# Secondary Bonding Interactions in Some Di- and Trihaloanilinium Halides

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Six solvent-free structures of di- and trihaloanilinium halides are presented. All involve clearly defined hydrophilic regions built up from classical hydrogen bonding systems. The 2,4-dibromo-, 2,6-dichloro-, 2,4,6-trichloro- and 2,4,6-tribromoanilinium derivatives form ribbon structures involving annelated  $R_4^2(8)$  rings with NH<sub>2</sub> donors (two hydrogens from the positively charged NH<sub>3</sub> groups) and halide acceptors. The 2,5-dibromo- and 2,4,5-trichloro derivatives form layers with two types of ring,  $R_4^2(8)$  and  $R_8^4(16)$ . All structures also involve other secondary interactions (C-H...X hydrogen bonds and/or X...X contacts, X = halogen), some of which link the ribbons or layers into a second or third dimension. The shortest X...X contacts generally involve the anions. In the 2,4-dibromo, 2,4,6-trichloro and tribromo derivatives, somewhat more extensive halogen aggregates (triangles, angled  $X_3$  or  $X_4$  chains) are formed between neutral halogens. In two appendices, the packing patterns of (I) the disordered structure 3,4,5-trichloroanilinium chloride and (II) the known structures of unsubstituted anilinium halides are briefly presented.

Key words: Anilinium, Halides, Hydrogen Bonds, Halogen-Halogen Contacts

### Introduction

In previous papers [1, 2] we described the roles of classical hydrogen bonds and other secondary contacts in the crystal packing of various monohalo- and dichloroanilinium halides. Except for 3-iodoanilinium iodide, the classical hydrogen bonds (from the positively charged NH<sub>3</sub> groups to the halide ions) formed clearly defined polar regions. The extended structures of these regions were of three basic types: corrugated ribbon (ladder) structures with successive rings of type  $R_4^2(8)$ , with neighbouring ribbons all arranged parallel to form a layer; layer structures with  $R_6^3(12)$  rings; and layer structures with  $R_4^2(8)$  and  $R_8^4(16)$  rings. In the hierarchy of secondary interactions, non-classical hydrogen bonds of the form C-H... $X^-$  (X = general halogen throughout) and halogen-halogen interactions generally either played a supporting role within the polar regions, or connected neighbouring polar regions. In the pure layer structures, the hydrophobic regions of neighbouring layers were appreciably interdigitated, but those of the ribbon structures were not.

The generally accepted polarisation pattern for a C-X bond is that there is a positive region in the extension of the C-X bond beyond X, and a negative region at X perpendicular to the bond. Thus the shortest halogen-halogen contacts  $C-X...X^-$  are generally linear at the central X atom [3], and contacts  $C-X...X^-$ C are of "type II" [4] (one C-X...X angle about 90°, one about 180°) if a significant attractive interaction is involved. The "type I" interactions (C-X...X angles approximately equal) are attributed to non-specific features such as crystal packing symmetry and atom anisotropy; however, the objection could be raised that this does not satisfactorily account for their frequency.

Here we extend our studies to dibromo- and trihaloanilinium halides, and also include a dichloro derivative that we were previously unable to crystallise. All six compounds were obtained as solventfree crystals.

#### **Results and Discussion**

### Preliminary Remarks

Abbreviations for the compound names conform to the principle 2,4-Br = 2,4-dibromoanilinium bromide, *etc.* The ring numbering is standard (the nitrogenbearing carbon is C1). The halogens of the cation are numbered beginning with 1 at the lowest-numbered

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Fig. 1. Structures of the formula unit of all six compounds: (a) **2,4-Br**; (b) **2,5-Br**; (c) **2,6-Cl**; (d) **2,4,5-Cl**; (e) **2,4,6-Cl**; (f) **2,4,6-Br**. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

carbon, with the highest number for the halide anion. Hydrogens bonded to carbon are given the same number as their parent atom; those of the  $NH_3$  groups are numbered 01 to 03.

The compound **2,6-Cl** was previously only obtained as a 1:1 methanol solvate [2].

All compounds crystallise without imposed symmetry and with one formula unit in the asymmetric unit. None are isotypic to any other structures in the series. Bond lengths and angles may be regarded as normal. The formula units are displayed as thermal ellipsoid diagrams in Fig. 1a-f. The secondary contacts are summarised for all compounds in Table 1 (classical and non-classical hydrogen bonds) and Table 2 (halogen-halogen contacts); our first paper [1] comments on the values used for van der Waals radii and explains the calculation of normalised hydrogen bond distances. Note that the "borderline cases" in the Tables are classified thus on the basis of longer contact distances, which may not be a completely objective criterion; the inverse correlation of length with strength may not apply strictly to such interactions.

As previously observed, all compounds form classical hydrogen bonds N- H...X<sup>-</sup> from all three hydrogens of the  $NH_3^+$  groups, and thus each halide accepts three hydrogen bonds. The extended structure in each case presents clearly defined hydrophilic regions.

# **Ribbon Structures**

Four of the structures reported here crystallise in the ribbon (corrugated ladder) structure. The compound **2,4-Br** (Fig. 2) forms ribbons parallel to the *x* axis. Within the ribbons, the approximately linear halogen-halogen contact Br1...Br3, 3.6357(3) Å, connects the



E. López-Duplá <i>et al.</i> Secondary Bonding Interactions in Some Di- and Trihaloanilinium	Hali	ide
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Compound	H bond	D-H	HA	DA	D-HA	Operator of A
2,4-Br	N-H01Br3	1.01	2.28	3.268	165	
	N-H02Br3	1.01	2.28	3.276	167	1 + x, y, z
	N-H03Br3	1.01	2.33	3.299	160	1 - x, -y, 1 - z
	C5-H5Br3	1.08	3.04	3.704	120	1 - x, 1 - y, 1 - z
	C6-H6Br3	1.08	2.87	3.631	128	1-x, 1-y, 1-z
	C3-H3Br2	1.08	3.07	4.057	152	-x, 1-y, -z
	C5-H5Br1	1.08	3.28	4.022	127	x, 1+y, z
2,5-Br	N-H01Br3	1.01	2.31	3.313	170	x, 1/2 - y, 1/2 + z t
	N-H02Br3	1.01	2.29	3.257	160	I
	N-H03Br3	1.01	2.32	3.262	155	2-x, 1/2+y, 1/2-z
	C3-H3Br2	1.08	3.10	3.786	129	$x, \frac{11}{2} - y, \frac{1}{2} - z$
	C4-H4Br3	1.08	2.86	3.917	165	1 - x, 1 - y, -z
	C6-H6Br3	1.08	2.96	3.805	135	x, 1/2 - y, 1/2 + z
2,6-Cl	N-H01Cl3	1.01	2.12	3.128	178	-x, 1-y, 1-z
	N-H02Cl3	1.01	2.12	3.122	169	
	N-H03Cl3	1.01	2.27	3.203	153	1 - x, 1 - y, 1 - z
	C3-H3Cl3	1.08	2.64	3.512	137	-x, -1/2 + y, 11/2 - z
	C3-H3Cl2	1.08	3.03	3.954	143	-1+x, 1/2-y, 1/2+z
2,4,5-Cl	N-H01Cl4	1.01	2.07	3.056	162	x, 1/2 - y, 1/2 + z
	N-H02Cl4	1.01	2.16	3.083	151	
	N-H03Cl4	1.01	2.05	3.060	173	-x, -y, -z
	C6-H6Cl4	1.08	2.93	3.336	103	-x, -1/2 + y, 1/2 - z
	C6-H6Cl4	1.08	2.99	3.754	128	-x, -y, -z
	C6-H6Cl1	1.08	2.92	3.961	161	x, -1 + y, z
	<i>C3-H3Cl3</i>	1.08	2.90	3.938	161	x, 1+y, z
2,4,6-Cl	N-H01Cl4	1.01	2.13	3.134	174	1 - x, 1 - y, -z
	N-H02Cl4	1.01	2.24	3.163	151	
	N-H03Cl4	1.01	2.12	3.114	170	-1+x,y,z
	C5-H5Cl4	1.08	2.51	3.571	167	-1 + x, -1 + y, z
0.4 C D	C3-H3CII	1.08	2.84	3.856	157	1-x,-y,1-z
2,4,6-Br	N-H01Br4	1.01	2.33	3.336	173	1 - x, -y, 1 - z
	N-H02Br4	1.01	2.49	3.405	150	1+x,y,z
, anh	N-H03Br4	1.01	2.31	3.307	169	1 / .
Anilinium-Cl <sup>o</sup>	N-H01Cl	1.01	2.14	3.145	177	x, -y, 1/2 + z
	N-H02Cl	1.01	2.08	3.087	173	1 1/
	N-H03Cl	1.01	2.11	3.102	167	x, 1-y, 1/2+z
	$C_3$ -H $_5$ $C_l$	1.08	2.90	3./18	133	-1/2 + x, 1/2 + y, z
Anilinium Dube	CO-HOCl	1.08	2.90	3./30	154	$x, -y, \frac{1}{2} + z$
Anilinium-Br <sup>b,c</sup>	N-HUIBr	1.03	2.54	3.322	159	1 - x, 2 - y, 1 - z
	IN-HU2Bf	1.04	2.29	3.322 2.244	1/0	1 1 1
	N-HU3Br	1.04	2.36	5.544	158	1 - x, 1 - y, 1 - z
	C2-H2Br	1.09	3.13	3.981	135	1 - x, 1 - y, 1 - z

Table 1. Normalised hydrogen bond dimensions  $(\text{\AA}, \circ)^a$ .

<sup>a</sup> Several borderline cases (in italics) are included for completeness. D = donor, A = acceptor; <sup>b</sup> see Appendix II; <sup>c</sup> data are calculated or taken directly from ref. [8] and are not normalised (neutron diffraction data).

opposite uprights of the "ladder", presumably contributing to its cohesion. Such contacts are a common feature of haloanilinium halides when there are halogen substituents *ortho* to the NH<sub>3</sub><sup>+</sup> group, although these are of necessity relatively close to a halide ion. Neighbouring ribbons are related by a **b** translation to form a layer parallel to the *xy* plane *via* the bifurcated hydrogen bond (H5,H6)...Br3, which forms five-membered rings. The polar areas are at  $z \approx 0.5$ , 1.5, *etc.*, and the layer repeat is thus the **c** translation. The most significant contact between ribbons is however the type I interaction Br2...Br2, 3.6106(5) Å, between layers related by the **c** translation of 11.14 Å (Fig. 3). The next longest bromine-bromine contact, also connecting the layers, is Br1...Br2, 3.8879(4) Å, which is approximately type II, but is rather longer than the double van der Waals radius; the combination of these contacts gives angled  $Br_4$  chains, which link with the anions (as described above) to form an extensive region of bromine atoms. The contact H5...Br1, 3.28 Å, could be considered as the second component of a three-centre hydrogen bond from H5 but also is probably too long. Nevertheless, we should stress that a clear distance limit for significance can never be defined for secondary interactions.

The compound **2,6-Cl** forms ribbons parallel to the *x* axis (Fig. 4), in which the short linear contact Cl1...Cl3, 3.3533(4) Å, connects the opposite uprights

Compound	Contact	XX Å	$ heta_1(^\circ)^{b}$	$ heta_2(^\circ)^{\mathrm{b}}$	Operator	Table 2. Halogen-halo
2,4-Br	C2-Br1Br3	3.6357(3)	156.96(6)		-x, -y, 1-z	tuets .
	C4-Br2Br2-C4	3.6106(5)	145.23(6)	c	-x, 2-y, -z	
	C2-Br1Br2-C4	3.8879(4)	97.34(6)	142.56(6)	-x, 1-y, -z	<sup>a</sup> Several borderline cas
	C2-Br1Br3	3.9734(3)	80.76(6)			ics) are included for con
2,5-Br	C2-Br1Br3	3.5755(3)	162.13(7)		2 - x, 1 - y, -z	<sup>b</sup> the $\theta$ angles are defined as the second secon
	C5-Br2Br3	3.5400(3)	160.02(7)		$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	XX and XX-C [4].
	C2-Br1Br1-C2	3.8344(5)	127.73(7)	c	2 - x, 1 - y, -z	second halogen is an a
	C2-Br1Br2-C5	3.9334(4)	75.08(7)	102.99(6)	1 - x, 1 - y, -z	not defined, but the she
2,6-Cl	C2-Cl1Cl3	3.3533(4)	161.43(4)		-1 + x, y, z	interactions have $\theta_1 \approx$
	C2-Cl1Cl2-C6	3.4353(4)	106.19(4)	153.88(4)	$-1+x, \frac{1}{2}-y, \frac{1}{2}+z$	$^{c}$ $\theta_{1}$ and $\theta_{2}$ are equal b
	C2-Cl1Cl3	3.6206(4)	97.72(4)			try.
	C6-Cl2Cl3	3.6463(4)	109.33(4)	106.19(4)	1 - x, 1 - y, 1 - z	
2,4,5-Cl	C2-Cl1Cl4	3.4143(7)	158.24(6)		-x, 1-y, -z	
	C4-Cl2Cl3-C5	3.3791(8)	165.45(8)	138.41(7)	$1 - x, \frac{1}{2} + y, \frac{11}{2} - z$	
	<i>Cl4Cl4</i>	3.6588(9)			-x, 1-y, -z	
2,4,6-Cl	C6-Cl3Cl4	3.3029(4)	166.53(4)		-x, 1-y, -z	
	C6-Cl3Cl3-C6	3.4833(6)	79.91(4)	c	-x, -y, -z	
	C4-Cl2Cl2-C4	3.5353(6)	167.25(5)	c	-x, 1-y, 1-z	
	C2-Cl1Cl4	3.5941(4)	108.90(4)			
	C2-Cl1Cl2-C4	3.6059(5)	108.20(4)	130.13(4)	x, 1 + y, z	
	C2-Cl1Cl2-C4	3.6757(5)	85.32(4)	107.81(4)	-x, -y, 1-z	
	C6-Cl3Cl4	3.6759(4)	94.52(4)		1 - x, 1 - y, -z	
2,4,6-Br	C2-Br1Br4	3.3046(4)	169.15(8)		-x, -y, 1-z	
	C6-Br3Br4	3.3147(4)	167.79(8)		2-x, 1-y, 1-z	
	C2-Br1Br2-C4	3.7959(4)	69.65(8)	112.46(8)	1 - x, -y, -z	
	C4-Br2Br2-C4	3.8184(6)	72.14(8)	с	1 - x, 1 - y, -z	
	C2-Br1Br4	3 8358(5)	90.83(8)		$1 - x_1 - y_1 - z_1$	



ses (in italnpleteness; ined as C-Where the nion,  $\theta_2$  is ortest such 180° [3]; by symme-



Fig. 2. Packing diagram of 2,4-Br viewed parallel to the z axis. Classical hydrogen bonds are shown as thick and Br...Br contacts as thin dashed lines; non-classical hydrogen bonds are shown as thin unbroken lines (note the associated formation of five-membered rings). Hydrogens H3, which are not involved in secondary interactions, are omitted.

of the ladder. The packing represents a new substructure type, insofar as the ribbons are not connected by translation to form layers (for this reason only one rib-



Fig. 3. Packing diagram of 2,4-Br viewed perpendicular to the yz plane. The contacts Br1...Br2 and Br2...Br2 are shown as thick dashed lines, all other secondary interactions as thin dashed lines. Hydrogen atoms are omitted.

bon is shown in Fig. 4). Instead, they form a threedimensional, pseudo-centred arrangement, Fig. 5 (the view parallel to the ribbon direction), in which the hydrophilic areas are at  $y \approx 0$ ,  $z \approx 0$  and  $y \approx 0.5$ ,  $z \approx 0.5$ , etc.; the ribbons are connected via the type I interaction Cl1...Cl2, 3.4353(4) Å, and the short C-H...Cl hydrogen bond C3-H3...Cl3.



Fig. 4. Packing diagram of 2,6-Cl; view of one ribbon. The view direction is approximately perpendicular to the *xy* plane. Classical hydrogen bonds are shown as thick dashed lines, Cl. . . Cl contacts as thin double dashed lines.



Fig. 5. Packing diagram of 2,6-Cl viewed parallel to the *x* axis. The interactions H3...Cl3 and Cl1...Cl2 are emphasised with thick dashed bonds, other secondary interactions are shown as thin dashed bonds. H atoms not involved in hydrogen bonding are omitted.

It is noteworthy that, if the ribbon structure of solvent-free **2,6-Cl** is taken, and two methanol molecules are inserted into every second  $R_4^2(8)$  ring (making it  $R_6^4(12)$ ), then the ribbon structure of the methanol solvate [2] is generated – albeit the ribbon packings are quite different.

The trihalogen derivative **2,4,6-Cl** also forms a ribbon structure parallel to the *x* axis (Fig. 6), with neighbouring ribbons lying in a layer parallel to the *xz* plane; again, there is a contact from an *ortho*-chlorine to the chloride of the opposite upright, Cl3...Cl4 3.3029(4) Å. In contrast to previous "layered ribbon" structures, there are no short contacts between adjacent ribbons in the layer. The hydrophilic region is  $z \approx 0$ , and the layers are related by the **c** translation



Fig. 6. Packing diagram of **2,4,6-Cl** viewed parallel to the *y* axis. Classical hydrogen bonds are shown as thick dashed lines, Cl...Cl contacts as thin dashed lines.



Fig. 7. Packing diagram of **2,4,6-Cl** viewed parallel to the *x* axis. The hydrogen bond H5...Cl4, the contact Cl3...Cl3 and the chlorine triangles (see text) are drawn with thick dashed bonds for emphasis. Secondary interactions in the ribbons (*cf.* Fig. 6) are drawn as thin dashed lines. The longer contact H3...Cl1 is omitted for clarity.

of 11.55 Å. The view parallel to the ribbon direction, Fig. 7, shows that the ribbons are connected by the short hydrogen bond C5-H5...Cl4 with H...Cl only 2.51 Å, the type I interaction Cl3...Cl3, 3.4833(6) Å, and, more strikingly, an approximately equilateral trangle of type I interactions, Cl1...Cl2 3.6059(5) and 3.6757(5) and Cl2...Cl2 3.5353(6) Å (angles 58– 62°). Although these distances lie above the double van der Waals radius, the triangular assemblies represent a significant feature of the packing (*cf.* the quadrilaterals of chlorine atoms in **3,5-Cl** 1/4-hydrate [2]).

The compound **2,4,6-Br** is not isostructural to its chlorine analogue despite crystallising in the same space group with closely similar axis lengths. It



Fig. 8. Packing diagram of 2,4,6-Br viewed parallel to the *z* axis. Classical hydrogen bonds and Br... Br contacts are shown as thick dashed lines.



Fig. 9. Packing diagram of **2,4,6-Br** viewed parallel to the x axis. The contacts Br1...Br2 and Br2...Br2 are drawn with thick dashed bonds for emphasis. Other secondary interactions (*cf.* Fig. 8) are drawn as thin dashed lines. All hydrogen atoms are omitted for clarity.

too forms a ribbon structure parallel to the *x* axis (Fig. 8). There are two very short bromine-bromine contacts, Br1...Br4, 3.3046 Å (within the ribbons) and Br3...Br4, 3.3147(4) Å, connecting the ribbons to form layers parallel to the *xy* plane. The layers lie at  $z \approx 0.5$ , 1.5, *etc.*, and are thus related by the **c** translation of 11.99 Å. The layers are connected (Fig. 9) by Br1...Br2 3.7959(4) Å and Br2...Br2 3.8184(6) Å (the latter type II and the former unclassifiable), and these interactions lead for the first time in this series to some interdigitation between the layers of a ribbon-type structure. There are no significant H...Br interactions and the next longest Br...Br not involving the anion is 3.93 Å.

#### Layer structures

The compound **2,5-Br** crystallises with the  $R_4^2(8)/R_8^4(16)$  layer structure (Fig. 10). The hydrophilic



Fig. 10. Packing diagram of 2,5-Br viewed perpendicular to the yz plane. Classical hydrogen bonds are shown as thick dashed lines, Br1...Br3 contacts as double dashed lines and Br1...Br1 contacts as single dashed lines. Ring hydrogens are omitted for clarity.



Fig. 11. Packing diagram of 2,5-Br viewed parallel to the *z* axis. The deeply indented nature of the layers (seen here from the side) is made clear by the use of open bonds for the lower layer. The contacts Br2...Br3 and H4...Br3 are drawn with thick dashed bonds for emphasis. Other secondary interactions (*cf.* Fig. 10) are drawn as thin dashed lines. Hydrogen atoms H3 and H6 are omitted for clarity.

regions are parallel to the *yz* plane at  $x \approx 0,1$ , *etc.*, and are thus separated by the **a** translation of 10.53 Å. Within the layer, the bromine-bromine contacts Br1...Br3, 3.5755(3) Å and Br1...Br1, a type I contact of 3.8344(5) Å, are observed; the contacts



Fig. 12. Packing diagram of **2,4,5-Cl** viewed perpendicular to the *yz* plane. Classical hydrogen bonds are shown as thick dashed lines, Cl. . . Cl contacts as single dashed lines. Ring hydrogens are omitted for clarity.



Fig. 13. Packing diagram of **2,4,5-Cl** viewed approximately parallel to the *y* axis. All secondary interactions are drawn as thick dashed lines. Note the Cl. . . Cl interactions in the region  $x \approx 0.5$ . Ring hydrogen atoms are omitted for clarity.

H3...Br2 and H6...Br3 (the latter an *ortho* type) may provide additional stability but are quite long. The layers are far from planar and the crests of one project into the troughs of the next. In this way the otherwise one-sided coordination of the anions is completed by the contacts Br2...Br3, 3.5400(3) Å and H4...Br3, 2.86 Å (Fig. 11).

Finally, the compound **2,4,5-Cl** also crystallises with the  $R_4^2(8)/R_8^4(16)$  layer structure (Fig. 12). The

hydrophilic regions are parallel to the *yz* plane at  $x \approx 0,1, etc.$ , and are thus separated by the **a** translation of 15.26 Å. Within the layer, the short chlorine-chlorine contact Cl1...Cl4, 3.4143(7) Å is observed. Adjacent layers are linked solely by the type I contact Cl2...Cl3, 3.3791(8) Å (Fig. 13), and there is no interdigitation of the rings from adjacent layers, consistent with the long *x* axis. There are no H...Cl contacts < 2.9 Å.

# Conclusions

Even in more highly substituted haloanilinium species, the effects of the classical hydrogen bonds dominate; there are only three basic structural patterns (one ribbon type, with minor variations, and two layer types) for the whole series of 16 solvent-free haloanilinium halides, except for the 3-iodo derivative, which does not form a layer structure at all. All structures display one or more halogen-halogen contacts involving the anion, and these tend to be the shortest such contacts, as would be expected for a charge-assisted system. Only in the 2,4-dibromo, 2,4,6-trichloro and -tribromo derivatives are more extensive aggregates (triangles or angled X<sub>3</sub> or X<sub>4</sub> chains) of uncharged halogens formed. As would be expected, the increased extent of halogen substitution tends to increase the number of halogen-halogen interactions at the expense of C-H... $X^-$  hydrogen bonds.

### Appendix I: Structure of 3,4,5-Cl

X-ray data were recorded for the compound 3,4,5-Cl, which crystallises in the space group  $Pna2_1$  with a = 7.3135(4), b = 29.5929(16), c = 4.0777(2) Å, Z = 4 at -140 °C. The structure could be solved, but the hydrogens of the  $NH_3^+$  group are disordered and the refinement could not be satisfactorily completed. Hydrophilic layers are formed at  $y \approx 0.25, 0.75, etc.$ , in which the nitrogen atom is approximately equidistant from four chlorides rather than the usual three. Similar effects were noted for the disordered hightemperature forms of anilinium bromide [5] and iodide [6], but, in contrast to those compounds, there was no phase transition on cooling 3,4,5-Cl. Additional short N...Cl<sup>-</sup> distances apparently not connected with hydrogen bonding were also observed by us in previous ribbon structures [1,2] (but did not lead to disorder of the NH<sub>3</sub><sup>+</sup> hydrogens), e.g. 3.28 Å in **3,5-Cl**, where adjacent ribbons are extremely close. It is possible, though we rejected this interpretation at the time, that the short contacts are associated with very long and angled components of three-centre hydrogen bonds. The ribbon structures presented here have no additional  $N...Cl^-$  contacts < 4.5 Å, presumably because of the effects, whether negative (steric) or positive (additional secondary contacts) of the additional substituents.

# Appendix II: Structures of Unsubstituted Anilinium Halides

The structure of anilinium chloride was determined in 1949 [7]; although, as was not unusual at the time, the hydrogen atoms were not located, the packing was correctly analysed in terms of hydrogen bonding, and the layer structure with  $R_6^3(12)$  rings was correctly identified (although not using this notation). We have redetermined the structure more precisely with modern instrumentation; the formula unit is shown in Fig. 14 and the packing in Fig. 15. Adjacent layers are related by the *C*-centring operator and are thus separated by  $c/2 \approx 4.2$  Å. This distance is so short because the *z* axis is polar; the aromatic rings from a given layer are followed directly by the hydrophilic region of the next layer rather than interdigitating or forming other contacts with its rings.

The low-temperature phase of anilinium bromide was investigated by neutron diffraction [8] and is ordered, although twinned. The space group is  $P2_1/a$ , with cell constants 16.760, 6.005, 6.809 Å, 90, 91.32, 90°. Hydrogen bonds were correctly identified, but the extended packing was not presented. For completeness, we present here the ribbon-type packing (Fig. 16), in which the ribbons are parallel to the *y* axis and form hydrophilic layers parallel to the *yz* plane at  $x \approx 0, 0.5, etc.$ , layer separation *ca.* 8.4 Å. There is an additional short N...Br<sup>-</sup> contact of 3.57 Å between adjacent ribbons.



Fig. 14. Formula unit of anilinium chloride in the crystal. Ellipsoids represent 50% probability levels. See Appendix II.



Fig. 15. Packing diagram of anilinium chloride viewed approximately perpendicular to the *yz* plane. Hydrogen bonds are drawn as thick dashed lines. Ring hydrogen atoms are omitted for clarity.



Fig. 16. Packing diagram of anilinium bromide [8] viewed approximately perpendicular to the *xy* plane. Hydrogen bonds are drawn as thick dashed lines. Ring hydrogen atoms are omitted for clarity.

The low-temperature form of anilinium iodide [6] is isostructural to the bromide and is therefore not further analysed here.

### **Experimental Section**

The free bases were obtained commercially and used without further purification. All the salts were prepared by one of the two methods described previously [1]. Elemental analyses and NMR spectra accorded with expectation. Recrystallisation: **2,4-** and **2,5-Br**, ethanol/diisopropyl

Table 3. Crystal d	ata.						
Compound	2,4-Br	2,5-Br	2,6-CI	2,4,5-CI	2,4,6-CI	2,4,6-Br	Anilinium chloride
Formula	$C_6H_6Br_3N$	$C_6H_6Br_3N$	C <sub>6</sub> H <sub>6</sub> Cl <sub>3</sub> N	C <sub>6</sub> H <sub>5</sub> Cl <sub>4</sub> N	C <sub>6</sub> H <sub>5</sub> Cl <sub>4</sub> N	$C_6H_5Br_4N$	C <sub>6</sub> H <sub>8</sub> CIN
$M_r$	331.85	331.85	198.47	232.91	232.91	410.75	129.58
Habit	colourless tablet	colourless tablet	colourless lath	colourless plate	colourless tablet	colourless tablet	colourless plate
Crystal size (mm)	$0.46 \times 0.15 \times 0.09$	0.25  imes 0.24  imes 0.12	0.5 imes 0.14 imes 0.08	0.26  imes 0.26  imes 0.02	0.5 imes 0.35 imes 0.10	0.09  imes 0.07  imes 0.04	0.17 imes 0.15 imes 0.04
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	P(-1)	$P2_1/c$	$P2_1/c$	$P2_1/c$	P(-1)	P(-1)	Cc
Cell constants:							
a (Å)	5.2286(4)	10.5309(6)	5.0302(4)	15.2656(18)	4.9741(3)	5.2667(6)	15.735(3)
b (Å)	8.2022(4)	8.3864(6)	14.2664(12)	7.6615(9)	7.9478(4)	8.0197(8)	5.3094(12)
<i>c</i> (Å)	11.1401(6)	10.5721(6)	11.2045(11)	7.5829(9)	11.5476(6)	11.9918(12)	8.397(2)
$\alpha$ (°)	81.585(4)	90	90	60	81.845(3)	95.352(3)	90
β (°)	85.186(4)	108.167(3)	100.323(4)	101.103(2)	82.413(3)	95.826(3)	101.029(6)
χ(°)	73.347(4)	90	90	90	82.162(3)	103.428(3)	90
$V(\text{\AA}^3)$	452.34(5)	887.15(10)	791.05(12)	870.28(18)	444.71(4)	486.52(9)	688.6(3)
Z	2	4	4	4	2	2	4
$D_{\rm X} ({\rm Mg}~{\rm m}^{-3})$	2.436	2.485	1.666	1.778	1.739	2.804	1.250
$\mu \ (\mathrm{mm}^{-1})$	13.3	13.6	1.08	1.29	1.26	16.5	0.45
F(000)	308	616	400	464	232	376	272
T (°C)	-140	-140	-140	-140	-140	-140	-140
$2\theta_{\rm max}$	09	09	09	60	09	60	09
Abs. correction	Face indexed	SADABS	SADABS	SADABS	SADABS	SADABS	SADABS
Transmissions	0.066-0.37	0.28-0.49	0.71-0.93	0.77-0.93	0.58-0.93	0.40- 0.65	0.74-0.96
No. of refl.:							
measured	9531	17402	16172	15611	9020	9822	3953
indep.	2639	2586	2297	2553	2574	2836	1883
$R_{ m int}$	0.035	0.035	0.027	0.042	0.021	0.029	0.024
Parameters	103	104	103	112	112	112	85
Restraints	0	3	0	0	0	0	2
$wR(F^2, all refl.)$	0.048	0.056	0.058	0.090	0.064	0.050	0.070
$R(F,>4\sigma(F))$	0.019	0.021	0.020	0.035	0.023	0.022	0.030
S	1.05	1.06	1.08	1.05	1.05	0.99	1.00
max. $\Delta  ho$ (e Å <sup>-3</sup> )	0.66	0.74	0.39	0.60	0.43	0.96	0.27

ether; **2,6-Cl**, ethanol/petroleum ether; anilinium chloride, *n*-butanol/diethyl ether; others, ethanol/diethyl ether.

#### X-ray structure determinations

Crystals were mounted in inert oil on glass fibres. Data were measured using Mo- $K_{\alpha}$  radiation on a Bruker SMART 1000 CCD diffractometer. Absorption corrections were performed with the program SADABS (exception: **2,4-Br** by face-indexing). The structures were refined anisotropically on  $F^2$  using all reflections (program SHELXL-97 [9]). The acidic H atoms were located and refined freely (exception: **2,5-Br** with N-H distances restrained equal); other H atoms were included using a riding model. The Flack parameter for

anilinium chloride refined to 0.02(7). Crystal data and numerical details of refinement are given in Table 3.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-192071 (**2,4-Br**), 192072 (**2,5-Br**), 192073 (**2,6-Cl**), 192074 (**2,4,5-Cl**), 192075 (**2,4,6-Cl**), 192076 (**2,4,6-Br**), 196349 (anilinium chloride). 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).

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