

Secondary Bonding Interactions in Some Dichloroanilinium Chlorides

Lilian Gray and Peter G. Jones

Institut für Anorganische und Analytische Chemie, Technical University of Braunschweig,
Postfach 3329, 38023 Braunschweig, Germany

Reprint requests to Prof. Dr. P. G. Jones. E-mail: p.jones@tu-bs.de

Z. Naturforsch. 57 b, 73–82 (2002); received October 1, 2001

Anilinium, Halides, Hydrogen Bonds

Of the six structures presented here, five involve clearly defined hydrophilic layers built up from classical hydrogen bonding systems. Of three solvent-free structures, 2,4- and 3,5-dichloroanilinium chlorides both form ribbon structures involving annelated $R_4^2(8)$ rings with NH_2 donors (two hydrogen atoms from the positively charged NH_3 groups) and chloride acceptors. The ribbons are linked by weaker interactions to form layers. 2,5-Dichloroanilinium chloride forms a layer structure directly, with rings $R_6^3(12)$ exactly analogous to those previously observed in 2-chloroanilinium chloride. 2,6-Dichloroanilinium chloride methanol solvate forms a different type of ribbon structure, with alternating $R_4^2(8)$ and $R_6^4(12)$ rings; the latter involve two chlorides, two NH_2 groups and two methanols. These ribbons too are linked to form layers. 2,3-Dichloroanilinium chloride hydrate forms layers with two types of ring $R_5^3(10)$; one involves two NH_2 , two chlorides and the OH part of a water, whereas in the other, an NH_2 is replaced by OH_2 . In all these structures the aromatic groups project approximately perpendicular to the layers to form hydrophobic regions; for all except 3,5-dichloroanilinium chloride, neighbouring layers are linked by weaker interactions such as $C-H \cdots Cl$ hydrogen bonds or $Cl \cdots Cl$ contacts. The final structure, 3,5-dichloroanilinium chloride $1/4$ -hydrate, is completely different; it involves two types of columns, one built up from quadrilaterals of $Cl \cdots Cl$ contacts between cations and the other consisting of "nanotubes" of NH_3 groups and chloride anions linked by two- and three-centre hydrogen bonds. The columns are in turn linked by cation-anion $Cl \cdots Cl$ interactions.

Introduction

In the preceding paper [1] we described the roles of hydrogen bonds and halogen-halogen contacts in the crystal packing of various (mono)haloanilinium halides. Except for 3-iodoanilinium iodide, the classical hydrogen bonds (from the positively charged NH_3 groups to the halide ions) formed clearly defined polar regions, thereby leaving only a minor role for any halogen-halogen interactions. We expected to be able to redress this imbalance by using systems with more halogen substituents. Here we present the structures of some dichloroanilinium chlorides.

Results and Discussion

Preliminary remarks

Abbreviations for the compound names conform to the principle 2,6-Cl = 2,6-dichloroanilinium chloride, etc. The ring numbering is standard (the nitrogen-bearing carbon is C1). The chlorines of the

cation are numbered 1 (at the lower-numbered carbon) and 2, and the chloride anion 3. Hydrogen atoms bonded to carbon atoms are given the same number as their parent atom; those of the NH_3 groups are numbered 01 to 03, and hydrogen bond donors of solvent from 04 onwards.

Only the compounds 2,4-Cl, 2,5-Cl and 3,5-Cl could be obtained solvent-free; 2,3-Cl was obtained as a monohydrate, 2,6-Cl as a 1:1 methanol solvate and 3,5-Cl additionally as a $1/4$ -hydrate.

The secondary contacts are summarised for all compounds in Table 1 (hydrogen bonds) and Table 2 (chlorine-chlorine contacts). The preceding paper [1] comments on the values used for van der Waals radii and explains the calculation of normalised hydrogen bond distances.

Two solvent-free ribbon structures with clearly defined hydrophilic regions

The asymmetric units of 2,4-Cl and 3,5-Cl are shown in Figs. 1 and 2; the former compound in-

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

H Bond	D-H	H	D	D-H	Operator of A
	...A	...A	...A	...A	
<i>Compound 2,4-Cl:</i>					
N-H01...Cl3'	1.01	2.21	3.158	157	$1+x,y,z$
N-H02...Cl3	1.01	2.17	3.125	158	
N-H03...Cl3	1.01	2.26	3.233	161	$1-x,-y,-z$
N'-H01'...Cl3'	1.01	2.19	3.157	159	$1-x,1-y,-z$
N'-H02'...Cl3	1.01	2.07	3.057	166	$-x,1-y,-z$
N'-H03'...Cl3	1.01	2.19	3.112	151	
C5-H5...Cl1	1.08	2.79	3.656	137	$x,-1+y,z$
C6-H6...Cl3	1.08	2.77	3.635	137	$1-x,-y,-z$
C3'-H3'...Cl2'	1.08	2.79	3.735	147	$1-x,2-y,1-z$
C6-H6...Cl3	1.08	2.97	3.761	130	$x,-1+y,z$
<i>Compound 3,5-Cl:</i>					
N-H01...Cl3	1.01	2.26	3.222	159	
N-H02...Cl3	1.01	2.25	3.168	150	$x,1+y,z$
N-H03...Cl3	1.01	2.12	3.117	172	$1-x,1-y,1-z$
C6-H6...Cl1	1.08	2.84	3.744	141	$1+x,-1+y,z$
C2-H2...Cl3	1.08	2.79	3.764	150	$-1+x,1+y,z$
C6-H6...Cl3	1.08	2.91	3.736	133	
<i>Compound 2,5-Cl:</i>					
N-H01...Cl3	1.01	2.14	3.147	173	
N-H02...Cl3	1.01	2.23	3.192	159	$1/2-x,-1/2+y,1/2-z$
N-H03...Cl3	1.01	2.16	3.166	177	$1^{1/2}-x,-1^{1/2}+y,1^{1/2}-z$
C4-H4...Cl3	1.08	2.65	3.669	156	$1-x,1-y,1-z$
C6-H6...Cl3 ^b	1.08	2.90	3.740	135	$1^{1/2}-x,-1^{1/2}+y,1^{1/2}-z$
C6-H6...Cl2 ^b	1.08	2.84	3.830	152	$2-x,-y,1-z$
C3-H3...Cl1	1.08	2.74	3.711	150	$-x,1-y,1-z$

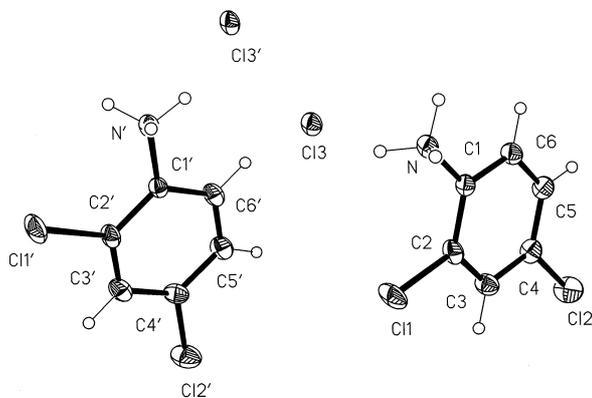


Fig. 1. Structure of the asymmetric unit of compound 2,4-Cl in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

volves two independent formula units. Both compounds form classical hydrogen bonds $\text{N-H}\cdots\text{X}^-$ from all three hydrogen atoms of the NH_3 group(s), each to a halide ion; accordingly, each halide ion accepts three hydrogen bonds.

Table 1 (continued).

H Bond	D-H	H	D	D-H	Operator of A
	...A	...A	...A	...A	
<i>Compound 2,6-Cl · MeOH:</i>					
N-H01...O	1.01	1.74	2.704	158	
N-H02...Cl3	1.01	2.23	3.156	151	
N-H03...Cl3	1.01	2.08	3.072	167	$1-x,1-y,-z$
O-H04...Cl3	0.98	2.10	3.082	175	$-x,1-y,-z$
C4-H4...Cl3	1.08	2.86	3.613	127	$x,y,1+z$
<i>Compound 2,3-Cl · H₂O:</i>					
N-H01...O1W	1.01	1.66	2.666	175	
N-H02...Cl3	1.01	2.16	3.152	166	$1-x,-1/2+y,1^{1/2}-z$
N-H03...Cl3	1.01	2.18	3.165	166	$1^{1/2}-x,2-y,-1/2+z$
O1W-H04...Cl3	0.98	2.18	3.152	173	$1^{1/2}-x,1-y,-1/2+z$
O1W-H05...Cl3	0.98	2.17	3.112	162	$2-x,-1/2+y,1^{1/2}-z$
C6-H6...Cl1 ^b	1.08	2.95	3.816	137	$x,1+y,z$
C2-H2...Cl3 ^b	1.08	2.90	3.745	135	$1^{1/2}-x,2-y,-1/2+z$
<i>Compound 3,5-Cl · 1/4H₂O:</i>					
N-H01...Cl3	1.01	2.13	3.125	168	$1/2+x,-1/2+y,-z$
N-H02...Cl3'	1.01	2.20	3.157	159	$y,1/2-x,1/2-z$
N-H03...Cl3 ^b	1.01	2.34	3.120	142	$1-x,1-y,-z$
N-H03...Cl3 ^b	1.01	2.65	3.237	117	$y,1/2-x,1/2-z$
N'-H01'...Cl3	1.01	2.09	3.084	168	$1-x,1-y,-z$
N'-H02'...Cl3'	1.01	2.19	3.141	156	$1^{1/2}-y,x,1/2-z$
N'-H03'...Cl3 ^b	1.01	2.42	3.202	134	$1-x,1-y,-z$
N'-H03'...Cl3 ^b	1.01	2.58	3.260	125	$y,1/2-x,1/2-z$
C6'-H6'...Cl3	1.08	2.67	3.539	137	$y,1/2-x,1/2-z$
C2-H2...Cl3'	1.08	2.80	3.672	137	$1-x,1-y,-z$
C6-H6...Cl3'	1.08	2.85	3.618	128	$y,1/2-x,1/2-z$

^a Several borderline cases (in italics) are included for completeness, D = donor, A = acceptor; ^b three-centre hydrogen bond.

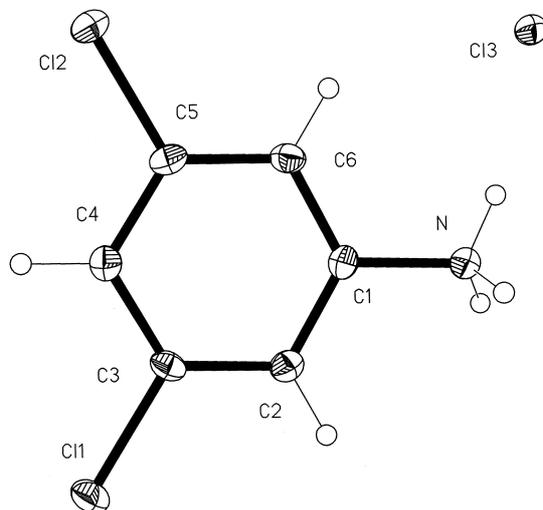


Fig. 2. Structure of the formula unit of compound 3,5-Cl in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

Table 2. Chlorine-chlorine contacts^a.

Contact	X...X (Å)	θ_1 (°) ^b / θ_2 (°) ^b	Operator
<i>Compound 2,4-Cl</i> :			
C2'-Cl1'...Cl3	3.5539(12)	153.00(11)	$x, 1+y, z$
C2-Cl1...Cl2'-Cl4'	3.6977(14)	81.70(10)/ 132.59(11)	$1-x, 1-y, 1-z$
Cl3...Cl3'	3.7166(14)		
Cl3'...Cl3'	3.7095(16)		$-x, -y, -z$
C2-Cl1...Cl3'	3.7227(13)	99.27(10)	$1+x, y, z$
<i>Compound 3,5-Cl</i> :			
C3-Cl1...Cl2-C5	3.3068(9)	164.50(7)/ 102.68(7)	$-1+x, 1+y, z$
C3-Cl1...Cl2-C5	3.5586(10)	88.76(7)/ 75.89(7)	$x, 1+y, z$
Cl3...Cl3	3.6293(12)		$2-x, 1-y, 1-z$
C5-Cl2...Cl2-C5	3.6424(12)	88.43(7)	$1-x, 1-y, -z$
<i>Compound 2,5-Cl</i> :			
C2-Cl1...Cl3	3.3142(4)	168.53(3)	$2-x, 1/2+y, 1/2-z$
C5-Cl2...Cl3	3.3983(4)	156.25(4)	$1/2+x, 1/2-y, 1/2+z$
C2-Cl1...Cl3	3.5716(5)	83.12(3)	$1/2-x, -1/2+y, 1/2-z$
C2-Cl1...Cl3	3.7027(4)	89.86(3)	
<i>Compound 2,6-Cl · MeOH</i> :			
C2-Cl1...Cl3	3.3430(5)	169.99(5)	$x, 1+y, z$
C2-Cl1...Cl2-C6	3.5982(5)	106.23(5)/ 153.37(4)	$x, 1+y, z$
C6-Cl2...Cl3	3.6987(5)	107.98(4)	
<i>Compound 2,3-Cl · H₂O</i> :			
C3-Cl2...Cl3	3.3763(5)	165.85(5)	$x, -1+y, z$
<i>Compound 3,5-Cl · 1/4H₂O</i> :			
C5'-Cl2'...Cl2-C5	3.4410(6)	170.02(5)/ 101.02(5)	$1-x, 1-y, 1-z$
C5-Cl2...Cl2'-C5'	3.4229(6)	167.32(5)/ 100.89(5)	$-1/2+x, -1/2+y, 1-z$
C3'-Cl1'...Cl3	3.4475(6)	164.49(5)	$1+x, y, z$
C3-Cl1...Cl3'	3.7262(6)	162.13(5)	

^a Several borderline cases (in italics) are included for completeness; ^b the θ angles are defined as C-Cl...Cl and Cl...Cl-C; $\theta_1 \approx 90^\circ$, $\theta_2 \approx 180^\circ$ (or *vice versa*) is classified as a type II contact, usually held to be associated with a genuine attractive interaction [4]; where the second chlorine is an anion, θ_2 is not defined, but the shortest such interactions have $\theta_1 \approx 180^\circ$ [5].

In 2,4-Cl the basic feature of the packing is a ribbon or ladder structure parallel to [110], involving annelated rings of graph set $R_4^2(8)$ [2] (Fig. 3); the rings each contain two chloride ions and two NH₂ moieties (two hydrogen atoms from an NH₃ group). The rungs of the ladder are formed by the hydrogen bonds H02...Cl3' and H02'...Cl3. Topologically equivalent ribbons were observed for 3-chloroanilinium chloride and its bromo analogue [1]; rings of general graph set $R_{2n}^n(4n)$ arose

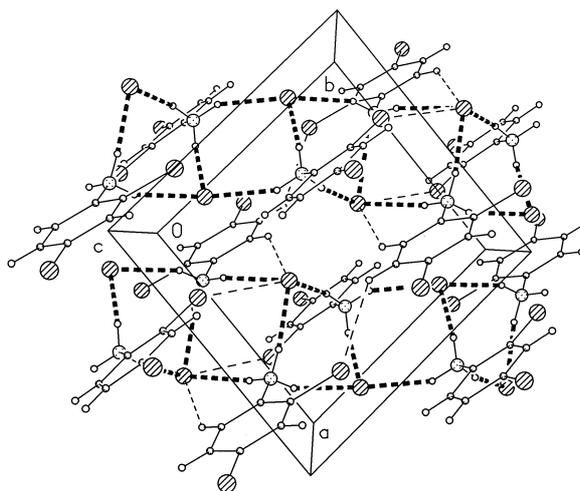


Fig. 3. Packing diagram of 2,4-Cl viewed parallel to the z axis. Classical hydrogen bonds are shown as thick, non-classical hydrogen bonds and Cl...Cl contacts as thin dashed lines. The rings of the first independent cation project into the spaces between ribbons; those of the second cation lie above and below the ribbons.

frequently in the monohalogenated series, being formed from equal numbers of NH₂ and halide units.

Of the non-classical, “weaker” hydrogen bonds [3], H6...Cl3 is found within individual ribbons, and may possibly be attributed to its position next to the NH₃ group. H5...Cl1 links the ribbons to form polar layers parallel to the xy plane at $z \approx 0, 1$, etc. The aromatic rings project from the layers but rings from adjacent layers do not overlap significantly (interlayer repeat distance $c = 14.00$ Å), they are linked by the interaction H3'...Cl2' (Fig. 4). We have already noted [1] that the ribbon structures seem to preclude significant overlap or interdigitation of aromatic rings from neighbouring layers.

The introduction of the extra chlorine atom has not succeeded in promoting short Cl...Cl contacts. The shortest such contact [Cl1'...Cl3, 3.5539(12) Å] is found within the ribbons, and there are no others < 3.69 Å.

In 3,5-Cl the same pleated ribbon or ladder motif is again observed (Fig. 5), and must thus be considered a robust supramolecular unit. The rungs are formed by the hydrogen bonds H03...Cl3. The ribbons run parallel to the y axis and are connected *inter alia* (see below) by the interactions H6...Cl1 and H2...Cl3 to neighbouring ribbons to form polar layers parallel to the xy plane at $z \approx 1/2, 1 1/2$,

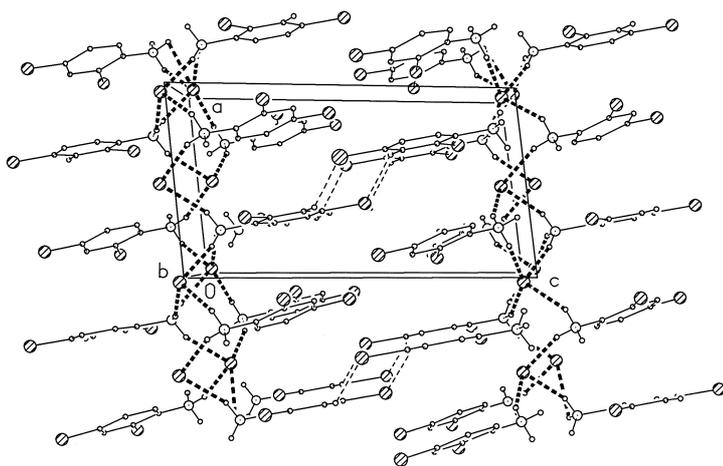


Fig. 4. Packing diagram of 2,4-Cl viewed parallel to the y axis. Classical hydrogen bonds are shown as thick, non-classical hydrogen bonds as thin dashed lines. Note the non-classical C-H...Cl hydrogen bonds formed in the region $z \approx 1/2$. Other H atoms not involved in classical H bonding are omitted.

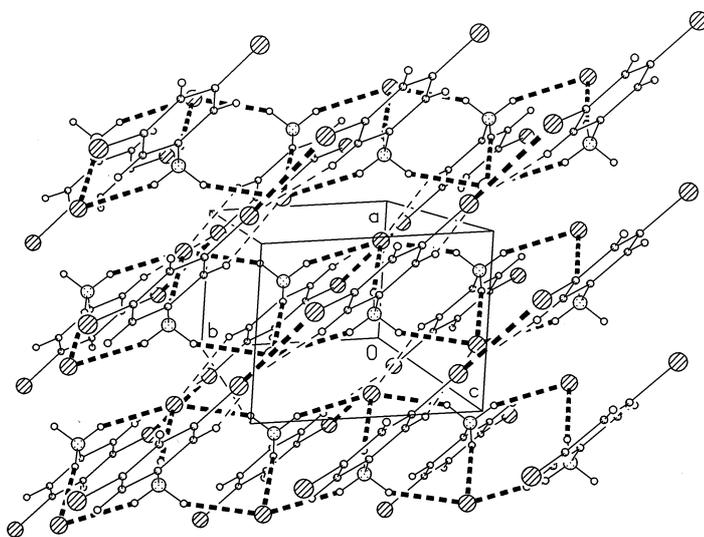


Fig. 5. Packing diagram of 3,5-Cl. The view direction is approximately perpendicular to the xy plane. Classical hydrogen bonds and Cl...Cl contacts are shown as thick dashed lines, C-H...Cl interactions as thin dashed lines. Note that all the latter run parallel to the diagonal (a-b). The second part of a three-centre hydrogen bond (H6...Cl3) is omitted for clarity.

etc., with a layer repeat distance of $c = 14.60$ Å. These weaker interactions run parallel to the diagonal (a - b).

A more striking feature connecting the ribbons is however a very short Cl1...Cl2 contact of 3.3068(9) Å. With C-Cl...Cl angles θ of 164.5 and 102.7° at Cl1 and Cl2 respectively, this can be classified as a "type II contact" [4] ($\theta_1 \approx 90^\circ$, $\theta_2 \approx 180^\circ$), which is thought more likely to arise from attractive forces (*cf.* type I contacts, which have $\theta_1 \approx \theta_2$). In our previous publications [5], where the predominant interhalogen interactions tended to involve a cation halogen and a halide ion (and thus be "charge-assisted"), it was not necessary to intro-

duce this classification of directionality. It will be used again below.

The hydrophobic regions do not overlap or interdigitate significantly, and there appear to be no secondary contacts that connect such regions of neighbouring layers; the shortest connection is a Cl2...Cl2 contact of 3.6424(12) Å, significantly above the van der Waals diameter.

The cell constants of 3,5-Cl for the projection of Fig. 5 are typical of the ribbon structure type, with $a = 4.678$, $b = 5.965$ Å, $\gamma = 96.59^\circ$ [1]. However, those of 2,4-Cl do not conform to this standard type because there are two ribbons per unit cell projection area rather than one.

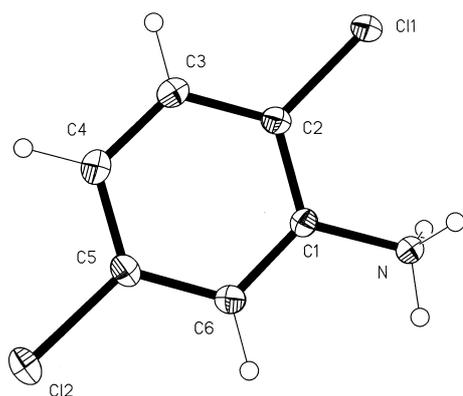


Fig. 6. Structure of the formula unit of compound 2,5-Cl in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

A solvent-free layer structure

The formula unit of compound 2,5-Cl is shown in Fig. 6. The crystal packing involves the usual set of hydrogen bonds from NH_3 to chloride, whereby the extended structure consists of layers parallel to the xy plane that involve (apart from translation) only the 2_1 screw axis as symmetry operator. The hydrophilic regions lie at $z \approx 1/4, 3/4$, and the inter-layer repeat distance is thus $c/2 \approx 8.48 \text{ \AA}$; successive layers are related by inversion.

The layers consist of rings of graph set $R_6^3(12)$ (Fig. 7), with a short $\text{Cl1} \cdots \text{Cl3}$ contact of $3.3142(4) \text{ \AA}$ across each ring. Exactly the same arrangement within layers was seen in 2-Cl [1], and

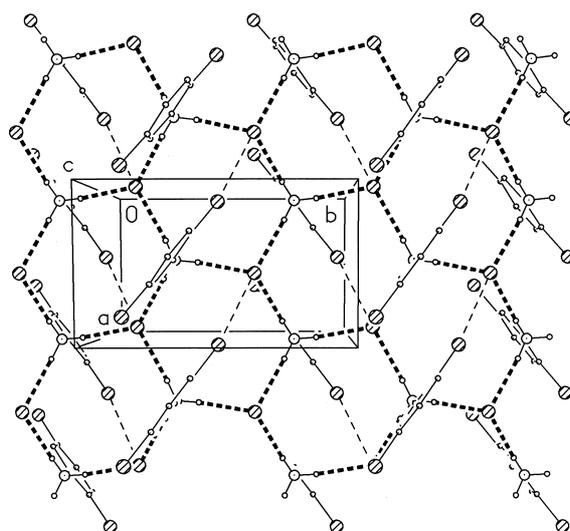


Fig. 7. Packing diagram of 2,5-Cl viewed parallel to the z axis. Classical hydrogen bonds are shown as thick dashed lines, $\text{Cl} \cdots \text{Cl}$ contacts as thin dashed lines. H atoms not involved in hydrogen bonding are omitted.

the relevant cell constants in projection are very similar: 2-Cl, $b = 5.324$, $c = 8.698 \text{ \AA}$, $\beta = 90^\circ$; 2,5-Cl, $a = 5.415$, $b = 8.907 \text{ \AA}$, $\beta = 98.4^\circ$. Because the two structures are not isotypic, however, one would expect to see a difference in the weak interactions linking the interdigitating aromatic rings, and this is indeed the case (Fig. 8). In 2,5-Cl four such interactions are involved, namely the hydrogen bonds $\text{H4} \cdots \text{Cl3}$, $\text{H6} \cdots \text{Cl2}$ and $\text{H3} \cdots \text{Cl1}$, and also the chlorine-chlorine interaction $\text{Cl2} \cdots \text{Cl3}$,

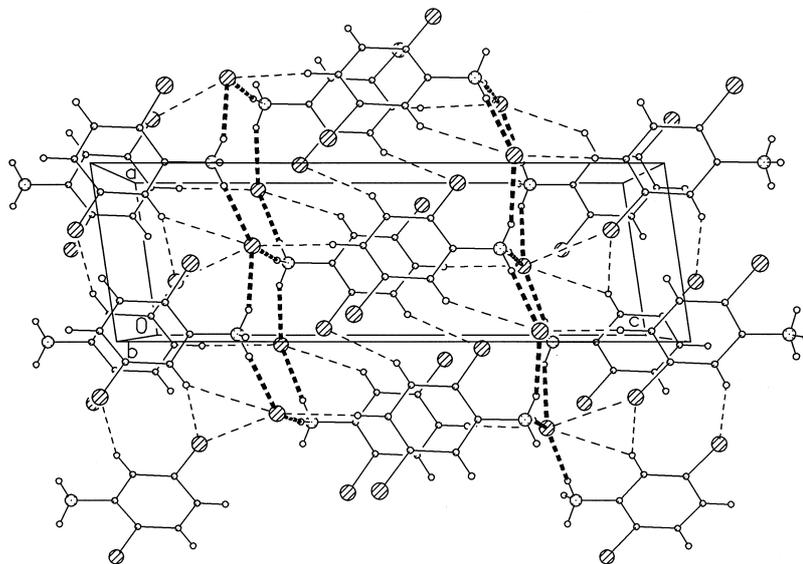


Fig. 8. Packing diagram of 2,5-Cl viewed parallel to the y axis. Classical hydrogen bonds are shown as thick dashed lines, $\text{H} \cdots \text{Cl}$ and $\text{Cl2} \cdots \text{Cl3}$ contacts as thin dashed lines. The $\text{Cl1} \cdots \text{Cl2}$ contacts are omitted for clarity. The triangles (*e.g.* bottom left) are built up from a three-centre hydrogen bond and the $\text{Cl2} \cdots \text{Cl3}$ interaction (see text). The interactions $\text{H3} \cdots \text{Cl1}$ can be seen in the hydrophobic regions at $z \approx 1/2$.

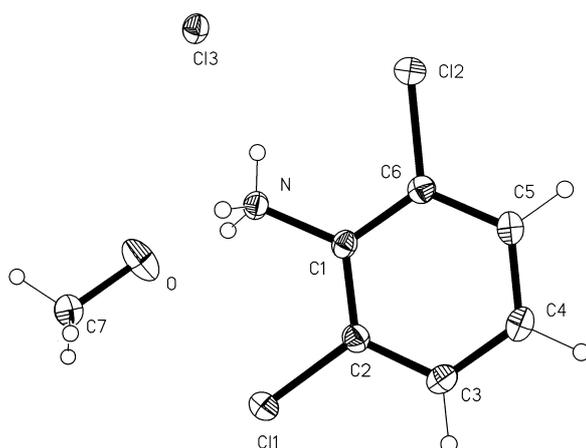


Fig. 9. Structure of the formula unit of compound 2,6-Cl methanol solvate in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary. The hydrogen atom of the methanol hydroxy group is obscured.

3.3983(4) Å. The interaction H6...Cl3 occurs within the layers and forms part of a three-centre hydrogen bond.

A ribbon structure involving solvent

It is a truism that structural comparisons rely on the availability of strictly comparable structures. Thus we have attempted, where possible, to obtain solvent-free single crystals. In the dichloroanilinium chloride series, two compounds have, despite our best efforts, so far only yielded solvates: 2,6-Cl methanol solvate and 2,3-Cl hydrate. These structures are presented in this and the next section.

The formula unit of 2,6-Cl methanol solvate is shown in Fig. 9. The presence of the methanol molecule relaxes the constraint that N-H groups and chloride ions are the only classical hydrogen bond donors and acceptors respectively; the methanol

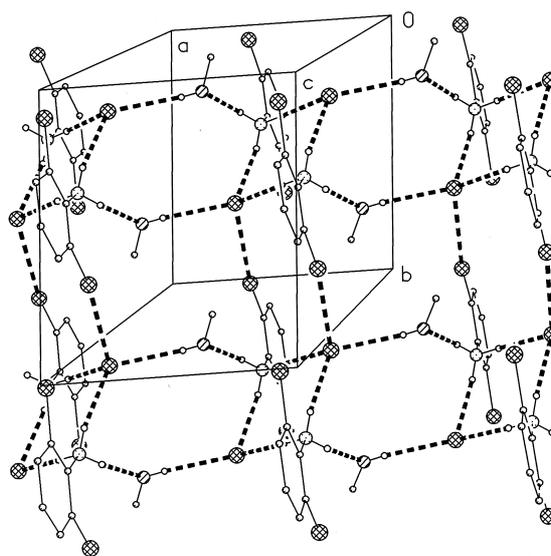


Fig. 10. Packing diagram of 2,6-Cl methanol solvate viewed perpendicular to the xy plane. Classical hydrogen bonds and Cl1...Cl3 contacts are shown as thick dashed lines. The rather longer Cl1...Cl2 contacts are not drawn explicitly; they run horizontally across the centre of the Figure. Hydrogen atoms not involved in hydrogen bonding are omitted.

oxygen atom accepts a hydrogen bond from N-H01, and its OH group is a donor towards chloride, which thus accepts three classical hydrogen bonds as in the solvent-free structures presented above.

The hydrogen bonds combine to form a ribbon structure (Fig. 10), but of a different type from that previously observed in these compounds. The annelated rings are of two types, the well-known $R_4^2(8)$ with two chlorides and two NH_2 moieties, and $R_6^4(12)$ with two chlorides, two NH_2 and two methanols. The common rungs are provided by the hydrogen bond H02...Cl3. The ribbons run parallel to the x axis and are connected by the short Cl1...Cl3

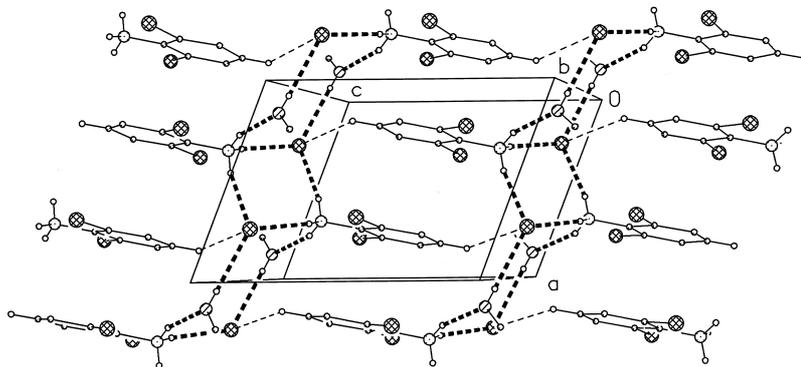


Fig. 11. Packing diagram of 2,6-Cl methanol solvate viewed approximately perpendicular to the xz plane. Classical hydrogen bonds and Cl1...Cl3 contacts are shown as thick dashed lines, C-H...Cl interactions linking the layers as thin dashed lines.

contact of 3.3430(5) Å (and also by the appreciably longer Cl1...Cl2 3.5982(5) Å) to form hydrophilic layers parallel to the xy plane at $z \approx 0, 1, \text{etc.}$ The hydrophobic groups of neighbouring layers overlap appreciably in the region $z \approx 1/2$, and the layers are connected by the (rather long and narrow-angled) weak hydrogen bond H4...Cl3 (Fig. 11). This is the first ribbon structure of the anilinium series to display such overlap, which is presumably facilitated by the larger 12-membered rings. However, the repeat distance of $c = 9.414$ Å is rather long for a layer structure with overlap of the aromatic rings (*cf.* earlier values), which may be connected with the steric effect of the methanol molecule with its methyl group.

A hydrate with layer structure

The formula unit of 2,3-Cl hydrate is shown in Fig. 12. The water molecule accepts a hydrogen bond from an NH group and donates two to chlorides; the chloride ion also accepts two hydrogen bonds from NH groups, and thus four in total. The classical hydrogen bonds combine to form hydrophilic layers parallel to the xy plane at $z \approx 0, 1/2, 1, \text{etc.}$; one such layer is shown in Fig. 13. The layers consist of rings of graph set $R_5^3(10)$, of which there are two different kinds; one contains two NH_2 moieties, two chlorides and the OH part of a water molecule, whereas, in the second type, one NH_2 is replaced by a topologically equivalent OH_2 . The layer repeat distance is $c/2 \approx 8.33$ Å, which implies considerable overlap of the aromatic rings from neighbouring layers. Fig. 14 confirms this, and shows that the layers are connected by a short chlor-

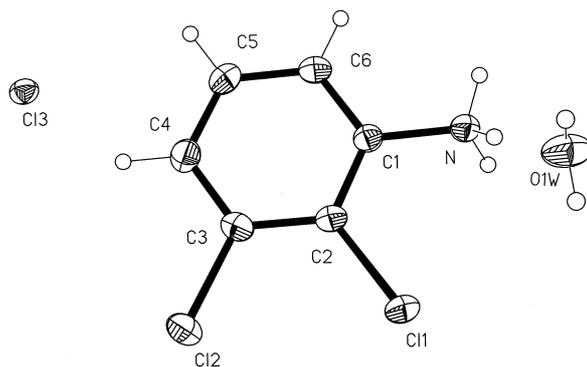


Fig. 12. Structure of the formula unit of compound 2,3-Cl hydrate in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

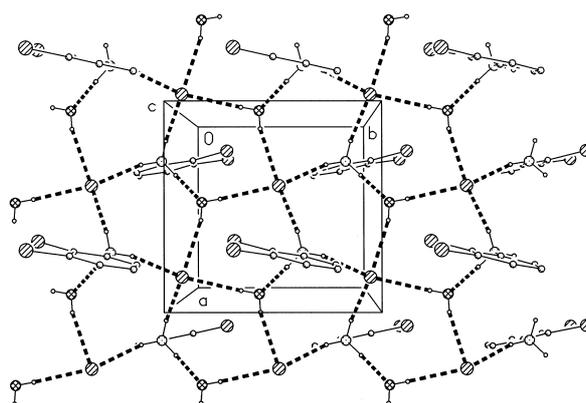


Fig. 13. Packing diagram of 2,3-Cl hydrate viewed parallel to the z axis. Classical hydrogen bonds are shown as thick dashed lines. Hydrogen atoms not involved in hydrogen bonding are omitted.

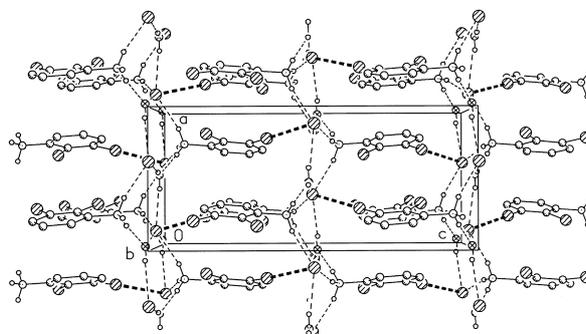


Fig. 14. Packing diagram of 2,3-Cl hydrate viewed parallel to the y axis. Classical hydrogen bonds are shown as thin dashed lines, Cl...Cl contacts as thick dashed lines. Hydrogen atoms not involved in hydrogen bonding are omitted.

ine-chlorine contact Cl2...Cl3 3.3763(5) Å (and related by inversion about $(0, 0, 1/2)$). The π -stacking implied by Fig. 14 is an optical illusion; in projection parallel to the x axis (not shown here) the rings are staggered.

A new structure type for anilinium halides: hydrogen-bonded nanotubes

First attempts to crystallise the compound 3,5-Cl led to a phase that retained small amounts of water. The tetragonal cell was different from that of the solvent-free material (presented above). The structure determination revealed a completely different structure type from the ribbon and layer structures previously described for this series. The asymmet-

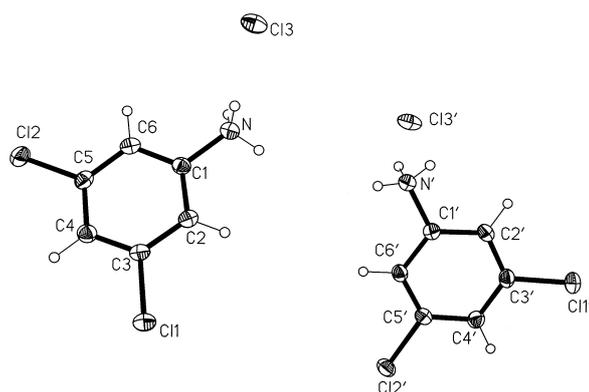


Fig. 15. Structure of the asymmetric unit of compound 3,5-Cl $^{1/4}$ -hydrate in the crystal (solvent omitted). Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

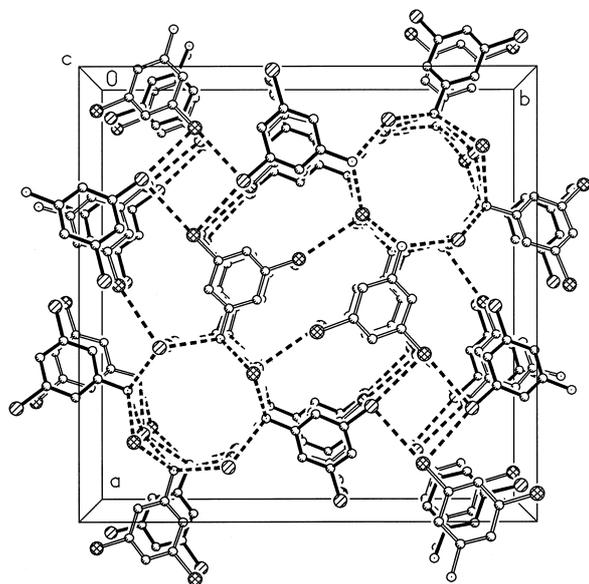


Fig. 16. Packing diagram of 3,5-Cl $^{1/4}$ -hydrate viewed parallel to the z axis. Hydrogen atoms are omitted for clarity. Classical hydrogen bonds (as $N \cdots Cl^-$) and $Cl \cdots Cl$ contacts are shown as thick dashed lines. The first independent formula unit is depicted with thick bonds and diagonally shaded chlorines; the second independent unit with open bonds and crosshatched chlorines.

ric unit, which contains two formula units of 3,5-Cl, is shown (except for disordered water) in Fig. 15. Atoms of the second formula unit are distinguished by a prime.

A general impression of the packing is given in Fig. 16, a view parallel to the z axis. The most

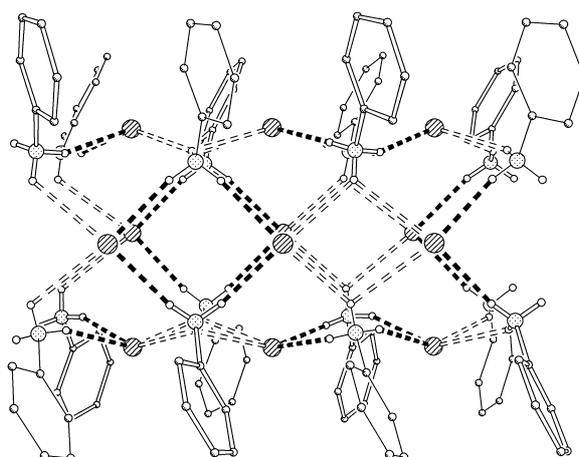


Fig. 17. Packing diagram of 3,5-Cl $^{1/4}$ -hydrate: hydrogen-bonded channel viewed from the side. Two-centre hydrogen bonds are shown as thick dashed lines, three-centre hydrogen bonds as open dashed lines. The second independent cation is drawn with open bonds. The chlorine substituents of the rings are omitted for clarity.

striking features are columnar arrays, namely the approximately circular channels at *e.g.* $x \approx 1/4$, $y \approx 3/4$, involving hydrogen bonding (see below), and the square (in projection) assemblies of chlorine-chlorine contacts at *e.g.* $x \approx 1/4$, $y \approx 1/4$.

The "square" arrays are in fact appreciably non-planar (deviations ± 0.52 Å from the best plane). They involve the two independent contacts $Cl2 \cdots Cl2'$, 3.4410(6) and 3.4229(6) Å, and are completed by twofold symmetry about $1/4, 1/4, z$. The C-Cl \cdots Cl angles (Table 2) classify the contacts unambiguously as "type II", and these are well-suited to the formation of quadrilateral arrays. In passing it may be noted that a further short chlorine-chlorine contact, but this time involving an anion [$Cl1' \cdots Cl3$, 3.4475(6) Å], links the two types of columns *via* common cations.

The hydrogen-bonded channel is shown as a side view in Fig. 17. The centre of the channel is the 4_2 axis at $1/4, 3/4, z$, and its overall architecture is that of a "nanotube". The hydrogen bonds fall into two types: conventional two-centre bonds, which form $R_4^2(8)$ rings of the customary type, and three-centre bonds (from H03 of both cations), which form $R_2^2(4)$ rings. The hybrid rings that link these two types (seen edge on in Fig. 17) are also $R_4^2(8)$. The exact role of the water molecule in the channels remains unclear in view of its disorder, but a

Table 3. Crystal data.

Compound	2,4-Cl	3,5-Cl	2,5-Cl	2,6-Cl · MeOH	2,3-Cl · H ₂ O	3,5-Cl · 1/4H ₂ O
Formula	C ₆ H ₆ Cl ₃ N	C ₆ H ₆ Cl ₃ N	C ₆ H ₆ Cl ₃ N	C ₇ H ₁₀ Cl ₃ NO	C ₆ H ₈ Cl ₃ NO	C ₆ H _{6.5} Cl ₃ NO _{0.25}
<i>M_r</i>	198.47	198.47	198.47	230.51	216.48	202.97
Habit	colourless plate	colourless plate	colourless tablet	colourless tablet	colourless prism	colourless prism
Crystal size (mm)	0.5 × 0.2 × 0.02	0.4 × 0.17 × 0.04	0.48 × 0.32 × 0.21	0.38 × 0.31 × 0.16	0.31 × 0.10 × 0.09	0.32 × 0.18 × 0.16
Crystal system	triclinic	triclinic	monoclinic	triclinic	orthorhombic	tetragonal
Space group	<i>P</i> (-1)	<i>P</i> (-1)	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> (-1)	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 4 ₂ / <i>n</i>
Cell constants:						
<i>a</i> (Å)	7.756(2)	4.6872(12)	5.4148(6)	7.0902(4)	7.3399(6)	20.1542(16)
<i>b</i> (Å)	7.865(2)	5.9654(14)	8.9067(12)	8.2633(6)	7.4778(6)	20.1542(16)
<i>c</i> (Å)	13.997(3)	14.595(3)	16.965(2)	9.4141(6)	16.6578(12)	8.3057(10)
α (°)	99.757(8)	98.609(6)	90	72.854(3)	90	90
β (°)	95.617(8)	95.594(6)	98.359(3)	69.322(3)	90	90
γ (°)	94.964(8)	96.585(6)	90	86.286(3)	90	90
<i>V</i> (Å ³)	832.7(4)	398.09(16)	809.48(18)	492.61(6)	914.29(12)	3373.7(6)
<i>Z</i>	4	2	4	2	4	16
<i>D_x</i> (Mg m ⁻³)	1.583	1.656	1.629	1.554	1.573	1.598
μ (mm ⁻¹)	1.02	1.07	1.05	0.88	0.95	1.01
<i>F</i> (000)	400	200	400	236	440	1640
<i>T</i> (°C)	-130	-130	-130	-130	-130	-130
2 θ _{max}	56.2	57	60	60	61	60
Transmissions	0.70 - 0.98	0.62 - 0.98	0.79 - 0.96	0.64 - 0.98	0.73 - 0.96	0.86 - 0.99
Measured refls	12304	5895	9360	10408	20550	56743
Independent refls	4220	2011	2366	2873	2799	4931
<i>R</i> _{int}	0.091	0.067	0.027	0.039	0.054	0.056
Parameters	205	103	103	126	120	210
Restraints	15	3	3	3	4	15
<i>wR</i> (<i>F</i> ² , all refl.)	0.121	0.094	0.056	0.088	0.054	0.086
<i>R</i> (<i>F</i> , > 4 σ (<i>F</i>))	0.051	0.038	0.021	0.032	0.023	0.030
<i>S</i>	0.96	1.00	1.06	1.03	0.99	1.00
Max. $\Delta\rho$ (e Å ⁻³)	0.78	0.52	0.49	0.56	0.32	0.57

reasonable speculation is that it is hydrogen bonded to the chloride anions.

All three short C-H...Cl contacts involve hydrogen atoms ortho to the NH₃ groups, and these may be considered as supporting the classical hydrogen bonds to which they are adjacent.

Conclusions

The introduction of a second chlorine was intended to promote chlorine-chlorine interactions, possibly at the expense of classical hydrogen bonds, in comparison to the previously studied monohalo derivatives. Nevertheless, five of the six structures display hydrogen-bonded layer structures reminiscent of (or even exactly analogous to) those of the mono-substituted derivatives. The weaker interactions (C-H...Cl and Cl...Cl) in general play a subordinate role in determining the interactions between layers or parts thereof. However, 3,5-dichloroanilinium chloride does show, in both its solvent-free and hydrated structure, the unusual feature

of short Cl...Cl interactions between cations. In the 1/4-hydrate, these associate to form columns of four-membered rings of chlorine atoms. Clearly, to break the near-monopoly of the classical hydrogen bonds, different types of compounds are needed; possibilities include the use of softer halogens (which however form appreciably less stable derivatives), even higher degrees of halogen substitution (also associated with lower stability) or blocking some N-H functions by alkylation. Corresponding systems are now being investigated.

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. Method 2: 2,4-Cl, 3,5-Cl 1/4-hydrate (recrystallized by diffusion of diethyl ether into a methanol solution at -18 °C or R. T., respectively). Method 1: 3,5-Cl (solvent-free, recrystallized by cooling solutions in *n*-butanol), 2,5-Cl, 2,6-Cl (both recrystallized by diffusion of diethyl

ether into methanol solutions at R. T.), 2,3-Cl (recrystallized by evaporation of a methanol solution).

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. Absorption corrections were performed with the program SADABS. The structures were refined anisotropically on F^2 using all reflections (program SHELXL-97 [6]). The acidic H atoms were located and refined freely, but with N-H (and O-H, where applicable) distances restrained equal; 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. 2,3-Cl hydrate: Flack parameter refined to $-0.08(5)$. 3,5-Cl $^{1/4}$ H $_2$ O: A difference peak in the channels around the fourfold axis was

tentatively refined as a water oxygen atom, although its anisotropic U components were very asymmetric and it is probably disordered along the channels. Its hydrogen atoms were not located.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers 170633 (2,4-Cl), 170634 (3,5-Cl), 170635 (2,5-Cl), 170636 (2,6-Cl methanol solvate), 170637 (2,3-Cl hydrate), 170638 (3,5-Cl $^{1/4}$ -hydrate). 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

We thank the Fonds der Chemischen Industrie for financial support. L.G. was financed by the Erasmus scheme.

-
- [1] L. Gray, P. G. Jones, *Z. Naturforsch.* **57b**, 61 (2002).
[2] J. Bernstein, R. E. Davis, L. Shimoni, N.-L. Chang, *Angew. Chem.* **107**, 1689 (1995) and references therein.
[3] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford (1999).
[4] V.R. Pedireddi, D.S. Reddy, B.S. Goud, D.C. Craig, A.D. Rae, G.R. Desiraju, *J. Chem. Soc., Perkin Trans 2*, 2353 (1994).
[5] see *e.g.* P. G. Jones, M. Freytag, B. Ahrens, A.K. Fischer, *New J. Chem.* **23**, 1137 (1999); M. Freytag, P. G. Jones, *Z. Naturforsch.* **56b**, 889 (2001).
[6] G. M. Sheldrick, "SHELXL-97, a program for refining crystal structures". Univ. of Göttingen, Germany (1997).