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The Structure of the Hydrated Salt of 3,5-Dichlorosalicylaldehyde and 4-Aminopyridine, $C_5H_7N_2^+.C_7H_3Cl_2O_2^-.H_2O$

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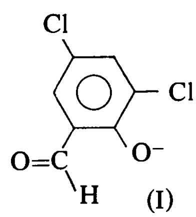
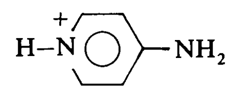
Abstract. $M_r = 303\cdot15$, orthorhombic, $Pna2_1$, $a = 22\cdot897$ (5), $b = 3\cdot9476$ (6), $c = 30\cdot398$ (6) Å, $V = 2747$ (4) Å^3, $Z = 8$, $D_x = 1\cdot466$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\mu = 43\cdot9$ cm^{-1}, $F(000) = 1248$. Final $R = 0\cdot049$, $R_w = 0\cdot045$ for 963 observed reflections. There are two crystallographically independent groups of cations and anions in the asymmetric unit arranged separately in chains along **a** and held together by H bonds. Two neighboring chains are also linked by H bonds *via* water molecules. The aldehyde and aminopyridine ions are in an appropriate relative geometry to react and form a Schiff base.

Introduction. In continuation of our studies on the molecular structure and behavior of 2-(pyridyliminomethyl)phenols (Moustakali-Mavridis, Hadjoudis & Mavridis, 1978, 1980), the crystallization of a number of derivatives of 2-(4-pyridyliminomethyl)phenol was attempted. This proved to be not an easy task because, when left in solution, the compounds either polymerized or hydrolyzed yielding crystals of 4-aminopyridine (Chao & Schempp, 1977). Finally the derivative 4,6-dichloro-2-(4-pyridyliminomethyl)phenol gave good quality yellow crystals from a mixture of ethanol and chlorobenzene. To our surprise the X-ray study showed that the crystals are formed from a co-crystallization of the hydrolysis products of the above derivative, namely the phenolic anion (I) and the pyridinium cation (II) with a water molecule.



(I)



(II)

Single crystals of the above salt (m.p.=357 K) are destroyed when heated above 318 K yielding an orange powder (m.p.=447 K) that exhibits photochromic behavior, a fact indicating that the molecules react in the solid state to form the Schiff base. The latter is again easily hydrolyzed.

Experimental. $0\cdot4 \times 0\cdot1 \times 0\cdot1$ mm, mounted along **b**, systematic absences $0kl$:$k + l = 2n$, $h0l$:$h = 2n$, $Pnam$ or $Pna2_1$, unit-cell parameters by least-squares from setting angles of 12 reflections, $45 < 2\theta < 60°$; room temperature, Cu $K\alpha$, Picker 4-circle diffractometer (Vandlen & Tulinsky, 1971), $1 < 2\theta < 110°$, 'wandering' ω step scan, balanced Ni/Co filters, alignment and decay of the crystal monitored every 100 reflections and automatically corrected for, no radiation damage; 1936 reflections measured (including 356 systematically absent), 963 observed $[I \geq 2\sigma(I)]$, correc-

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ted for absorption (North, Phillips & Mathews, 1968), converted to relative structure amplitudes by usual correction factors; direct methods and Fourier techniques, *MULTAN* (Germain, Main & Woolfson, 1971), all non-H atoms could have been recognized among highest peaks of first E map calculated with 300 E's ($E \geq 1{\cdot}32$), but initial interpretation was hindered by the assumption that the initial compound had remained intact; 26 non-H atoms found, other non-H from Fourier maps, isotropic full-matrix unit-weight least squares gave $R = 0{\cdot}12$; H atoms from difference Fourier map, isotropic temperature factors 25% greater than those of the atoms to which they are bonded, non-H anisotropic, $R = 0{\cdot}049$, $R_w = 0{\cdot}045$, $w = 1/\sigma(F)$, *ORFLS* (Busing, Martin & Levy, 1962); refinement in *Pnam* not successful, scattering factors from Doyle & Turner (1968) for non-H, from Stewart, Davidson & Simpson (1965) for H atoms, final difference Fourier map had no significant features except positive density of 0·16e$Å^{-3}$ near a Cl atom (mean peak heights 12·4 and 4·1 e$Å^{-3}$ for the Cl and C atoms respectively).

Disscussion. The asymmetric unit contains two crystallographically independent hydrated salt 'molecules', hereafter referred to as molecules A and B, related by a pseudo center of symmetry. Final coordinates and equivalent isotropic temperature factors are listed in Table 1.*

Molecules A are almost parallel to molecules B [dihedral angles are 4·8 (1)° and 1·6 (1)° between the aldehyde and pyridine entities respectively] and form separate zig-zag chains almost parallel to **a**, which are held together by strong H bonds: the phenolate O(2) to the H(N1) of the pyridinium cation, and the carbonyl O(1) to the NH_2 group of another pyridinium cation. Two neighboring chains composed of molecules A and B are linked by H bonds *via* the water molecules and form a sort of double chain. The latter are stacked antiparallel along **c** interacting weakly by van der Waals forces (see Fig. 1 and Table 2).

Molecules A and B interact with their environment in a very similar fashion. Some variability is probably a result of finding different ways of relieving close contacts. Bond lengths and angles and the atom notation are shown in Fig. 2.

The ring atoms are coplanar and the deviations of the peripheral atoms from the mean molecular planes are small.*

The participation of H(N1) of the pyridinium cation in a H bond and the presence of a water molecule close to C(8) [the distance O(3)···C(8) is 3·18 (2) Å for A and 3·37 (2) Å for B] has introduced asymmetry in this ion. An enlargement of the C(8)N(1)C(12) angle noted by Rerat (1962) in crystals of pyridine hydrochloride is clearly apparent. The amino-ring bond lengths of 1·35 (2) and 1·38 (2) Å for molecules A and B

Table 1. *Positional parameters (with e.s.d.'s in parentheses) and equivalent isotropic thermal parameters*

$B_{eq} = 8\pi^2 \langle u^2 \rangle$ (Willis & Pryor, 1975).

	x	y	z	B_{eq}(Å^2)
Molecule A				
C(1)	0·0176 (8)	0·691 (4)	0·3505 (6)	7·3 (7)
C(2)	−0·0385 (8)	0·820 (3)	0·3461 (6)	6·7 (7)
C(3)	−0·0608 (5)	0·961 (3)	0·3855 (5)	5·3 (5)
C(4)	−0·0346 (7)	0·954 (4)	0·4268 (5)	6·7 (7)
C(5)	0·0212 (7)	0·818 (4)	0·4265 (4)	6·5 (7)
C(6)	0·0513 (7)	0·688 (4)	0·3914 (5)	7·2 (7)
C(7)	0·0483 (7)	0·570 (4)	0·3103 (5)	8·0 (8)
C(8)	0·3127 (7)	0·782 (4)	0·2476 (5)	8·3 (7)
C(9)	0·2605 (7)	0·906 (4)	0·2307 (5)	7·4 (7)
C(10)	0·2129 (7)	1·010 (4)	0·2565 (4)	7·4 (8)
C(11)	0·2210 (7)	0·975 (4)	0·3000 (6)	8·1 (8)
C(12)	0·2707 (9)	0·861 (4)	0·3192 (6)	8·3 (8)
Cl(1)	−0·1326 (2)	1·1268 (11)	0·3858	7·1 (2)
Cl(2)	0·0573 (2)	0·7901 (13)	0·4783 (2)	9·3 (2)
N(1)	0·3145 (6)	0·758 (3)	0·2930 (5)	7·2 (6)
N(2)	0·1640 (6)	1·155 (3)	0·2394 (4)	7·2 (6)
O(1)	0·0976 (5)	0·444 (3)	0·3101 (3)	8·9 (6)
O(2)	−0·0706 (5)	0·825 (2)	0·3102 (4)	6·8 (4)
O(3)	−0·0662 (6)	0·323 (3)	0·2527 (4)	8·6 (5)
H(C4)	−0·051 (5)	1·21 (3)	0·452 (4)	7·6
H(C6)	0·093 (4)	0·60 (3)	0·394 (4)	8·5
H(C7)	0·034 (5)	0·67 (3)	0·286 (4)	7·4
H(C8)	0·341 (5)	0·65 (3)	0·234 (4)	8·1
H(C9)	0·257 (5)	0·95 (3)	0·204 (4)	7·9
H(C11)	0·196 (5)	0·93 (3)	0·314 (4)	8·8
H(C12)	0·263 (6)	0·72 (3)	0·350 (4)	7·9
H(N1)	−0·151 (5)	0·81 (3)	0·305 (5)	7·4
H1(N2)	0·166 (4)	1·11 (3)	0·206 (3)	7·7
H2(N2)	0·145 (5)	1·31 (3)	0·253 (4)	7·7
H1(O3)	−0·065 (5)	0·10 (3)	0·269 (4)	8·2
H2(O3)	−0·059 (6)	0·20 (3)	0·231 (5)	8·2
Molecule B				
C(1)	0·2326 (7)	0·293 (4)	0·5458 (6)	6·0 (6)
C(2)	0·2930 (7)	0·195 (4)	0·5494 (6)	6·4 (7)
C(3)	0·3161 (6)	0·050 (4)	0·5118 (5)	6·9 (7)
C(4)	0·2855 (6)	0·025 (4)	0·4731 (5)	6·0 (6)
C(5)	0·2296 (7)	0·140 (4)	0·4691 (5)	7·2 (8)
C(6)	0·2049 (6)	0·278 (4)	0·5079 (6)	6·9 (6)
C(7)	0·2046 (7)	0·440 (4)	0·5858 (5)	7·4 (7)
C(8)	−0·0549 (7)	0·186 (4)	0·6459 (6)	7·7 (8)
C(9)	−0·0084 (7)	0·055 (4)	0·6686 (5)	7·4 (7)
C(10)	0·0383 (7)	−0·036 (3)	0·6406 (5)	6·5 (6)
C(11)	0·0355 (7)	−0·004 (4)	0·5938 (5)	8·1 (8)
C(12)	−0·0156 (7)	0·132 (5)	0·5768 (5)	7·9 (8)
Cl(1)	0·3881 (2)	−0·0979 (11)	0·5142 (2)	7·6 (2)
Cl(2)	0·1931 (2)	0·1157 (13)	0·4200 (2)	10·0 (3)
N(1)	−0·0612 (7)	0·207 (3)	0·6037 (6)	8·0 (6)
N(2)	0·0873 (6)	−0·173 (3)	0·6600 (5)	8·2 (6)
O(1)	0·1551 (5)	0·531 (3)	0·5852 (4)	8·8 (6)
O(2)	0·3219 (5)	0·223 (2)	0·5859 (4)	7·2 (5)
O(3)	0·3169 (5)	0·734 (3)	0·6471 (3)	8·2 (6)
H(C4)	0·306 (4)	−0·11 (3)	0·447 (4)	7·1
H(C6)	0·164 (4)	0·36 (3)	0·501 (4)	7·2
H(C7)	0·221 (6)	0·30 (3)	0·610 (4)	9·4
H(C8)	−0·092 (5)	0·15 (3)	0·659 (4)	8·0
H(C9)	0·000 (5)	0·13 (3)	0·697 (4)	8·3
H(C11)	0·062 (4)	0·11 (3)	0·588 (4)	7·9
H(C12)	−0·017 (6)	0·24 (3)	0·546 (5)	9·9
H(N1)	0·399 (6)	0·24 (3)	0·592 (5)	8·4
H1(N2)	0·110 (6)	−0·29 (3)	0·642 (5)	8·8
H2(N2)	0·087 (5)	−0·40 (3)	0·678 (3)	8·8
H1(O3)	0·321 (5)	0·59 (3)	0·624 (4)	9·1
H2(O3)	0·313 (6)	0·84 (3)	0·666 (5)	9·1

* Lists of structure factors, anisotropic thermal parameters and mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38212 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

respectively, both shorter than the C_{ar}—N distance of 1·43 Å (*International Tables for X-ray Crystallography*, 1968), reflect their partial double-bond character (Chao & Schempp, 1977). The ionic character of the salicylaldehyde molecules is reflected in the short C(2)—O(2) distance.

Table 2. *Short intermolecular distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

A—$B\cdots C$	$A\cdots C$	$B\cdots C$	$\angle ABC$
$N(1A)$—$H(N1A^{i})\cdots O(2A^{iv})$	2·70 (2)	1·8 (1)	163 (10)
$N(1B)$—$H(N1B^{iv})\cdots O(2B^{i})$	2·75 (2)	1·7 (1)	153 (12)
$N(2A)$—$H2(N2A^{iii})\cdots O(1A^{i})$	2·87 (2)	1·8 (1)	164 (9)
$N(2B)$—$H1(N2B^{ii})\cdots O(1B^{i})$	2·99 (2)	1·9 (1)	164 (10)
$O(3A)$—$H1(O3A^{ii})\cdots O(2A^{i})$	2·64 (1)	1·6 (1)	160 (10)
$O(3B)$—$H1(O3B^{i})\cdots O(2B^{i})$	2·75 (2)	1·8 (1)	170 (11)
$N(2A)$—$H1(N2A^{i})\cdots O(3B^{v})$	2·85 (1)	2·0 (1)	145 (10)
$O(3B)$—$H2(O3B^{v})\cdots N(2A^{i})$		2·3 (1)	145 (14)
$N(2B)$—$H2(N2B^{v})\cdots O(3A^{iv})$	2·91 (2)	2·1 (1)	125 (8)
$O(3A)$—$H2(O3A^{iv})\cdots N(2B^{v})$		2·3 (1)	149 (14)
$Cl(2A^{i})\cdots Cl(2B^{ii})$		3·805 (8)	
$Cl(1A^{iv})\cdots Cl(2B^{i})$		5·058 (7)	
$Cl(2A^{i})\cdots Cl(1B^{vi})$		4·095 (7)	

Symmetry code
(i) x,y,z (iv) $\frac{1}{2}+x,\frac{1}{2}-y,z$
(ii) $x,1+y,z$ (v) $\frac{1}{2}-x,\frac{1}{2}+y,z-\frac{1}{2}$
(iii) $x,y-1,z$ (vi) $x-\frac{1}{2},\frac{1}{2}-y,z$

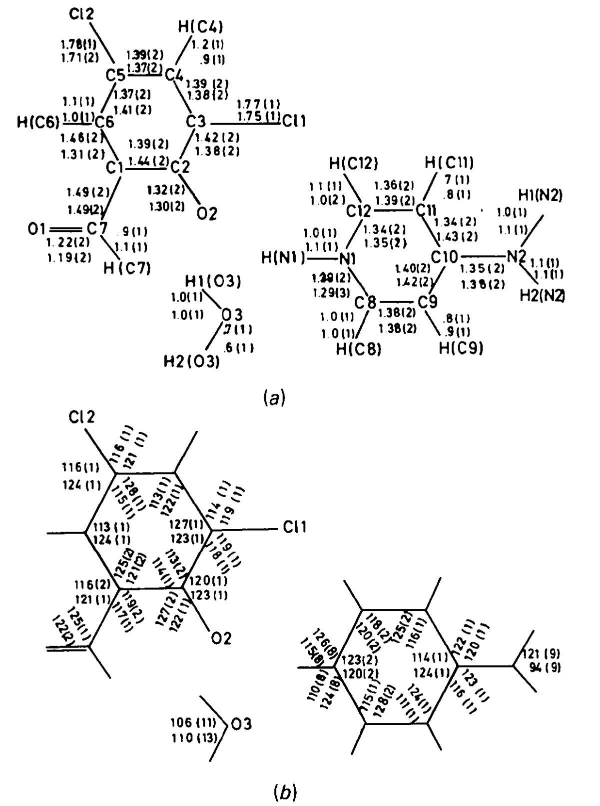

Fig. 2. (*a*) Bond lengths (Å) and atom numbering system; (*b*) angles (°). E.s.d.'s are in parentheses. The upper values correspond to molecules *A* and the lower to molecules *B*.

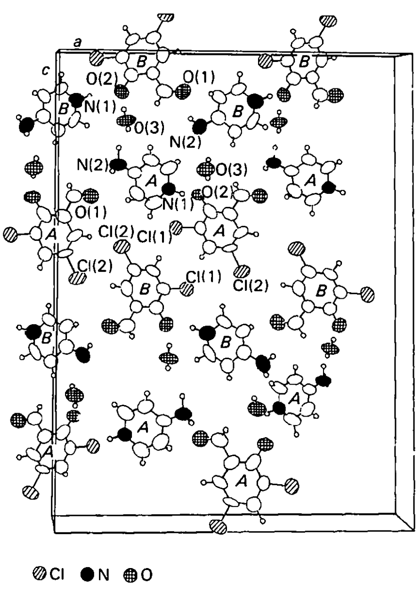

Fig. 1. Projection of the crystal structure along **b** (Johnson, 1965).

The very extensive net of H bonds involving all six molecules of the asymmetric unit forms a dimer-like arrangement. The H bonds between the charged atoms N(1) and O(2) and also the H bonds of O(2) to the water molecule and that of the carbonyl O(1) to the NH_2 group are very strong (Fig. 1 and Table 2). The water molecule and the NH_2 group act as both hydrogen donors and acceptors forming longer H bonds. This constraint may cause the N(2)···H—O(3) and O(3)···H—N(2) angles to deviate strongly from the expected value of ~ 180° (Ölovsson & Jönsson, 1976).

The aldehyde and 4-aminopyridine molecules are in an appropriate relative geometry to react and form the Schiff base. The N(2)···O(1) distances are 2·87 (2) and 3·00 (2) Å and the dihedral angles between the ring planes are 14 (1) and 19 (1)° for *A* and *B* respectively. However, the resulting Schiff base will not have the OH group close to the bridge N atom and consequently no internal H bond will be formed. Therefore, concomitant with the removal of a water molecule a rotation of the aldehydic moiety about the C(1)—C(7) bond should take place to give a Schiff base of the known geometry (Moustakali-Mavridis *et al.*, 1978, 1980).

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14β-Hydroxysteroide. VII.* 14β-Hydroxyhecogeninacetat,† $C_{29}H_{44}O_6$

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Abstract. $M_r = 488{\cdot}67$, monoclinic, $P2_1$, $a = 13{\cdot}248\,(10)$, $b = 6{\cdot}762\,(7)$, $c = 16{\cdot}09\,(4)$ Å, $\beta = 108{\cdot}9\,(1)°$, $V = 1363{\cdot}7$ Å^3, $D_x = 1{\cdot}190$, $D_m = 1{\cdot}16$ g cm^{-3} (in an aqueous solution of K_2HgI_4), $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}762$ cm^{-1}, $F(000) = 532$, $T = 295$ K, $R_w = 3{\cdot}4\%$ (1260 reflections). The 13β-methyl and 14β-hydroxy configuration of the steroid was confirmed.

Einleitung. Das 12-Oxosteroid Hecogeninacetat (mit *trans*-verknüpften Ringen *C* und *D*) lagert sich photochemisch durch α-Spaltung und Wasserstoffverschiebung von C(14) nach C(12) in einen ungesättigten Secoaldehyd um, aus dem durch intramolekulare Prins-Reaktion und anschliessende Oxidation 14β-Hydroxyhecogeninacetat (mit *cis*-verknüpften Ringen *C* and *D*) entsteht (Bladon, McMeekin & Williams, 1963; Welzel, Janssen & Duddeck, 1981; Welzel, 1981). Diese bequeme Methode zur 14β-Hydroxylierung ist kürzlich bei der Synthese medizinisch wichtiger Cardenolide angewendet worden (Welzel & Stein, 1981; Milkova, Stein, Ponty, Böttger & Welzel, 1982). Wir beschreiben hier die Röntgenstrukturanalyse des 14β-Hydroxyhecogeninacetats.

* 14β-Hydroxysteroide VI: Milkova, Stein, Ponty, Böttger & Welzel (1982).
† (25*R*)-3β-Acetoxy-14β-hydroxy-12-oxo-5α-spirostan.

Experimentelles. Der verwendete Einkristall (0,16 × 0,11 × 0,10 mm) wurde zum Schutz und zur besseren Handhabung in ein Markröhrchen eingeschmolzen. Es war nicht möglich, ein besseres Kristallmaterial zu erhalten. Rechnergesteuertes Einkristalldiffraktometer der Firma Siemens (Hoppe, 1965; Kobelt & Paulus, 1979); Mo $K\alpha$-Strahlung; $\theta_{max} = 28°$; 3530 unabhängige Reflexe, davon 1794 mit $I > \sigma(I)$; direkte Phasenbestimmung (Germain, Main & Woolfson, 1970; Germain & Woolfson, 1968). Nach anfänglichen Schwierigkeiten war es möglich geworden mit dem Programmsystem *SHELXTL* (Sheldrick, 1981) zum Ziele zu kommen: Die Phasen von 12 Reflexen wurden permutiert, was 864 Phasensätze gab. In der '*E* map' aus dem Phasensatz mit den besten 'figures of merit' liessen sich 27 Atome chemisch sinnvoll zuordnen, die restlichen acht Atome konnten mit sukzessiven '*E* maps' nach dem Kriterium eines minimalen *R*-Wertes ('*FIND* routine' in *SHELXTL*) mühelos gefunden werden. Die Atomparameterverfeinerung wurde mit der Methode der Kleinsten-Quadrate durchgeführt. Die Atomformfaktoren wurden den *International Tables for X-ray Crystallography* (1974) entnommen. Nur 1260 Reflexe mit Intensitätswerten grösser als vier Standardabweichungen wurden zur Verfeinerung herangezogen. Es war nicht möglich, die Wasserstoffatomlagen einer Differenzfouriersynthese der Elektronendichte zu entnehmen, was bei dem relativ schlechten erhaltbaren Kristallmaterial nicht weiter

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