (3)	0.0456 (3)	0.000	−0.0093 (3)	0.000
Br1	0.040 (3)	0.0568 (5)	0.045 (2)	0.000	0.0048 (19)	0.000
Br2	0.0468 (6)	0.0470 (4)	0.0460 (5)	0.000	0.0023 (4)	0.000
Br3	0.1209 (18)	0.0587 (4)	0.0424 (4)	0.000	−0.0016 (6)	0.000
I7	0.040 (3)	0.0568 (5)	0.045 (2)	0.000	0.0048 (19)	0.000
O1	0.050 (3)	0.053 (2)	0.049 (2)	0.002 (2)	0.006 (2)	0.0011 (18)
O2	0.051 (3)	0.068 (3)	0.056 (3)	0.002 (2)	−0.015 (2)	0.004 (2)
N1	0.045 (3)	0.048 (2)	0.053 (3)	0.002 (2)	0.005 (3)	0.002 (2)
N2	0.047 (4)	0.059 (3)	0.059 (3)	−0.005 (3)	−0.010 (3)	0.004 (2)
C1	0.041 (4)	0.051 (3)	0.059 (4)	0.002 (3)	0.006 (3)	0.004 (3)
C2	0.044 (4)	0.051 (3)	0.041 (3)	0.007 (3)	0.000 (3)	0.002 (2)
C3	0.047 (4)	0.055 (3)	0.040 (3)	−0.002 (3)	−0.005 (3)	0.006 (2)
C4	0.047 (4)	0.055 (3)	0.054 (4)	0.007 (3)	0.000 (3)	0.006 (3)
C5	0.050 (4)	0.054 (3)	0.054 (4)	−0.003 (3)	−0.003 (3)	0.005 (3)
C6	0.050 (4)	0.063 (4)	0.051 (4)	−0.008 (3)	−0.005 (3)	0.008 (3)
C7	0.048 (4)	0.067 (4)	0.044 (3)	0.002 (3)	−0.002 (3)	0.006 (3)
C8	0.045 (4)	0.055 (3)	0.049 (4)	0.006 (3)	−0.007 (3)	0.000 (3)
C9	0.046 (4)	0.075 (4)	0.061 (4)	−0.009 (3)	−0.008 (3)	0.007 (3)
C10	0.048 (4)	0.065 (4)	0.048 (4)	−0.008 (3)	−0.005 (3)	0.005 (3)
C11	0.047 (4)	0.071 (4)	0.045 (3)	−0.008 (3)	−0.004 (3)	0.001 (3)
C12	0.054 (5)	0.071 (4)	0.059 (4)	−0.016 (4)	−0.013 (4)	0.009 (3)
C13	0.077 (6)	0.077 (4)	0.052 (4)	−0.013 (4)	−0.011 (4)	−0.001 (3)
C14	0.055 (5)	0.114 (7)	0.044 (4)	−0.022 (5)	−0.004 (3)	0.000 (4)
C15	0.049 (5)	0.107 (6)	0.056 (4)	0.006 (4)	−0.013 (4)	−0.009 (4)
C16	0.046 (4)	0.087 (5)	0.051 (4)	0.003 (4)	−0.007 (3)	−0.006 (3)

Geometric parameters (Å, º)

I1—I2	2.7285 (9)	C4—H4	0.9500
I3—I4	2.7462 (9)	C5—C6	1.384 (11)
I5—I6	2.7678 (12)	C5—H5	0.9500
I6—Br3	2.926 (17)	C6—C7	1.384 (10)
I6—Br1	2.944 (18)	C6—H6	0.9500
I6—I7	3.06 (3)	C7—C8	1.400 (11)

O1—C2	1.261 (8)	C7—H7	0.9500
O1—H1H	0.8802	C8—H8	0.9500
O2—C10	1.267 (9)	C9—C10	1.489 (10)
O2—H2H	0.8788	C9—H9A	0.9800
N1—C2	1.319 (9)	C9—H9B	0.9800
N1—C3	1.424 (9)	C9—H9C	0.9800
N1—H1N	0.878 (10)	C11—C16	1.379 (11)
N2—C10	1.323 (10)	C11—C12	1.391 (11)
N2—C11	1.418 (9)	C12—C13	1.396 (11)
N2—H2N	0.878 (10)	C12—H12	0.9500
C1—C2	1.504 (9)	C13—C14	1.369 (14)
C1—H1A	0.9800	C13—H13	0.9500
C1—H1B	0.9800	C14—C15	1.386 (14)
C1—H1C	0.9800	C14—H14	0.9500
C3—C8	1.395 (10)	C15—C16	1.382 (11)
C3—C4	1.397 (9)	C15—H15	0.9500
C4—C5	1.399 (10)	C16—H16	0.9500
I5—I6—Br1	177.6 (4)	C6—C7—H7	120.1
Br3—I6—I7	166.4 (9)	C8—C7—H7	120.1
C2—O1—H1H	115.3	C3—C8—C7	119.8 (6)
C10—O2—H2H	104.0	C3—C8—H8	120.1
C2—N1—C3	130.4 (6)	C7—C8—H8	120.1
C2—N1—H1N	115 (5)	C10—C9—H9A	109.5
C3—N1—H1N	114 (5)	C10—C9—H9B	109.5
C10—N2—C11	130.7 (6)	H9A—C9—H9B	109.5
C10—N2—H2N	121 (5)	C10—C9—H9C	109.5
C11—N2—H2N	109 (5)	H9A—C9—H9C	109.5
C2—C1—H1A	109.5	H9B—C9—H9C	109.5
C2—C1—H1B	109.5	O2—C10—N2	121.0 (7)
H1A—C1—H1B	109.5	O2—C10—C9	120.7 (7)
C2—C1—H1C	109.5	N2—C10—C9	118.3 (7)
H1A—C1—H1C	109.5	C16—C11—C12	120.2 (7)
H1B—C1—H1C	109.5	C16—C11—N2	115.6 (7)
O1—C2—N1	121.9 (6)	C12—C11—N2	124.2 (7)
O1—C2—C1	120.3 (6)	C11—C12—C13	117.9 (8)
N1—C2—C1	117.7 (5)	C11—C12—H12	121.0
C8—C3—C4	120.4 (7)	C13—C12—H12	121.0
C8—C3—N1	115.8 (6)	C14—C13—C12	121.8 (9)
C4—C3—N1	123.8 (7)	C14—C13—H13	119.1
C3—C4—C5	119.0 (7)	C12—C13—H13	119.1
C3—C4—H4	120.5	C13—C14—C15	119.8 (8)
C5—C4—H4	120.5	C13—C14—H14	120.1
C6—C5—C4	120.5 (6)	C15—C14—H14	120.1
C6—C5—H5	119.7	C16—C15—C14	119.1 (8)
C4—C5—H5	119.7	C16—C15—H15	120.4
C7—C6—C5	120.5 (7)	C14—C15—H15	120.4
C7—C6—H6	119.7	C11—C16—C15	121.1 (8)

| C5—C6—H6 | 119.7 | C11—C16—H16 | 119.4 |
| C6—C7—C8 | 119.7 (8) | C15—C16—H16 | 119.4 |

C3—N1—C2—O1	2.3 (11)	C11—N2—C10—O2	−4.2 (13)
C3—N1—C2—C1	−178.8 (6)	C11—N2—C10—C9	178.2 (8)
C2—N1—C3—C8	173.9 (7)	C10—N2—C11—C16	−172.1 (8)
C2—N1—C3—C4	−6.8 (11)	C10—N2—C11—C12	9.7 (14)
C8—C3—C4—C5	−0.9 (10)	C16—C11—C12—C13	2.5 (12)
N1—C3—C4—C5	179.7 (6)	N2—C11—C12—C13	−179.3 (8)
C3—C4—C5—C6	−0.3 (10)	C11—C12—C13—C14	−0.9 (14)
C4—C5—C6—C7	1.5 (11)	C12—C13—C14—C15	−0.5 (14)
C5—C6—C7—C8	−1.6 (11)	C13—C14—C15—C16	0.2 (14)
C4—C3—C8—C7	0.9 (10)	C12—C11—C16—C15	−2.9 (13)
N1—C3—C8—C7	−179.7 (6)	N2—C11—C16—C15	178.8 (8)
C6—C7—C8—C3	0.3 (10)	C14—C15—C16—C11	1.5 (14)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···Br2	0.88 (1)	2.49 (1)	3.367 (5)	175 (7)
N2—H2*N*···Br1	0.88 (1)	2.69 (2)	3.546 (10)	164 (7)
O1—H1*H*···O1[i]	0.88	1.62	2.442 (10)	155
O2—H2*H*···O2[ii]	0.88	1.58	2.434 (10)	164

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