

Secondary Bonding Interactions in Some Haloanilinium Halides

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The crystal packing in the structures of various solvent-free (mono)haloanilinium halides involves with one exception the formation of approximately planar hydrophilic regions that contain classical hydrogen bonds $N-H \cdots X^-$ ($X = \text{halogen}$). Common to the substructures of all layers are rings of general graph set $R_{2n}^z(4n)$, involving equal numbers of chloride acceptors and NH_2 moieties (two hydrogen atoms of the positively charged NH_3 groups). The 2-substituted derivatives contain the shortest $X \cdots X^-$ contacts, and these are within the layers; it could be argued that the contacts are forced upon the system by the 2-substitution pattern. In 3-chloroanilinium chloride and its bromine analogue, the layers consist of ribbons connected by short $C-H \cdots X^-$ interactions. In all these compounds, the aromatic groups project from the layers and form hydrophobic regions; the layers are linked by weak interactions of the form $X \cdots X$ or $C-H \cdots X$. There is appreciable interdigitation of hydrophobic groups from adjacent layers except for the ribbon structures. 3-Iodoanilinium iodide displays a completely different structure, in which all the atoms except some hydrogen atoms of the NH_3 groups lie in a crystallographic mirror plane, but without forming separate hydrophilic and hydrophobic regions. The salt 4-bromoanilinium bromide could only be obtained as a hemihydrate; it too forms hydrophilic layers, but these are highly puckered.

Introduction

We are interested in the interplay between secondary interactions, and in particular those between hydrogen bonds and halogen-halogen contacts in halide salts of halogen-substituted amines. We have recently described the infinite chain structures of 4-halopyridinium halides [1], in which the 4-substitution pattern promotes linear chains of ions with very short contacts between halide anion and halogen atoms of the cation (Cl 3.3352(14) Å, Br 3.3502(11) Å, I 3.5149(6) Å), and the more complex packing motifs of the 2- and 3-derivatives [2]. For a brief description of the phenomenon of halogen-halogen contacts, together with a review of the literature, the reader is referred to our publications [1 - 3]. We have now begun to study haloanilinium systems, in which there are more H-bond donors and where one would therefore expect a greater preponderance of hydrogen bonds over halogen-halogen contacts. Here we present the structures of 2-, 3- and 4-haloanilinium halides. The structure of 4-chloroanilinium chloride was taken from the literature [4].

Results and Discussion

Preliminary remarks

Abbreviations for the compound names conform to the principle 2-Cl = 2-chloroanilinium chloride, *etc.* The ring numbering is standard (the nitrogen-bearing carbon is C1). The halogen of the cation is always numbered 1 and the halide anion 2. For a general halogen the symbol X is used. Hydrogen atoms bonded to carbon are given the same number as their parent atom; those of the NH_3 groups are numbered 01 to 03.

We succeeded in synthesizing 4-I, but it has so far proved too unstable in solution to allow the growth of single crystals; 4-Br crystallizes, even from notionally dry solvents, either as microcrystalline material or as a hemihydrate. The complete series of structures of the solvent-free 2- and 3-substituted derivatives was however obtained.

The structures of the cations are unremarkable. The widening of the ring angle at C1, previously noted for 4-Cl [4], to values somewhat above 120° is observed in all structures but is marginal for 2-Cl and 2-Br (120.1 and 120.7° , respectively; otherwise

Table 1. Hydrogen bonds (Å, °)^a.

H Bond	D-H	H...A	D...A	D-H...A	Operator of A
<i>Compound 2-Cl:</i>					
N-H01...Cl2	1.01	2.17	3.169	169	1-x,2-y, ¹ / ₂ +z
N-H02...Cl2	1.01	2.13	3.136	172	
N-H03...Cl2	1.01	2.19	3.183	168	1-x,1-y, ¹ / ₂ +z
C5-H5...Cl1	1.08	2.78	3.736	147	¹ / ₂ -x,1+y, ¹ / ₂ +z
C3-H3...Cl2	1.08	2.88	3.632	127	- ¹ / ₂ +x,1-y,z
<i>Compound 2-Br:</i>					
N-H01...Br2	1.01	2.32	3.319	169	1-x,2-y, ¹ / ₂ +z
N-H02...Br2	1.01	2.32	3.299	165	
N-H03...Br2	1.01	2.33	3.325	169	1-x,1-y, ¹ / ₂ +z
C5-H5...Br1	1.08	2.89	3.833	147	¹ / ₂ -x,1+y, ¹ / ₂ +z
C3-H3...Br2	1.08	2.93	3.710	130	-1/ ₂ +x,1-y,z
<i>Compound 2-I:</i>					
N-H01...I2	1.01	2.58	3.518	156	2-x,1-y,1-z
N-H02...I2	1.01	2.52	3.525	176	
N-H03...I2	1.01	2.48	3.456	163	x, ¹ / ₂ -y,- ¹ / ₂ +z
C4-H4...I2	1.08	3.18	4.139	148	1-x, ¹ / ₂ +y, ¹ / ₂ -z
C5-H5...I2	1.08	3.13	3.904	130	1-x,1-y,1-z
C6-H6...I2	1.08	3.17	4.042	138	
<i>Compound 3-Cl:</i>					
N-H01...Cl2	1.01	2.21	3.165	157	
N-H02...Cl2	1.01	2.12	3.126	171	1-x,1-y,-z
N-H03...Cl2	1.01	2.21	3.183	162	x,1+y,z
C6-H6...Cl2	1.08	2.59	3.568	151	-1+x,1+y,z
C2-H2...Cl2	1.08	2.73	3.563	134	-1+x,y,z
C4-H4...Cl1	1.08	2.86	3.829	150	¹ / ₂ -x, ¹ / ₂ +y, ¹ / ₂ -z
<i>Compound 3-Br:</i>					
N-H01...Br2	1.01	2.35	3.355	176	
N-H02...Br2	1.01	2.35	3.335	165	1-x,-y,-z
N-H03...Br2	1.01	2.44	3.374	154	x,-1+y,z
C6-H6...Br2	1.08	2.69	3.655	149	1+x,-1+y,z
C2-H2...Br2	1.08	3.03	3.893	138	
<i>Compound 3-I:</i>					
N-H01...I2'	1.01	2.57	3.489	151	
N-H02...I2	1.01	2.61	3.479	141	1-x,1-y,1-z
N'-H01'...I2	1.01	2.62	3.619	170	1+x,y,-1+z
N'-H02'...I2'	1.01	2.68	3.511	140	2-x,1-y,-z
N'-H01''...I2'	1.01	2.61	3.617	179	x,y,-1+z
N'-H02''...I2'	1.01	2.67	3.511	141	2-x,-y,-z
C4-H4...I2'	1.08	2.94	4.020	176	-1+x,y,z
C4'-H4'...I2	1.08	3.19	4.098	143	x,y,-1+z
C5-H5...I1'	1.08	3.12	4.052	145	-1+x,y,z
C5-H5'...I1	1.08	3.05	4.128	177	x,y,-1+z
C6-H6...I2	1.08	2.90	3.945	164	x,y,-1+z
C6'-H6'...I2'	1.08	3.10	4.027	144	x,y,-1+z

121.4-122.8°). The C-N bond is significantly longer than in neutral aniline derivatives [4] and adopts here values of 1.457-1.468 Å, with one larger value in 3-I (1.480 Å).

Table 1 (continued).

H Bond	D-H	H...A	D...A	D-H...A	Operator of A
<i>Compound 4-Cl^b:</i>					
N-H01...Cl2	1.01	2.15	3.135	165	1+x,y,z
N-H02...Cl2	1.01	2.12	3.115	171	1+x, ¹ / ₂ -y, ¹ / ₂ +z
N-H03...Cl2	1.01	2.16	3.157	169	1-x,-y,1-z
C3-H3...Cl2	1.08	2.67	3.672	154	
<i>Compound 4-Br · ¹/₂H₂O:</i>					
N-H01...O	1.01	1.74	2.743	173	
N-H02...Br2'	1.01	2.33	3.317	167	¹ / ₂ -x,- ¹ / ₂ +y, ¹ / ₂ -z
N-H03...Br2	1.01	2.35	3.314	160	
N'-H01'...Br2'	1.01	2.31	3.288	164	
N'-H02'...Br2'	1.01	2.26	3.260	171	-x,2-y,1-z
N'-H03'...Br2	1.01	2.31	3.299	166	- ¹ / ₂ +x, ¹ / ₂ -y, ¹ / ₂ +z
O-H04...Br2	0.98	2.45	3.417	169	x,1+y,z
O-H05...Br2	0.98	2.33	3.304	171	¹ / ₂ -x, ¹ / ₂ +y, ¹ / ₂ -z
C5-H5...Br2'	1.08	2.82	3.901	172	1+x,-1+y,z
C2-H2...Br1'	1.08	2.88	3.922	162	¹ / ₂ -x,- ¹ / ₂ +y, ¹ / ₂ -z
C3'-H3'...Br2'	1.08	2.79	3.766	150	¹ / ₂ +x, ¹ / ₂ -y, ¹ / ₂ +z

^a Several borderline cases (in italics) are included for completeness, D = donor, A = acceptor; ^b taken or calculated from Ref. [4].

The non-bonding contacts form the main subject of interest and are summarised for all compounds in Table 1 (hydrogen bonds) and Table 2 (halogen-halogen contacts). Following Steiner [5], we have used idealised N-H, O-H and C-H distances of 1.009, 0.980 and 1.080 Å respectively to calculate normalised hydrogen bonding parameters. We have used the conservative values of 1.75, 1.85 and 1.98 Å respectively for the van der Waals radii of chlorine, bromine and iodine. These values are cited in many textbooks. However, at least one author presents larger values: Cl 1.81, Br 1.95, I 2.15 Å [6].

2-halo derivatives: structures with clearly defined hydrophilic regions

The formula units of 2-Cl, 2-Br and 2-I are shown in Figs 1 - 3. None of the compounds displays imposed symmetry. The compounds 2-Cl and 2-Br are isotopic. All three compounds form classical hydrogen bonds N-H...X⁻ from all three hydrogens of the NH₃⁺ group, each to a different halide ion; accordingly, each halide ion accepts three hydrogen bonds.

In 2-Cl the hydrogen bonds combine to form a layer structure (Fig. 4) parallel to the yz plane, with successive hydrophilic regions at $x \approx 0, \frac{1}{2}, 1, \text{etc.}$

Table 2. Halogen-halogen contacts ^a.

Contact	X...X (Å)	C-X...X (°)	Operator
<i>Compound 2-Cl:</i>			
C2-C11...Cl2	3.4118(5)	170.56(5)	$x, -1+y, z$
C2-C11...Cl2	3.6826(7)	85.36(5)	$1-x, 1-y, 1/2+z$
C2-C11...Cl2	3.7300(6)	90.05(5)	
<i>Compound 2-Br:</i>			
C2-Br1...Br2	3.4427(3)	170.19(7)	$x, -1+y, z$
C2-Br1...Br2	3.8741(5)	84.58(7)	$1-x, 1-y, 1/2+z$
C2-Br1...Br2	3.9410(4)	88.22(7)	
<i>Compound 2-I:</i>			
C2-I1...I2	3.6916(3)	170.16(7)	$2-x, 1/2+y, 1/2-z$
C2-I1...I2	4.3253(3)	94.54(7)	$2-x, 1-y, 1-z$
<i>Compound 3-Cl:</i>			
C3-C11...Cl2	3.6775(11)	150.47(3)	$2-x, -y, -z$
C3-C11...Cl2	3.7019(11)	100.70(3)	$2-x, 1-y, -z$
<i>Compound 3-Br:</i>			
C3-Br1...Br1	3.6178(7)	163.18(8) ^c	$1-x, 1-y, 1-z$
Br2...Br2	3.7155(6)		$-x, -y, -z$
<i>Compound 3-I:</i>			
C3-I1...I2	3.7820(6)	174.1(10)	
C3'-I1'...I2'	3.9241(6)	174.39(9)	
<i>Compound 4-Cl^b:</i>			
C4-C11...Cl2	3.635	166.6	$-x, 1/2+y, 1/2-z$
<i>Compound 4-Br · 1/2H₂O:</i>			
C4-Br1...Br2	3.7152(4)	155.27(7)	
C4'-Br1'...Br2	3.9895(4)	152.58(6)	

^a Several borderline cases (in italics) are included for completeness; ^b values calculated from Ref. [4]; ^c the other C-Br...Br angle of this interaction is equal by symmetry.

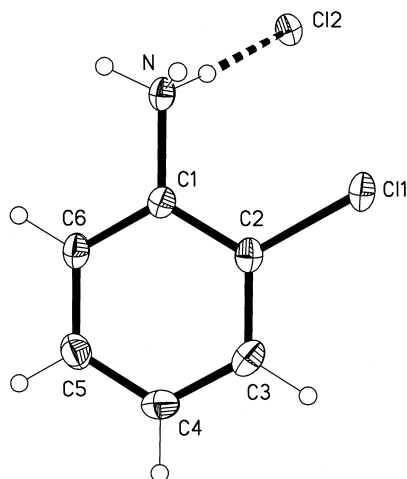


Fig. 1. Structure of the formula unit of compound 2-Cl in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

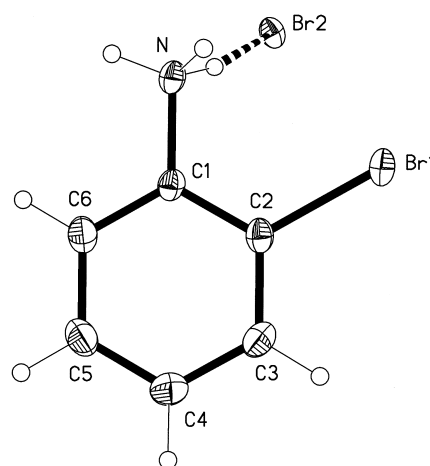


Fig. 2. Structure of the formula unit of compound 2-Br in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

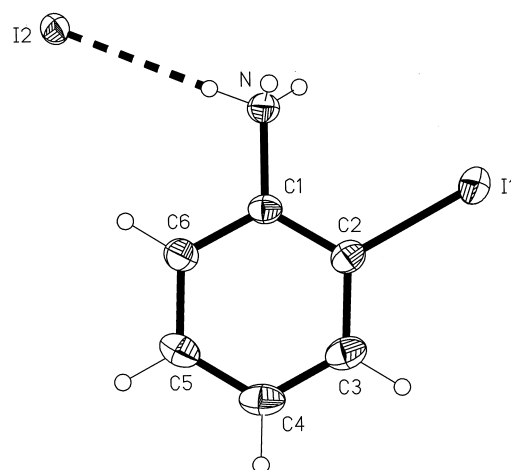


Fig. 3. Structure of the formula unit of compound 2-I in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

The layers are composed of prominent rings of type $R_6^3(12)$ [7] involving three chloride ions and three NH_2 moieties (two donor hydrogens from the positively charged NH_3 groups). Additionally, C11...Cl2 contacts of 3.4118(5) Å are observed, slightly but significantly (2.5%) shorter than the double van der Waals radius. Although the 2-substitution pattern must to some extent force Cl1 to be near the hydrogen bonding system, the essentially linear angle C-X...X⁻ was also observed for the even shorter X...X⁻ contacts of the 4-pyridinium series [1]. The aromatic rings project alternately above and below the hydrophilic layers, forming hydrophobic

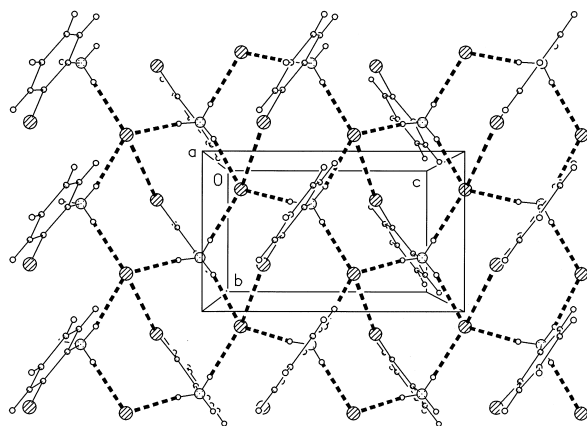


Fig. 4. Packing diagram of 2-Cl viewed parallel to the x axis. Classical hydrogen bonds and Cl...Cl contacts are shown as thick, non-classical as thin dashed lines.

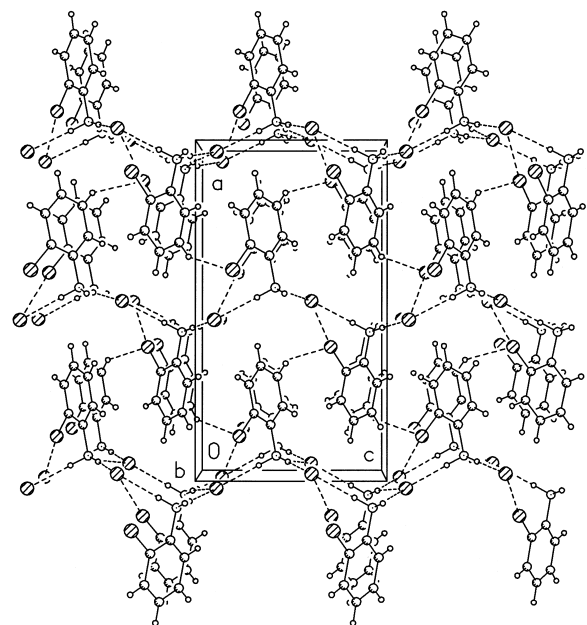


Fig. 5. Packing diagram of 2-Cl viewed parallel to the y axis. All secondary interactions are shown as thin dashed lines.

regions at $x \approx 1/4, 3/4, \text{etc.}$ Within these regions rings from both neighbouring hydrophilic layers (related by glide planes) overlap, consistent with the short layer repeat distance of $a/2 \approx 7.75 \text{ \AA}$. The layers are linked by one non-classical, "weak" [8] hydrogen bond C5-H5...Cl1 (Fig. 5), which, perhaps surprisingly, involves the cation chlorine atom (*cf.* 2-I below). Clearly, exactly analogous remarks apply to all aspects of the isomorphous 2-Br structure; its

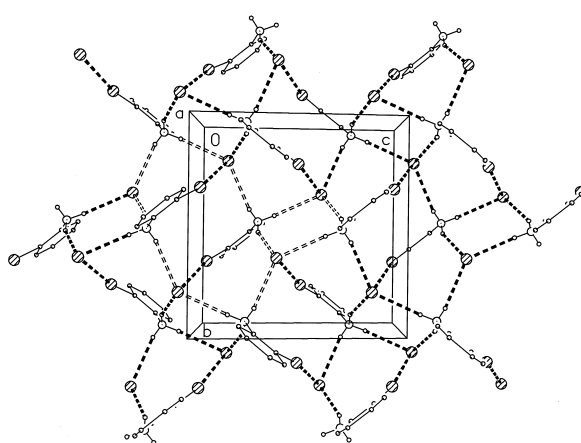


Fig. 6. Packing diagram of 2-I viewed parallel to the x axis. Classical hydrogen bonds and I...I contacts are shown as broken bonds; one of each kind of ring (see text) is highlighted with open bonds.

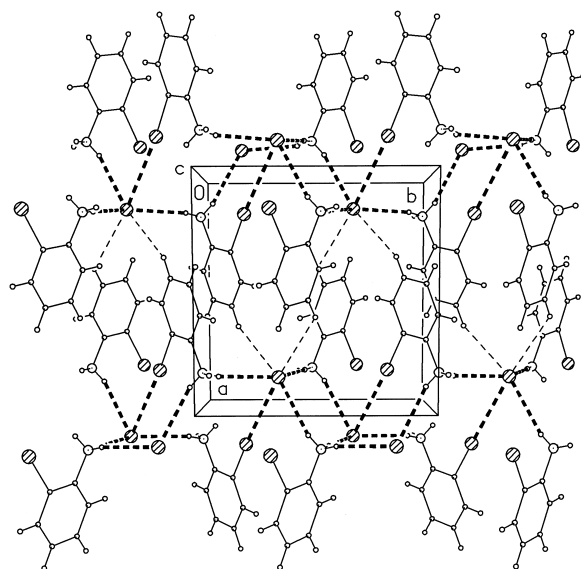


Fig. 7. Packing diagram of 2-I viewed parallel to the z axis. Classical hydrogen bonds and I...I contacts are shown as thick dashed lines, C-H...I interactions as thin dashed lines.

Br...Br contact is $3.4427(3) \text{ \AA}$, 7% below the van der Waals diameter, and its layer repeat distance is 7.98 \AA .

The extended structure of 2-I similarly consists of polar and non-polar regions. Fig. 6 shows one of the polar layers, which are parallel to yz and occupy the regions $x \approx 0, 1, \text{etc.}$ (being thus related by x translation). In contrast to 2-Cl, the hy-

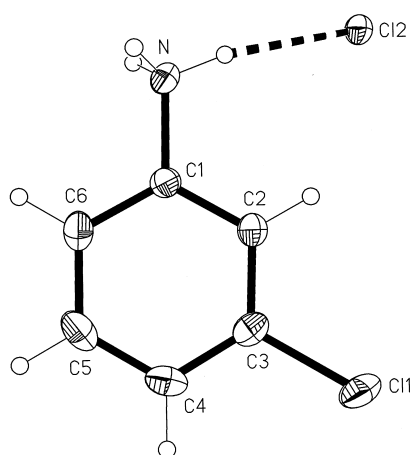


Fig. 8. Structure of the formula unit of compound 3-Cl in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

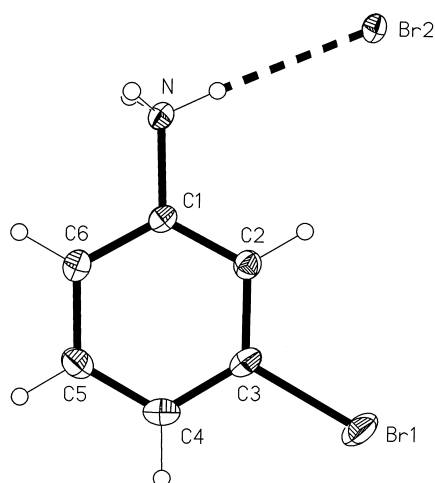


Fig. 9. Structure of the formula unit of compound 3-Br in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

hydrogen bonds form two sorts of rings, one $R_3^4(16)$ with donors H01 ($\times 2$), H02 ($\times 2$), H03 ($\times 4$) and one $R_4^2(8)$ with donors H01 ($\times 2$), H02 ($\times 2$); all acceptors are chloride ions. One of each type of ring is highlighted in Fig. 6. A short and linear C2-H11...I2 contact of 3.6916(3) Å (6.8% below the van der Waals diameter) is observed. The hydrophobic regions are composed of interdigitating aromatic rings from both neighbouring polar layers; these establish contacts to the polar layers via C-H...I⁻ interactions from H4 and H5 (Fig. 7). The layer repeat distance is $a = 10.01$ Å, appreciably greater than in 2-Cl, which may be at-

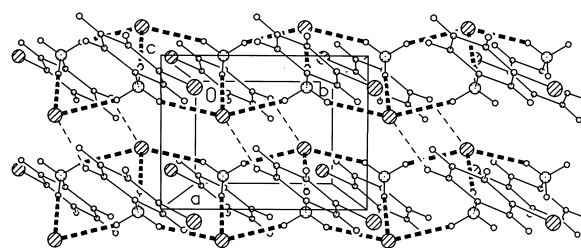


Fig. 10. Packing diagram of 3-Cl viewed parallel to the z axis. Classical hydrogen bonds are shown as thick dashed lines, C-H...Cl contacts as thin broken lines.

tributed to the greater intrinsic width of the polar regions.

3-Halo derivatives: two hydrophilic ribbon structures and one layer structure

The formula units of 3-Cl and 3-Br are shown in Figs 8 and 9. They display no imposed symmetry and are not isomorphous. As in the 2-derivatives, all three N-H units form hydrogen bonds, each to a different halide anion.

The packing of 3-Cl (Fig. 10) involves hydrophilic pleated ribbons of N-H...Cl⁻ hydrogen bonds, arranged in contiguous rings of graph set $R_4^2(8)$ parallel to the y axis. As usual the donors are NH₂ moieties and the acceptors are chloride anions. The pleating angle Cl⁻...N...Cl is 138°. The donors H01 and H03 form hydrogen bonds in the direction of this double chain, whereas the hydrogen bond from H02 joins the two single chain components to form a ladder-like arrangement (although the uprights are angled at every rung!). The ribbons are further linked by translation parallel to x via short hydrogen bonds C6-H6...Cl2 to form layers parallel to the xy plane with hydrophilic regions at $z \approx 0, 1/2, 1, \text{etc.}$ Contacts from H01 and H03 to Cl2 ions of the neighbouring ribbon are too unsuitable in terms both of distance (2.85, 2.88 Å) and angle (104, 102°) to be seriously considered as weak components of three-centre hydrogen bonds.

In contrast to the 2-derivatives, the aromatic rings that project from adjacent hydrophilic regions do not overlap significantly (Fig. 11) but are instead linked by (at best very weak) contacts C4-H4...Cl1 (2.86 Å); adjacent layers are related via the glide plane. The layer repeat distance is $c/2 \approx 14.35$ Å. The final C-H...Cl contact is C2-H2...Cl2, within the asymmetric unit and possibly imposed by the

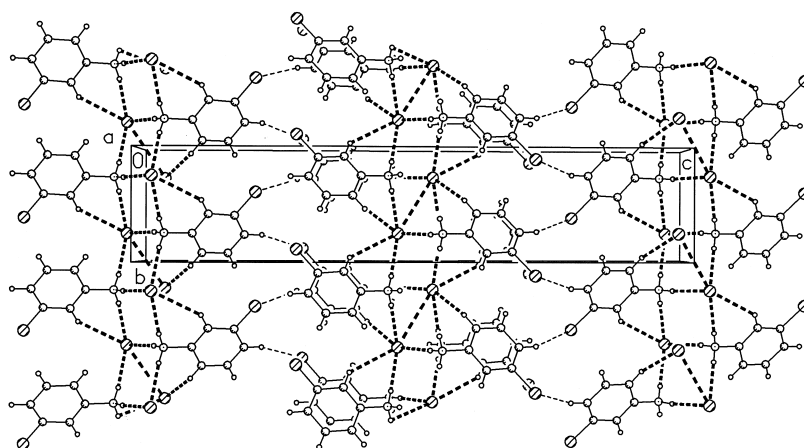


Fig. 11. Packing diagram of 3-Cl viewed parallel to the x axis. Classical hydrogen bonds are shown as thick dashed lines, C-H...Cl interactions linking the layers (at $z \approx 1/4, 3/4$) as thin dashed lines.

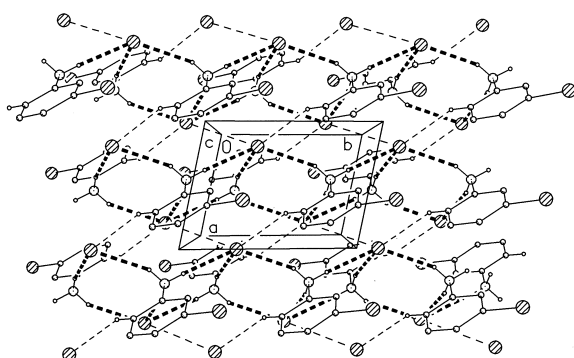


Fig. 12. Packing diagram of 3-Br viewed parallel to the z axis. Classical hydrogen bonds are shown as thick dashed lines, C-H...Br and Br⁻...Br⁻ contacts as thin broken lines. H atoms not involved in H bonding are omitted.

proximity to the classical H bond N-H1...Cl2. The shortest Cl1...Cl2 contact is 3.6775(11) Å, significantly above the double van der Waals radius of 3.5 Å.

The hydrogen bonding pattern of 3-Br is very similar to that of 3-Cl, as is reflected in the similar cell constants a and b . Ribbons topologically identical to those of 3-Cl are formed parallel to the y axis; these are linked by C6-H6...Br2 interactions to form layers parallel to xy with hydrophilic regions at $z \approx 0, 1$, etc. (Fig. 12), and the layer repeat distance is thus $c = 14.98$ Å. The pleating angle is 130°. Surprisingly, there are short anion...anion contacts of 3.7155(6) Å between ribbons. In the hydrophobic areas, the aromatic rings extending from neighbouring hydrophilic regions do not interdigitate; instead the layers are linked by Br1...Br1 contacts of 3.6178(8) Å across the inversion centre ($1/2,$

$1/2, 1/2$) (Fig. 13). The lack of isotopy to 3-Cl may be attributed to the differences in the weaker interactions. 3-Br represents the only case in this series with markedly short halogen-halogen contacts not involving halide anions. According to the classification of Pedireddi *et al.* [9] this is a "type I" contact, for which the two C-X...X angles θ are approximately equal (here exactly equal by symmetry, at 163.18(8)°). "Type II" contacts, in contrast, have $\theta_1 \approx 90^\circ$, $\theta_2 \approx 180^\circ$ (or *vice versa*) and are thought more likely to arise from true attractive interactions.

It is noteworthy that, of all layer-type structures reported here, only the two ribbon structures, 3-Cl and 3-Br, show no overlap or interdigitation of aromatic rings from adjacent hydrophilic layers. This may perhaps be attributed to the closer hydrophilic packing attained *via* the R₄²(8) rings, which leaves too little space for ring interdigitation; all the other structures have rings of dimension 10 or larger. In energy terms, one could speculate that a looser hydrophilic packing is in itself less favourable, but could be compensated by the weaker interactions attendant on ring interdigitation. The "efficiency" of packing is not an informative concept here in view of the trends in density: $\rho(2\text{-Cl}) > \rho(3\text{-Cl})$ but $\rho(2\text{-Br}) < \rho(3\text{-Br})$.

The structure of 3-I is completely different from all other structures reported here. There are no clearly separated polar regions. The entire structure except for some hydrogen atoms of the NH₃ groups lies in crystallographic mirror planes and there are two independent formula units (Fig. 14). Despite the apparently simple nature of the layers, an analysis of the secondary interactions is not completely

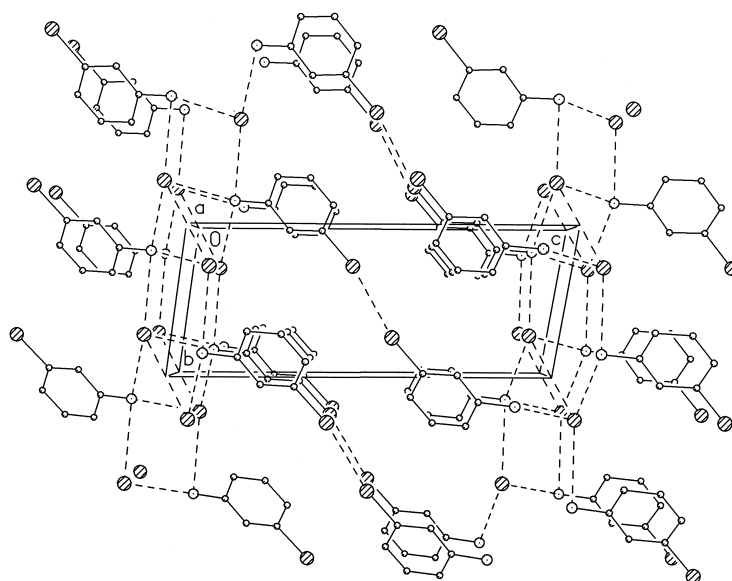


Fig. 13. Packing diagram of 3-Br viewed parallel to the x axis. All secondary contacts are shown as thin dashed lines. H atoms omitted. Note the Br...Br contacts at $z \approx 1/2$ (see text).

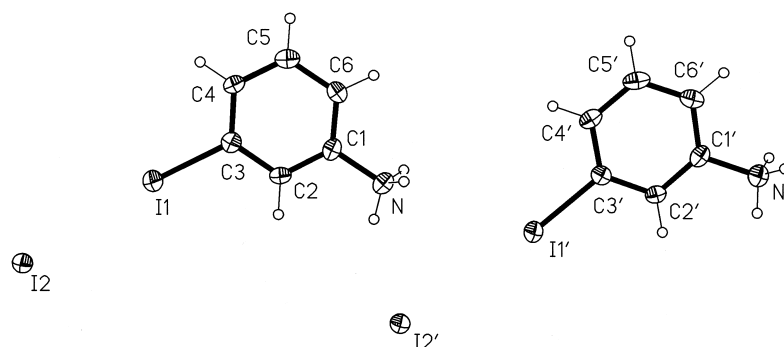


Fig. 14. Structure of the two independent formula units of compound 3-I in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

straightforward; in particular, there is no clear limit for the C-H...I interactions. Each independent formula unit forms chains parallel to the z axis, in which the residues are connected by I...I interactions (3.7820(6), 3.9241(6) Å) and hydrogen bonds C6-H6...I2 and C6'-H6'...I2'. The chains are connected by the classical hydrogen bonds N-H01...I2' and N'-H01'...I2 and the C-H...I interactions C4-H4...I2', C5-H5...I1' and C5'-H5'...I1. Possible bifurcated H bonds, in which two hydrogen atoms of an NH₃ group not lying in the mirror plane are the donors to an iodide acceptor, are not included in Fig. 15 (all H...I distances > 3.1 Å). One such NH₃ group is seen in Fig. 15 interrupting the cell edge $0 \rightarrow c$. The second disorder position of the NH₃ group at N' reverses the nature of the simple H bond to the neighbouring I2 and the bifurcated H bond to the neighbouring I2'. Finally, the layers are linked

by the H bonds N-H02...I2 and N'-H02'...I2' (in both disorder orientations of the latter group) (Fig. 16).

4-Chloroanilinium chloride revisited: more hydrophilic layers

The structure of 4-Cl was determined in 1985 at room temperature but with reasonable accuracy [4]. The secondary bonding was correctly described as being "composed of puckered layers ... held together by ionic forces and by hydrogen bonds to the chloride ions". Here we provide an extension of the previous discussion. Fig. 17 shows one of the hydrophilic layers, which are parallel to the yz plane and lie at $x \approx 0, 1, \text{etc.}$, thus being related by x translation. The layers contain rings analogous to those of 2-Br; the hydrogen bonds form one R₈⁴(16) ring with donors H01 (×2), H03 (×2), H02 (×4) and

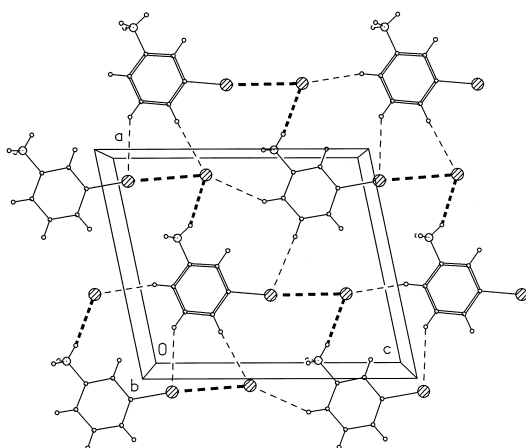


Fig. 15. Packing diagram of one layer of 3-I viewed parallel to the y axis. Short $N-H \cdots I$ hydrogen bonds and $I \cdots I$ contacts are shown as thick dashed lines, $C-H \cdots I$ contacts as thin broken lines. Bonds of the first independent formula unit (unprimed atoms in the text and tables) are shown as double, those of the second formula unit (primed atoms) as single lines. Possible bifurcated H bonds (see text) are not drawn explicitly. The second disorder component of the NH_3 group at N' is omitted.

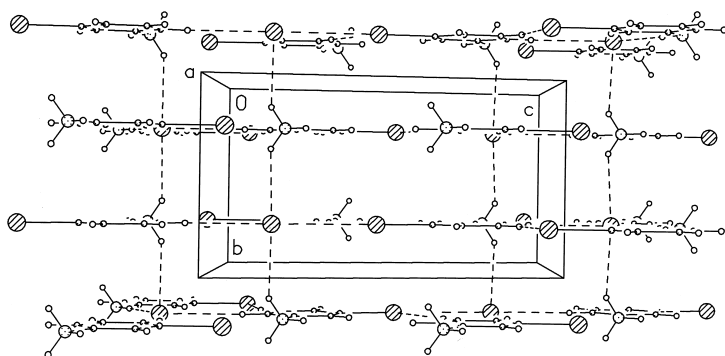


Fig. 16. Packing diagram of one layer of 3-I viewed parallel to the x axis, showing the $N-H \cdots I$ hydrogen bonds linking the layers.

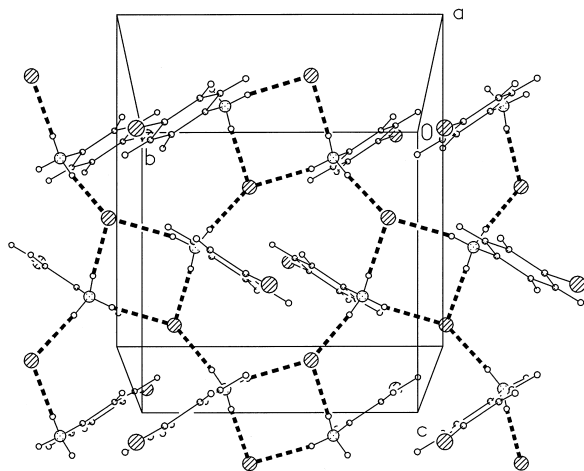


Fig. 17. Packing diagram of one layer of 4-Cl viewed perpendicular to the bc plane; hydrogen bonds are shown as dashed lines.

one $R_4^2(8)$ ring with donors $H01 (\times 2)$, $H03 (\times 2)$. The aromatic rings in the hydrophobic layers are interdigitated and are linked to the next polar layer

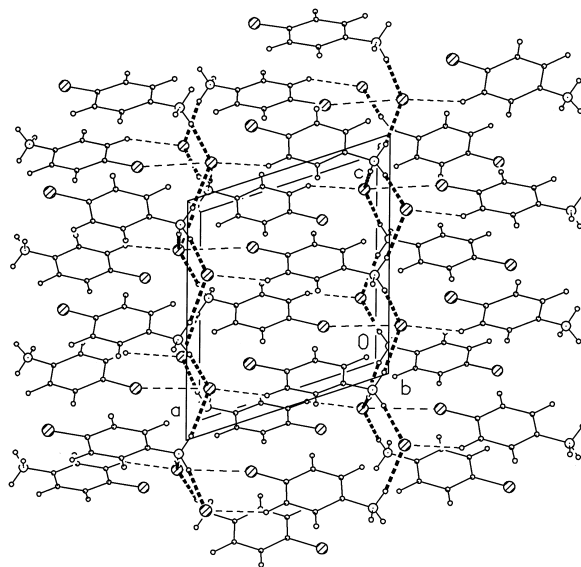


Fig. 18. Packing diagram of 4-Cl viewed parallel to the y axis; hydrogen bonds in the polar layers are shown as thick dashed lines. Thin dashed lines indicate $Cl \cdots Cl$ interactions and $C-H \cdots Cl$ hydrogen bonds.

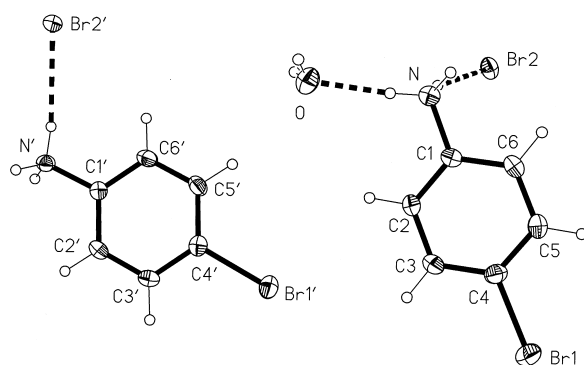


Fig. 19. Structure of the two independent formula units (and one water molecule) of 4-Br hemihydrate in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

via one rather long $C11 \cdots C12$ interaction and one quite short hydrogen bond $C3-H3 \cdots C12$ (2.67 Å), as shown in Fig. 18. The layer repeat distance is $a = 8.73$ Å.

4-Bromoanilinium bromide hemihydrate:
a highly puckered layer structure

Our attempts to recrystallize the compound 4-Br sometimes led to single crystals, but these always proved to be the hemihydrate; clearly the material can extract and tenaciously retain small quantities of water even from notionally dry solvents. The asymmetric unit, shown in Fig. 19, contains two independent formula units of 4-Br (in the following discussion, the second formula unit is distinguished by primed atom names) and one water molecule.

The two cations are almost parallel to each other (interplanar angle 6.8°). The NH_3 group of the first molecule donates hydrogen bonds to the water and to each bromide; the NH_3 group of the second molecule to $Br2'$ ($\times 2$) and $Br2$; and the water to $Br2$ ($\times 2$). The anion $Br2$ thus acts as acceptor to four classical hydrogen bonds, compared to a maximum of three in the anhydrous structures. There is a $Br1 \cdots Br2$ contact of 3.7152 Å and, finally, three short $C-H \cdots Br$ interactions.

All the classical hydrogen bonds form rings, which in turn combine to form highly puckered layers in planes perpendicular to the diagonal [101] (Fig. 20); there are two layers per diagonal length. The presence of water molecules leads to a departure from the general graph set form $R_{2n}^n(4n)$, with n halide anions and $2n$ hydrogen atoms from n NH_3 groups, as observed for the 2- and 3-derivatives. Although complicated at first sight, the layers in 4-Br hemihydrate are easy to analyse. Particularly striking are lines of rings parallel to the y axis. The first formula unit, together with the water molecule, forms annelated rings of graph set $R_5^3(10)$ (acceptors A are two bromides and one water; donors D are three water H and two H of an NH_3 group; the rings can be loosely described as "pentagons" excluding the H atoms); one such linear assemblage is seen in Fig. 20 obscuring the cell edge $0 \rightarrow b$. The second formula unit forms rings $R_4^2(8)$ (A : two bromides; D : four H from two NH_3 groups; overall form an approximate "square" excluding the H atoms) that are not linked directly to each other. The two

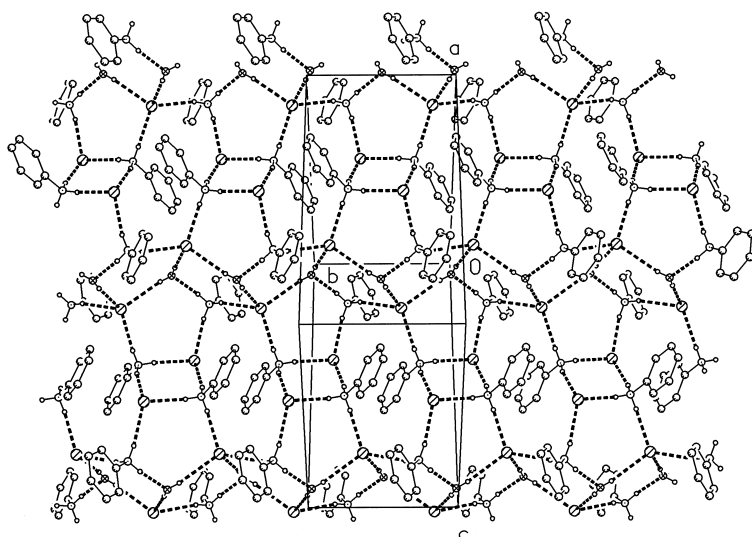


Fig. 20. One layer of 4-Br hemihydrate. For clarity, the aromatic rings are represented solely by their C atoms. Thick dashed lines represent classical H bonds. View direction parallel to the diagonal [101].

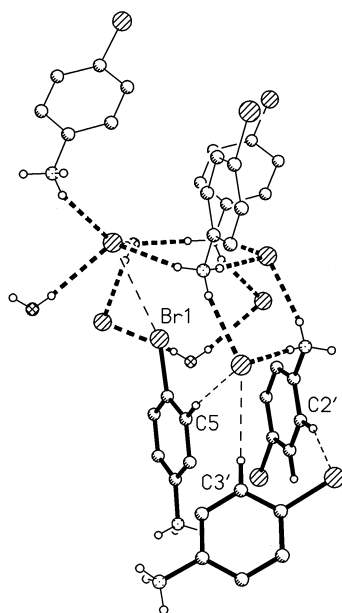


Fig. 21. The connection of neighbouring layers in 4-Br hemihydrate via $\text{Br}\cdots\text{Br}$ and $\text{C-H}\cdots\text{Br}$ interactions (thin dashed lines). The thick dashed lines represent classical hydrogen bonds of an upper layer, forming an appreciable hollow directed downwards. The atom Br1 can be seen projecting into this hollow from the lower layer. The same cation forms an H bond via H5 to Br2', which also accepts an H bond from H3'. Finally, the upper layer donates an H bond $\text{H2}'\cdots\text{Br1}'$ to the lower.

formula units are linked solely by the hydrogen bonds $\text{N-H02}\cdots\text{Br2}'$ and $\text{N-H03}'\cdots\text{Br}$, but these two additional interactions are sufficient to form further rings $\text{R}_5^3(10)$ (A and D qualitatively the same as above) and $\text{R}_6^4(16)$ (D: solely bromides, as for the 2- and 3-derivatives).

The necessarily two-dimensional nature of Fig. 20 does not make clear to what extent the layer is puckered. In particular, there are appreciable hollows formed about the $\text{R}_5^3(10)$ rings that connect the two formula units. The $\text{Br}\cdots\text{Br}$ interactions link the layers, with the Br1 atoms of the neighbouring layer projecting deep into the corresponding hollows. Around the edge of the hollows, the $\text{C-H}\cdots\text{Br}$ interactions also serve to link the layers (Fig. 21), which are related across those inversion centres whose x and z coordinates differ by integer values. The somewhat high layer repeat distance of $\frac{1}{2}(a+c) \approx 9.64 \text{ \AA}$ reflects the substantial intrinsic width of the puckered layers.

Conclusions

The large number of classical hydrogen bond donors (the positively charged NH_3 groups), together with the ability of halide anions to accept more than one hydrogen bond, are factors that promote the formation of extensive hydrophilic areas, generally layers, in the packing of haloanilinium halides. The halogen-halogen interactions, which are longer and presumably weaker than in *e.g.* 4-halopyridinium halides [1], play a subordinate role, as do non-classical hydrogen bonds of the form $\text{C-H}\cdots\text{X}$; these types of interaction can however play an important role in linking the hydrophilic layers. To increase the effect of the weaker interactions at the expense of classical hydrogen bonds, it will be necessary either to increase the number of halogen atoms on the ring or to block some of the hydrogen bond donors at the nitrogen atom. The structures of a number of dichloroanilinium chlorides are reported in the following paper.

Experimental Section

The free bases were obtained commercially and used without further purification. All the salts were prepared by one of two methods. *Method 1* (details as for 2-Cl): The free base (1.28 ml) was dissolved in 10 ml of ethanol and 1.01 ml of conc. aq. HCl was added slowly with stirring. A further 10 ml of ethanol was added and the solution stirred for 2 h. Then 25 ml of diethyl ether was added to precipitate the product, which was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 1.89 g (94.5%). Elemental analyses and NMR spectra accorded with expectation. Single crystals were obtained by liquid diffusion of diethyl ether into a solution in methanol / ethanol (2:1) at -15°C . This method was also used for: 2-Br (formed directly as single crystals), 2-I (recrystallized by diffusion of diethyl ether into a methanol solution at -15°C), 3-Cl (recrystallized by evaporation from methanol), 3-I (recrystallized from methanol / diethyl ether by evaporation), 4-Br (formed directly as single crystals, albeit as the hemihydrate). *Method 2* (for 3-Br): The free base (1.00 ml) was dissolved in 20 ml of dichloromethane and HBr gas passed until no further precipitation took place. The salt was filtered off, washed with petroleum ether and dried *in vacuo*. Yield 0.478 g (24%), not optimised. Single crystals were obtained by diffusion of diethyl ether into a solution in *n*-butanol.

Table 3. Crystal data.

Compound	2-Cl	2-Br	2-I	3-Cl	3-Br	3-I	4-Br · 1/2H ₂ O
Formula	C ₆ H ₇ Cl ₂ N	C ₆ H ₇ Br ₂ N	C ₆ H ₇ I ₂ N	C ₆ H ₇ Cl ₂ N	C ₆ H ₇ Br ₂ N	C ₆ H ₇ I ₂ N	C ₆ H ₈ Br ₂ NO _{0.5}
<i>M_r</i>	164.03	252.95	346.93	164.03	252.95	346.93	261.95
Habit	colourless plate	colourless tablet	pale brown block	colourless plate	colourless tablet	colourless lath	colourless prism
Crystal size (mm)	0.3 × 0.18 × 0.05	0.3 × 0.21 × 0.10	0.38 × 0.25 × 0.20	0.29 × 0.28 × 0.02	0.14 × 0.09 × 0.03	0.39 × 0.11 × 0.04	0.29 × 0.18 × 0.18
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>Pca</i> 2 ₁	<i>Pca</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> (-1)	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>n</i>
Cell constants:							
<i>a</i> (Å)	15.517(2)	15.9599(12)	10.0141(8)	4.3982(12)	4.4166(8)	10.7975(14)	13.7450(14)
<i>b</i> (Å)	5.3248(6)	5.5067(4)	9.7222(8)	5.9208(14)	6.0983(10)	6.8019(8)	7.8503(8)
<i>c</i> (Å)	8.6979(10)	8.9856(8)	9.5408(8)	28.696(7)	14.977(2)	12.5650(16)	16.0352(14)
α (°)	90	90	90	90	98.315(5)	90	90
β (°)	90	90	98.547(2)	92.644(9)	91.792(5)	101.704(5)	99.694(3)
γ (°)	90	90	90	90	101.524(5)	90	90
<i>V</i> (Å ³)	718.67(15)	789.71(11)	918.57(13)	746.5(3)	390.36(11)	903.6(2)	1705.5(3)
<i>Z</i>	4	4	4	4	2	4	8
<i>D_x</i> (Mg m ⁻³)	1.516	2.127	2.509	1.460	2.152	2.550	2.040
μ (mm ⁻¹)	0.81	10.2	6.77	0.78	10.3	6.89	9.43
<i>F</i> (000)	336	480	624	336	240	624	1000
<i>T</i> (°C)	-130	-130	-130	-130	-130	-130	-130
2θ _{max}	60	60	61	56.5	60	61	60
Abs. correction	SADABS	SADABS	SADABS	none	SADABS	face indexed	SADABS
Transmissions	0.69 - 0.98	0.23 - 0.49	0.60 - 0.93		0.60 - 0.98	0.44 - 0.77	0.53 - 0.86
Measured refls	8295	12499	10880	5351	7480	10301	29280
Independent refls	2099	2302	2801	1840	2273	2957	4974
<i>R</i> _{int}	0.042	0.050	0.035	0.073	0.047	0.059	0.052
Parameters	94	94	94	94	94	109	204
Restraints	1	1	0	3	3	30	16
<i>wR</i> (<i>F</i> ² , all refl.)	0.053	0.040	0.054	0.077	0.060	0.046	0.054
<i>R</i> (<i>F</i> , > 4σ(<i>F</i>))	0.024	0.019	0.024	0.037	0.027	0.025	0.026
<i>S</i>	1.01	1.01	1.12	0.95	0.98	0.93	0.93
Max. Δρ (e Å ⁻³)	0.30	0.34	1.15	0.54	1.03	0.95	0.78

X-ray structure determinations

Crystals were mounted in inert oil on glass fibres. Data were measured using Mo-*K*_α radiation on a Bruker SMART 1000 CCD diffractometer. The structures were refined anisotropically on *F*² using all reflections (program SHELXL-97 [10]). The acidic H atoms were generally located and refined freely; other H atoms were included using a riding model. Crystal data and numerical details of refinement are given in Table 3.

Special features of refinement. 2-Cl, Flack parameter refined to 0.03(6). 2-Br, Flack parameter refined to 0.040(12). 3-Cl and 3-Br, N-H bond lengths were restrained equal. 3-I, NH₃ groups were refined as idealised rigid groups; the hydrogen atoms at N' are disordered over two positions (distinguished in the Tables by one or two primes). Neighbouring atom *U* components were

restrained equal for light atoms (C,N) with the command DELU. 4-Br · 1/2H₂O, N-H bond lengths were restrained equal, as were O-H.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers 169439 (2-Cl), 169440 (2-Br), 169441 (2-I), 169442 (3-Cl), 169443 (3-Br), 169444 (3-I), 169445 (4-Br · 1/2H₂O). Copies may be requested free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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