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The Crystal and Molecular Structures of Two Pyridine Derivatives: 1-(2',6'-Dichlorobenzyl)-2-pyridone and 1-(2',6'-Dichlorobenzyl)-2-ethoxypyridinium Fluoroborate

By George L. Wheeler and Herman L. Ammon

Department of Chemistry, University of Maryland, College Park, Maryland 20742, *U.S.A.*

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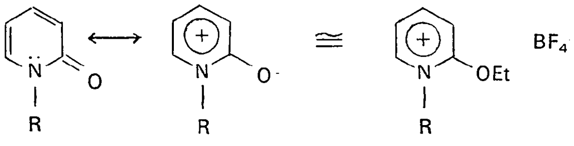
1-(2',6'-Dichlorobenzyl)-2-pyridone (I), $C_{12}H_9Cl_2NO$, crystallizes in the triclinic space group $P\bar{1}$: $a=9{\cdot}680$ (1), $b=8{\cdot}310$ (2), $c=8{\cdot}464$ (5) Å, $\alpha=118{\cdot}25$ (1), $\beta=78{\cdot}72$ (1) $\gamma=110{\cdot}82$ (2)°, $Z=2$. 1-(2',6'-Dichlorobenzyl)-2-ethoxypyridinium fluoroborate (II), $C_{14}H_{14}Cl_2NOBF_4$, crystallizes in the monoclinic space group $P2_1/c$: $a=10{\cdot}617$ (1), $b=10{\cdot}825$ (4), $c=15{\cdot}395$ (3) Å, $\beta=106{\cdot}76$ (1)°, $Z=4$. Mo $K\alpha$ intensity data were measured with a computer-controlled diffractometer and the initial phases were obtained by direct methods. The structures were refined by the full-matrix least-squares method with anisotropic temperature factors for the C, N, O, Cl, B and F atoms and isotropic terms for the H atoms. The final R values were 0·045 for the pyridone (I) and 0·069 for the pyridinium salt (II). The pyridone and pyridinium rings are inclined at angles of 85° and 87° to their respective dichlorobenzyl rings. The fluoroborate anion shows a twofold disorder. A comparison of bond lengths in the pyridinium and pyridone 6-rings indicates that π-delocalization is relatively small in the latter. Bond lengths in 1-hydro-2-pyridones (H on N) suggest that π-delocalization is slightly more extensive than in the 1-dichlorobenzyl derivative (I). The difference may arise from intermolecular H-bonding effects in the 1-hydro compounds.

Introduction

Although the extent of π-electron delocalization in 2-pyridones has been studied by spectroscopic and theoretical means, no totally satisfactory determination is available. Previous estimates of π-delocalization of 2-pyridone are in wide disagreement, varying from little or no delocalization (Ohtsuru, Tori & Watanabe, 1967) to a resonance energy of 25 kcal m^{-1} (Cook, Katritzky, Linda & Track, 1972). We have attempted to evaluate the degree of π-delocalization in 2-pyridones from structural data by studying a 1-alkyl-2-pyridone (I) ($R=2,6\text{-}Cl_2C_2H_3CH_2$) and a 1-alkyl-2-ethoxypyridinium salt (II).

The pyridinium compound was investigated as a structural model for the pyridinium oxide form (I*b*).



(I) (I*b*) (II)

The cation in (II) should be a satisfactory model for (I*b*) because of its positive charge and electron withdrawing group at C(2).

A second reason for these investigations was to provide structural benchmarks for the heterocyclic ring in the pseudoaromatic fulvalene, 1-benzyl-2-cyclopentadienylidene-1,2-dihydropyridine. This work will be the subject of a future paper.

Experimental

Compound preparation

The *N*-2,6-dichlorobenzyl substituent was used to enhance the compounds' crystallinity. Other derivatives, *viz*. *N*-alkyl and *N*-benzyl, are either liquids at room temperature or low-melting solids.

1-(2',6'-Dichlorobenzyl)-2-pyridone (I) was prepared from 1-(2',6'-dichlorobenzyl)pyridinium bromide (Krohnke, Ellegast & Bertram, 1956) by the general oxidation reaction reviewed by Abramovitch & Saha (1966). Two solutions, KOH (113 g, 2·0 mol in 330 ml H_2O) and $K_3Fe(CN)_6$ (210 g, 1·5 mol in 500 ml H_2O) were added simultaneously with vigorous stirring to a solution of the pyridinium salt (95 g, 0·3 mol in 500 ml H_2O) over a period of one half hour. The reaction mixture was extracted with chloroform, and evaporation of the solvent *in vacuo* left a black tar. A clear crystalline modification was obtained from the tar by repeated extraction with hot cyclohexane and treatment with charcoal; yield 15 g (20%), m.p. 115–6°C. The product structure was verified by n.m.r. and elemental analysis.

1-(2',6'-Dichlorobenzyl)-2-ethoxypyridinium fluoroborate (II) was prepared by the reaction of (I) with triethyloxonium fluoroborate (Meerwein, 1966). The alkylating agent (3·8 g, 0·02 mol) was added under nitrogen to a solution of the pyridone (5 g, 0·02 mol in 20 ml CH_2Cl_2), and stirred overnight at room temperature. Evaporation of the solvent *in vacuo* left a yellow solid which was recrystallized from nitrobenzene–ethyl ether, yielding 6·8 g (92%) of the salt, m.p. 151–2°. The structure was confirmed by n.m.r.

General X-ray diffraction

The Laue symmetry, space group and approximate lattice constants for each material were determined by a preliminary oscillation and Weissenberg photographic survey. Final cell parameters and intensity measurements were made on a Picker FACS-I diffractometer with Mo radiation and a highly oriented graphite monochromator (Mo $K\alpha=0\cdot71069$ Å, monochromator $2\theta=12\cdot16°$). Lenhert & Henry's (1970) PDP-8I dis-oriented program system was used for diffractometer control. Cell constants were calculated by least squares from 2θ's determined by manual measurement of $\pm 2\theta$ for each reflection. Intensity data were collected with the θ–2θ scan method and with two background measurements. Foil attenuators were automatically inserted to keep the maximum count rate below *ca.* 15000 counts s^{-1}. The reflection intensities (I) and standard deviations [$\sigma(I)$] were calculated from the following equations:

$$I=SA[I_s-K(I_{b1}+I_{b2})]\,,$$

and

$$\sigma(I)=\{S^2A^2[I_s+K^2(I_{b1}+I_{b2})]+DC^2\}^{1/2},$$

where I_s is the scan intensity, I_{b1} and I_{b2} are the backgrounds, K is the ratio (scan time)/(total background time), A is the attenuator factor, $C=I_s+I_{b1}+I_{b2}$, D is the instability factor (Stout & Jensen, 1968) and S is the reflection scale factor. D and S were evaluated from standard intensity measurements. Additional corrections were made for Lp; absorption corrections were not made. Crystal and intensity measurement data for the two compounds are summarized in Table 1.

The major crystallographic calculations were done on the University of Maryland's UNIVAC 1108 with the X-RAY System of Crystallographic Programs (1972).

Structure determinations

The structure of 1-(2',6'-dichlorobenzyl)-2-pyridone (I) was solved by direct methods. 46 phases determined by the direct method's program *PHASE* (X-RAY System, 1972) were expanded to 398 phases by tangent refinement. An E map computed with these terms revealed all of the C, N, O and Cl atoms.

The structure of 1-(2',6'-dichlorobenzyl)-2-ethoxypyridinium fluoroborate (II) was solved by direct methods with 677 phases determined by *PHASE*. The resulting E map contained the BF$_4$ tetrahedron and the dichlorobenzyl ring along with many smaller and less interpretable peaks. Electron density and difference electron density maps based on this partial structure revealed the remaining atoms along with an additional tetrahedron of F atoms about the B position. The peaks of the second tetrahedron were all somewhat smaller than those of the first, forming a hexahedral arrangement of eight peaks centered on the boron.

Refinement

Both structures were refined by full-matrix least squares with anisotropic temperature factors applied to the C, N, O, Cl, B and F atoms. The function minimized was $\sum 1/\sigma^2(F_o)\,(F_o-F_c)^2$. The data less than $3\sigma(I_o)$ were included in the calculation only where $I_c>3\sigma(I_o)$. The F_c's were corrected for isotropic secondary extinction [r^*; equation 22, Larson (1970)]. In Tables 2 and 3 the form of the anisotropic t.f.'s is $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots 2U_{23}klb^*c^*)$.†

For (I), the hydrogen atoms were located in a difference electron density map and refined with isotropic t.f.'s. H(3) behaved erratically during refinement, and it was finally fixed at its original difference-map position with $B=9\cdot0$ Å^2. The atomic parameters are pre-

Table 1. *Crystal data and data collection*

	1-(2',6'-Dichlorobenzyl)-2-pyridone (I)	1-(2',6'-Dichlorobenzyl)-2-ethoxypyridinium tetrafluoroborate (II)
Molecular formula	$C_{12}H_9Cl_2NO$	$C_{14}H_{14}Cl_2NOBF_4$
Crystallization solvent	Cyclohexane	Chloroform
Crystal size	Plate 0·4 × 0·4 × 0·2 mm	Needle 0·2 × 0·4 mm
Space group	$P\bar{1}$	$P2_1/c$
Unit-cell parameters (e.s.d.'s)	$a=9\cdot680$ (1), $b=8\cdot310$ (2), $c=8\cdot464$ (5) Å $\alpha=118\cdot25$ (1), $\beta=78\cdot72$ (1), $\gamma=110\cdot82$ (2)°	$a=10\cdot617$ (1), $b=10\cdot825$ (4), $c=15\cdot395$ (3) Å $\beta=106\cdot76$ (1)°
Average of $\lvert 2\theta_o-2\theta_c\rvert$	0·002° (for 17 reflections)	0·004° (for 14 reflections)
Z	2	4
V	560 Å^3	1694 Å^3
ϱ_{meas} (neutral buoyancy in aqueous KI)	1·512 g cm^{-3}	1·465 g cm^{-3}
$\varrho_{\text{X-ray}}$	1·506 g cm^{-3}	1·450 g cm^{-3}
Reciprocal lattice vector parallel to diffractometer φ axis	[2, −2,6]	[0,4,0]
2θ scan	2·7° at 1° min^{-1}	2·0° at 0·5° min^{-1}
Time for each background	40 s	40 s
Maximum 2θ ($\sin\theta/\lambda$)	55° (0·6497)	50° (0·5947)
Instability factor (D)	$3\cdot345\times10^{-5}$	$2\cdot618\times10^{-3}$
Total unique data (observed, 3σ above background)	2568 (2031)	2978 (2148)

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† The structure-factor tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30271 (51 pp., 1 microfiche). Copies of the tables may be obtained through the Executive Secretary, International Union of Crystallography 13 White Friars, Chester CH1 1NZ, England.

sented in Table 2. The final R ($\sum|F_o-F_c|/\sum F_o$) and weighted R [$\sum w(F_o-F_c)^2/\sum wF_o^2$, $w=1/\sigma^2(F_o)$] values were 0·045 and 0·038.

The two F tetrahedra in (II) can be readily interpreted as a disorder of the BF_4 moiety. Following initial refinement with anisotropic t.f.'s for C, N, O, B and F and with equal weights (0·5) assigned to the eight F atoms, a second round of refinement restricted the

Table 2. *Fractional coordinates, thermal parameters* (Å^2) *and e.s.d.'s* (*in parentheses*) *for* 1-(2',6'-*dichlorobenzyl*)-2-*pyridone*

$r^* = 0·00374$ (7)

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(2)	0·9983 (3)	0·1180 (4)	0·7985 (4)	0·042 (2)	0·058 (2)	0·061 (2)	0·029 (1)	0·002 (2)	0·022 (2)
C(3)	1·0147 (4)	−0·0702 (5)	0·7383 (5)	0·069 (2)	0·071 (2)	0·095 (3)	0·041 (2)	0·001 (2)	0·036 (2)
C(4)	0·9227 (4)	−0·2320 (5)	0·6208 (5)	0·065 (2)	0·049 (2)	0·085 (3)	0·034 (2)	0·018 (2)	0·025 (2)
C(5)	0·8059 (4)	−0·2243 (5)	0·5547 (5)	0·062 (2)	0·042 (2)	0·058 (2)	0·016 (2)	0·001 (2)	0·005 (2)
C(6)	0·7826 (3)	−0·0558 (4)	0·6123 (4)	0·055 (2)	0·049 (2)	0·050 (2)	0·021 (2)	−0·005 (2)	0·008 (2)
C(7)	0·8388 (3)	0·2927 (4)	0·7951 (4)	0·033 (1)	0·038 (2)	0·044 (2)	0·013 (1)	−0·002 (1)	0·016 (1)
C(1*A*)	0·6813 (3)	0·2768 (3)	0·8664 (3)	0·034 (1)	0·028 (1)	0·036 (1)	0·012 (1)	−0·003 (1)	0·010 (1)
C(2*A*)	0·5719 (3)	0·2674 (3)	0·7749 (3)	0·039 (1)	0·037 (1)	0·038 (2)	0·014 (1)	−0·004 (1)	0·014 (1)
C(3*A*)	0·4275 (3)	0·2556 (4)	0·8433 (4)	0·035 (2)	0·048 (2)	0·057 (2)	0·016 (1)	−0·009 (1)	0·016 (2)
C(4*A*)	0·3908 (3)	0·2511 (4)	1·0057 (5)	0·031 (2)	0·053 (2)	0·069 (2)	0·015 (1)	0·009 (2)	0·022 (2)
C(5*A*)	0·4943 (3)	0·2599 (4)	1·1016 (4)	0·057 (2)	0·052 (2)	0·045 (2)	0·020 (2)	0·012 (2)	0·023 (2)
C(6*A*)	0·6367 (3)	0·2728 (3)	1·0312 (3)	0·045 (2)	0·037 (1)	0·038 (2)	0·018 (1)	−0·002 (1)	0·015 (1)
N	0·8727 (2)	0·1114 (3)	0·7343 (3)	0·033 (1)	0·038 (1)	0·042 (1)	0·017 (1)	−0·002 (1)	0·009 (1)
O	1·0814 (2)	0·2703 (3)	0·8994 (3)	0·040 (1)	0·057 (1)	0·081 (2)	0·018 (1)	−0·021 (1)	0·014 (1)
Cl(2*A*)	0·61297 (8)	0·2716 (1)	0·5666 (1)	0·0593 (5)	0·0763 (6)	0·0491 (5)	0·0214 (4)	−0·0080 (4)	0·0321 (4)
Cl(6*A*)	0·76674 (9)	0·2862 (1)	1·1571 (1)	0·0717 (5)	0·0683 (5)	0·0461 (5)	0·0328 (4)	−0·0094 (4)	0·0240 (4)
H(3)	1·109	−0·054	0·796	0·114					
H(4)	0·934 (3)	−0·358 (4)	0·578 (4)	0·07 (1)					
H(5)	0·741 (3)	−0·328 (4)	0·476 (4)	0·054 (9)					
H(6)	0·698 (3)	−0·035 (4)	0·568 (4)	0·059 (9)					
H(3*A*)	0·361 (3)	0·252 (4)	0·774 (4)	0·050 (8)					
H(4*A*)	0·297 (3)	0·240 (3)	1·043 (3)	0·049 (8)					
H(5*A*)	0·463 (3)	0·250 (4)	1·209 (4)	0·056 (9)					
H(7*A*)	0·864 (3)	0·331 (4)	0·693 (4)	0·059 (9)					
H(7*B*)	0·911 (3)	0·403 (4)	0·897 (4)	0·054 (9)					

Table 3. *Fractional coordinates, thermal parameters* (Å) *and e.s.d.'s* (*in parentheses*) *for* 1-(2',6'-*dichlorobenzyl*)-2-*ethoxypyridinium fluoroborate*

$r^* = 0·0240$ (4)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(2)	0·8025 (5)	0·3268 (5)	0·4367 (3)	0·053 (3)	0·065 (4)	0·063 (3)	−0·008 (3)	0·015 (3)	0·004 (3)
C(3)	0·8602 (5)	0·4058 (5)	0·3864 (3)	0·075 (4)	0·077 (4)	0·076 (4)	−0·021 (3)	0·026 (3)	0·016 (3)
C(4)	0·9229 (6)	0·3536 (6)	0·3286 (4)	0·074 (4)	0·112 (5)	0·075 (4)	−0·028 (4)	0·026 (3)	0·019 (4)
C(5)	0·9287 (5)	0·2268 (7)	0·3186 (4)	0·074 (4)	0·112 (5)	0·074 (4)	−0·010 (4)	0·041 (3)	0·002 (4)
C(6)	0·8681 (5)	0·1513 (5)	0·3667 (3)	0·063 (3)	0·085 (4)	0·071 (3)	−0·002 (3)	0·031 (3)	−0·007 (3)
C(7)	0·7459 (4)	0·1175 (4)	0·4786 (3)	0·058 (3)	0·050 (3)	0·070 (3)	−0·001 (2)	0·031 (3)	0·013 (2)
C(8)	0·7461 (7)	0·4890 (5)	0·5222 (4)	0·140 (6)	0·052 (4)	0·115 (5)	−0·018 (4)	0·059 (5)	−0·018 (3)
C(9)	0·6897 (9)	0·4943 (5)	0·6011 (4)	0·242 (9)	0·063 (4)	0·128 (6)	−0·006 (5)	0·106 (6)	−0·018 (4)
C(1*A*)	0·5997 (4)	0·1389 (4)	0·4647 (3)	0·060 (3)	0·038 (3)	0·059 (3)	−0·008 (2)	0·024 (2)	0·004 (2)
C(2*A*)	0·5055 (5)	0·1289 (4)	0·3822 (3)	0·071 (3)	0·058 (3)	0·060 (3)	−0·007 (3)	0·026 (3)	0·010 (3)
C(3*A*)	0·3711 (5)	0·1479 (5)	0·3695 (4)	0·063 (3)	0·058 (3)	0·098 (4)	−0·006 (3)	0·013 (3)	0·023 (3)
C(4*A*)	0·3324 (5)	0·1754 (5)	0·4472 (4)	0·072 (4)	0·058 (3)	0·131 (5)	0·007 (3)	0·054 (4)	0·020 (3)
C(5*A*)	0·4208 (5)	0·1819 (4)	0·5310 (3)	0·070 (4)	0·054 (3)	0·093 (4)	0·000 (3)	0·040 (3)	0·002 (3)
C(6*A*)	0·5519 (5)	0·1657 (4)	0·5391 (3)	0·069 (4)	0·041 (3)	0·070 (3)	−0·007 (3)	0·028 (3)	0·000 (2)
B	0·1040 (6)	0·2782 (7)	0·1293 (5)	0·012 (4)	0·032 (4)	0·024 (4)	0·000 (4)	0·012 (3)	−0·001 (4)
N	0·8040 (3)	0·2028 (4)	0·4238 (2)	0·051 (2)	0·060 (3)	0·060 (2)	−0·005 (2)	0·023 (2)	0·006 (2)
O	0·7420 (3)	0·3603 (3)	0·4965 (2)	0·078 (2)	0·051 (2)	0·083 (2)	−0·012 (2)	0·040 (2)	−0·006 (2)
F(1*A*)	0·0059 (7)	0·1975 (8)	0·1202 (5)	0·097 (5)	0·127 (7)	0·129 (6)	−0·036 (5)	0·024 (4)	0·011 (5)
F(2*A*)	0·2156 (8)	0·2144 (8)	0·1390 (7)	0·113 (6)	0·146 (7)	0·200 (8)	0·024 (5)	0·062 (6)	0·026 (6)
F(3*A*)	0·0879 (8)	0·3494 (7)	0·0554 (5)	0·142 (6)	0·120 (6)	0·114 (5)	−0·019 (6)	0·020 (5)	0·038 (5)
F(4*A*)	0·115 (1)	0·3485 (8)	0·1983 (6)	0·24 (1)	0·156 (7)	0·140 (7)	−0·072 (8)	0·116 (8)	−0·062 (6)
F(1*B*)	0·009 (1)	0·359 (1)	0·1340 (9)	0·073 (7)	0·113 (9)	0·120 (9)	0·039 (7)	0·013 (7)	0·008 (7)
F(2*B*)	0·220 (1)	0·331 (1)	0·1697 (9)	0·093 (9)	0·16 (1)	0·13 (1)	−0·011 (9)	0·022 (7)	−0·047 (9)
F(3*B*)	0·099 (1)	0·245 (2)	0·0468 (8)	0·14 (1)	0·17 (1)	0·068 (7)	−0·01 (1)	0·037 (7)	−0·022 (9)
F(4*B*)	0·093 (2)	0·178 (1)	0·1764 (9)	0·18 (1)	0·078 (7)	0·14 (1)	0·045 (9)	0·10 (1)	0·037 (8)
Cl(2*A*)	0·5535 (1)	0·0845 (2)	0·28707 (9)	0·096 (1)	0·126 (1)	0·0603 (8)	−0·025 (1)	0·0299 (8)	−0·0100 (8)
Cl(6*A*)	0·6591 (1)	0·1742 (1)	0·64721 (8)	0·107 (1)	0·084 (1)	0·0617 (8)	−0·0204 (9)	0·0341 (8)	−0·0102 (7)

Table 3 (*cont.*)

	x	*y*	*z*	*U*
H(3)	0·856	0·502	0·393	0·150
H(4)	0·967	0·412	0·291	0·150
H(5)	0·978	0·189	0·275	0·150
H(6)	0·872	0·054	0·360	0·150
H(3*A*)	0·302	0·142	0·305	0·150
H(4*A*)	0·233	0·191	0·442	0·150
H(5*A*)	0·390	0·199	0·589	0·150
H(7*A*)	0·760	0·024	0·461	0·150
H(7*B*)	0·796	0·133	0·550	0·150
H(8*A*)	0·836	0·541	0·546	0·150
H(8*B*)	0·676	0·543	0·471	0·150
H(9*A*)	0·750	0·554	0·653	0·200
H(9*B*)	0·768	0·509	0·663	0·200
H(9*C*)	0·762	0·460	0·661	0·200
H(9*D*)	0·733	0·421	0·648	0·200
H(9*E*)	0·689	0·402	0·628	0·200
H(9*F*)	0·641	0·407	0·605	0·200
H(9*G*)	0·603	0·437	0·587	0·200
H(9*H*)	0·584	0·481	0·577	0·200
H(9*I*)	0·590	0·530	0·579	0·200
H(9*J*)	0·619	0·569	0·591	0·200
H(9*K*)	0·664	0·588	0·612	0·200
H(9*L*)	0·711	0·583	0·634	0·200

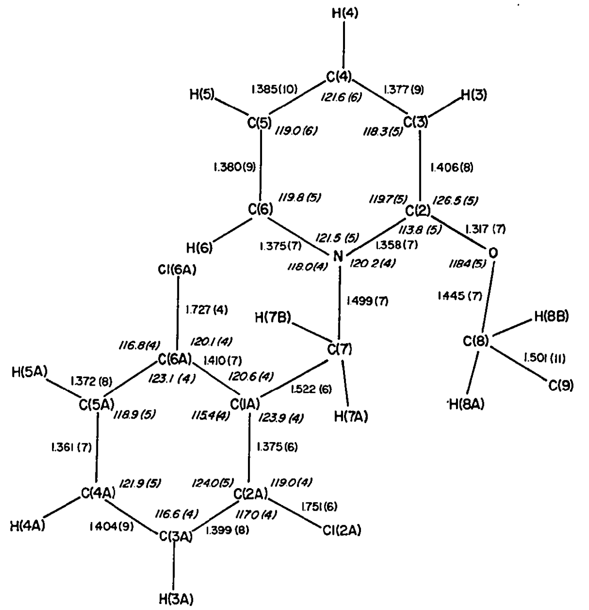


Fig. 2. Bond lengths (Å) and angles (°) for the 1-(2′,6′-dichlorobenzyl)-2-ethoxypyridinium cation. E.s.d.'s in parentheses. The fluoroborate quantities are given in Table 4.

populations of the two tetrahedra to *P* [for F(1*A*), F(2*A*), F(3*A*), F(4*A*)] and 1 − *P* [for F(1*B*), F(2*B*), F(3*B*), F(4*B*)]. A difference electron density map revealed several questionable hydrogen peaks and the methyl hydrogens appeared to be smeared together. This result, together with the relatively high t.f. of the methyl carbon C(9) suggested that the H's were disordered, and the methyl hydrogens were subsequently treated as a circle of 12 hydrogens (C–H = 1·08 Å), each with a population of 0·25 and isotropic t.f. (*U*) of 0·20 Å^2. The remaining H positions were calculated (C–H = 1·05 Å) from the heavy-atom positions and fixed with *U*'s of 0·15 Å^2. The final *R* and weighted *R* values are 0·069 and 0·068. The atomic parameters are presented in Table 3.

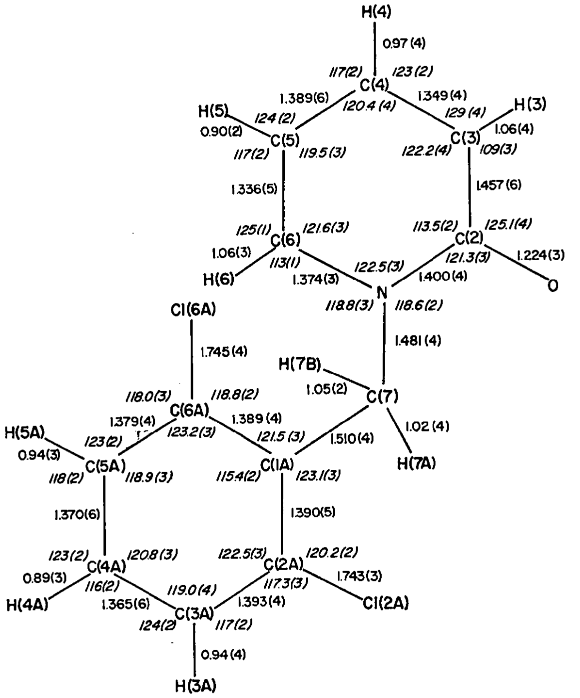


Fig. 1. Bond lengths (Å) and angles (°) for 1-(2′,6′-dichlorobenzyl)-2-pyridone. E.s.d.'s in parentheses.

Scattering factors for C, N, O, Cl, B and F were calculated from the analytical expressions of Cromer & Mann (1968). The hydrogen scattering factors were taken from the work of Stewart, Davidson & Simpson (1965).

Discussion

Bond distances and angles for the two structures are given in Figs. 1 and 2 and in Table 4. The two heterocyclic 6-rings and the two phenyl rings are individually planar (Tables 5 and 6), and the phenyl planes are inclined at angles of 85 and 87°, respectively, to the pyridone and pyridinium rings.

Table 4. BF_4^- *bond lengths and angles in* (II)

B–F(1*B*)	1·35 (1) Å	B–F(1*A*)	1·34 (1) Å
B–F(2*B*)	1·34 (1)	B–F(2*A*)	1·34 (1)
B–F(3*B*)	1·31 (1)	B–F(3*A*)	1·34 (1)
B–F(4*B*)	1·33 (1)	B–F(4*A*)	1·28 (1)
F(1*B*)–B–F(2*B*)	107 (1)°	F(1*A*)–B–F(2*A*)	108·2 (7)°
F(1*B*)–B–F(4*B*)	108 (1)	F(1*A*)–B–F(4*A*)	110·8 (9)
F(1*B*)–B–F(3*B*)	114 (1)	F(1*A*)–B–F(3*A*)	112·4 (6)
F(2*B*)–B–F(3*B*)	110 (1)	F(2*A*)–B–F(3*A*)	106·4 (8)
F(2*B*)–B–F(4*B*)	108 (1)	F(2*A*)–B–F(4*A*)	110·3 (8)
F(3*B*)–B–F(4*B*)	109 (1)	F(3*A*)–B–F(4*A*)	108·6 (7)

Table 5. *Least-squares planes in* 1-(2′,6′-*dichlorobenzyl*)-2-*pyridone* (I)

	Plane 1	Plane 2
N	0·027 Å*	−1·294 Å
C(2)	−0·032*	−1·321
C(3)	0·015*	−2·668
C(4)	0·010*	−3·762
C(5)	−0·018*	−3·637
C(6)	−0·001*	−2·427
C(7)	0·071	0·015
O	−0·081	−0·290
C(1*A*)	1·212	−0·004*
C(2*A*)	1·028	−0·002*
C(3*A*)	2·088	0·004*
C(4*A*)	3·360	−0·002*
C(5*A*)	3·599	−0·001*
C(6*A*)	2·530	0·002*
Cl(2*A*)	−0·576	−0·002
Cl(6*A*)	2·860	0·020

Plane 1 (pyridone ring):
$-3{\cdot}8454X-2{\cdot}7882Y+6{\cdot}8917Z=1{\cdot}3673$
Plane 2 (phenyl ring):
$-0{\cdot}6105X+7{\cdot}0926Y+0{\cdot}0218Z=1{\cdot}5666$

* Atoms used to define the least-squares planes.

Table 6. *Least-squares planes in* 1-(2′,6′-*dichlorobenzyl*)-2-*ethoxypyridinium fluoroborate* (II)

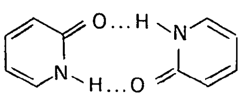
	Plane 1	Plane 2
N	−0·017 Å*	1·135 Å
C(2)	0·021*	2·408
C(3)	−0·009*	3·480
C(4)	−0·006*	3·194
C(5)	0·011*	1·890
C(6)	0·001*	0·856
C(7)	0·050	−0·018
O	0·058	2·494
C(8)	0·236	3·788
C(9)	0·467	3·528
C(1*A*)	−1·105	0·010*
C(2*A*)	−4·428	−0·014*
C(3*A*)	−3·491	0·004*
C(4*A*)	−3·153	0·011*
C(5*A*)	−1·858	−0·014*
C(6*A*)	−0·859	0·004*
Cl(2*A*)	−2·833	−0·136
Cl(6*A*)	0·763	−0·039

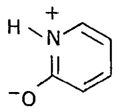
Plane 1 (pyridinium ring):
$7{\cdot}0733X-0{\cdot}4434Y+8{\cdot}0201Z=9{\cdot}0129$
Plane 2 (phenyl ring):
$1{\cdot}6271X+10{\cdot}5788Y-2{\cdot}8410Z=1{\cdot}1149$

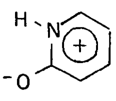
* Atoms used to define the least-squares planes.

A comparison of bond lengths in several pyridones and pyridinium derivatives is outlined in Table 7. The short-long-short pattern of bond distances in the C=C–C=C portion of (I), 5-chloro-2-pyridone and 2-pyridone indicates an appreciable degree of π-bond localization. The C=C lengths, C(3)–C(4) and C(5)–C(6), are close to the 1·34 Å, ethylenic value. Compared to these almost normal double-bond lengths, the C(4)–C(5) distances, average 1·40 Å, seem short for Csp^2–Csp^2 single bonds. The corresponding distances in the pyridinium ring of (II), 1·377–1·385–1·380 Å, are almost equal to each other, and show none of the pyridone-like alternation.

There is a fairly distinct difference between the N–C(2) and C(2)–O distances in (I) and the corresponding lengths in 5-chloro-2-pyridone and 2-pyridone (column 2). The formation of hydrogen-bonded dimers, similar to (III) in the crystals of the latter two compounds provides a mechanism for stabilization of the dipolar resonance form (IV). This kind of stabilization can not occur in (I) because the N's substituent is benzyl, not hydrogen. The comparatively long N–C(2) and short C(2)–O reflect the predominance of the nonpolar N–C=O form for the amide moiety in (I). There may also be some slight enhancement of the delocalized, dipolar form (V) in 5-chloro-2-pyridone and 2-pyridone compared to (I), suggested by the shorter C(6)–N and C(2)–C(3) distances, but there is no obvious effect on the C=C–C=C distances. Almlöf, Kvick & Olovsson (1971) performed CNDO calculations on the 2-pyridone monomer and dimer. Their data show a change in the monomer and dimer bond orders and charge densities, which reflects an increased amount of pyridinium oxide character in the dimer 2-pyridone. As might be expected, the largest change occurred in the N–C=O regions. However, π-bond order changes in the C=C–C=C portion amounted to no more than 0·01 in any bond.


(III)


(IV)


(V)

It is probable that the unassociated *N*-alkyl-pyridone (I) exhibits bond lengths characteristic of *N*-hydropyridone in the gas phase, and therefore the compound should be a superior model for molecular orbital calculations on 2-pyridones. Calculated bond lengths for 2-pyridone (Table 7, right-hand column) show two major differences from the experimental values for (I): the amounts of single-bond character in both C=O and C–C have been exaggerated. It is hoped that future calculations will be able to resolve these differences between theory and experiment.

There is good agreement between most of the 6-ring distances in 6-chloro-2-hydroxypyridine (column 4, Table 7) and (II). The largest differences are between the C(5)–C(6) and C(6)–N lengths. The differences are probably due to a bond-shortening effect of the C(6) Cl substituent in the hydroxypyridine.

There is ample bond-length evidence for (complete) π-delocalization in (II) and by virtue of the substantial differences between these parameters in (I) and (II), π-delocalization in (I) is judged to be minimal. A useful criterion for assessing relative degrees of delocalization from bond length data has been developed by

Table 7. *Pyridone and pyridinium bond lengths* (Å)

Estimated standard deviations in parentheses.

Bond	5-Chloro-2-pyridone*	2-Pyridone†	2-Pyridone‡	6-Chloro-2-hydroxy-pyridine§	(I)	(II)	2-Pyridone (calcd.‖)
N——C(2)	1·366 (6)	1·373 (4)	1·401	1·341 (3)	1·400 (4)	1·358 (7)	1·408
C(2)–C(3)	1·427 (4)	1·405 (6)	1·444	1·393 (4)	1·457 (6)	1·406 (8)	1·464
C(3)–C(4)	1·343 (5)	1·347 (6)	1·334	1·377 (4)	1·349 (4)	1·377 (9)	1·352
C(4)–C(5)	1·405 (5)	1·392 (6)	1·421	1·382 (4)	1·389 (6)	1·385 (10)	1·455
C(5)–C(6)	1·342 (4)	1·352 (6)	1·371	1·361 (4)	1·336 (5)	1·380 (9)	1·351
C(6)–N	1·356 (4)	1·357 (4)	1·335	1·332 (3)	1·374 (3)	1·375 (7)	1·376
C(2)–O	1·250 (3)	1·262 (4)	1·236	1·321 (3)	1·224 (3)	1·317 (7)	1·264

* Kvick & Booles (1972).
† From 2-pyridone-6-chloro-2-hydroxypyridine complex (Almlöf, Kvick & Olovsson, 1971).
‡ C–N, C–C and C–O σ's *ca.* 0·01 Å (Penfold, 1953).
§ Kvick & Olovsson (1968).
‖ Bodor, Dewar & Harget (1970).

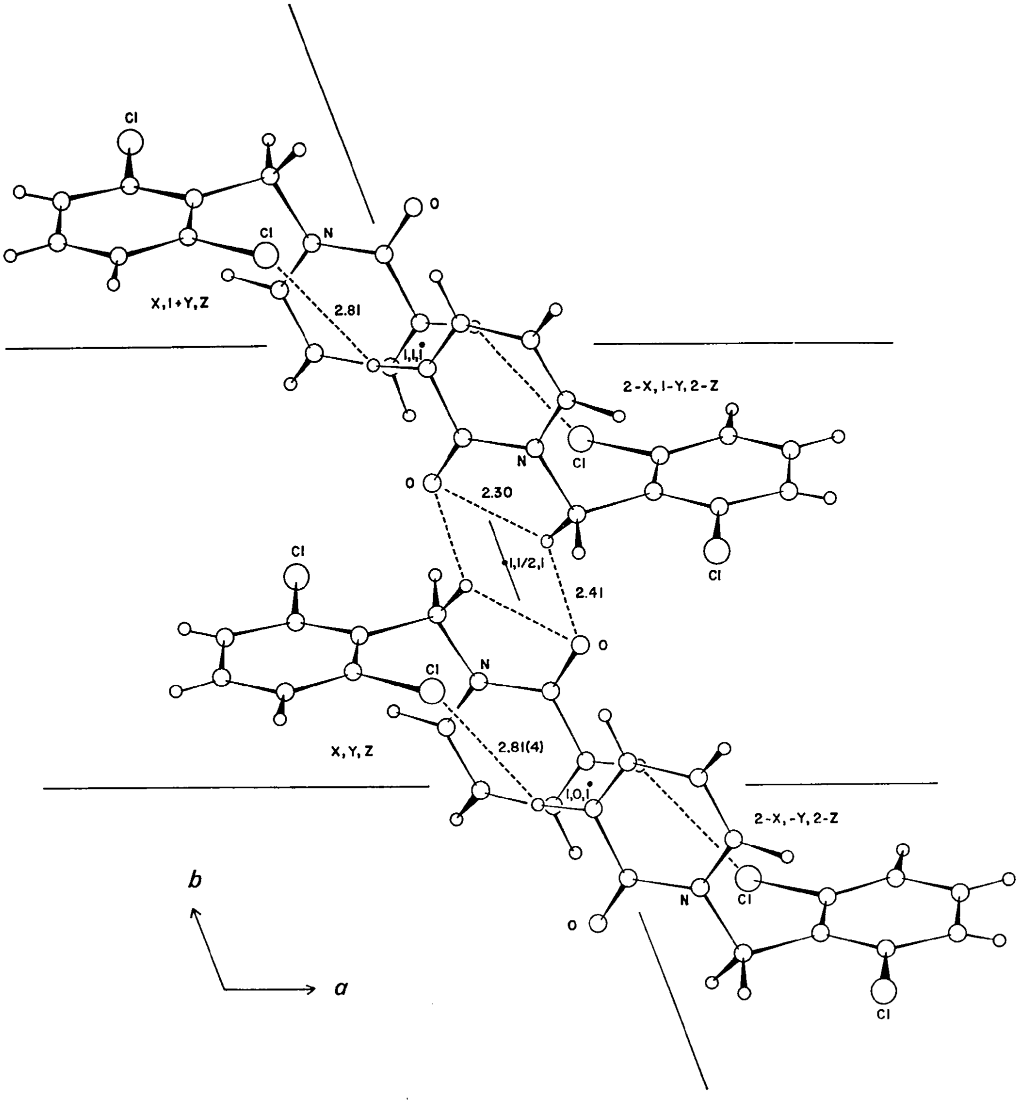


Fig. 3. Packing diagram for 1-(2′,6′-dichlorobenzyl)-2-pyridone viewed normal to the *ac* plane. Distances (Å) are given.

Julg & Francois (1967). In essence, the method is based on the uniformity of peripheral bond lengths, and uses the equation

$$A = 1 - \frac{225}{n}\sum_{i=1}^{n}\left(1 - \frac{d_i}{\hat{d}}\right)^2,$$

where A is an index of aromaticity, d_i is the ith bond length and $\hat{d}$ is the average of the n bond lengths. On this scale, benzene has $A = 1$ and a hypothetical Kekulé form of benzene (C=C = 1·34, C–C = 1·46 Å) has A = 0·59. Problems occur when the peripheral atoms are different. For example, Julg (1971) has modified his original expression to account for differences in the atomic charges. In our case, we have taken the differences in the C–C and C–N bonds into account by using different $\hat{d}$ values: $\hat{d}_{C-C} = 1{\cdot}395$ and $\hat{d}_{C-N} = 1{\cdot}340$ Å. The $\hat{d}$'s, taken from pyridine (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958), represent aromatic values for these bonds. This modification gave A values of 1·00 for pyridine, 0·95 for the pyridinium ring in (II) and 0·72 for the pyridone ring in (I). The 0·72 pyridone value is at the lower end of aromaticity (A) scale, and represents a small increase in π-delocalization over Kekulé benzene (A = 0·59) and fulvene (A = 0·62; Julg, 1971). Values of 0·85 for 5-chloro-2-pyridone and 0·89 for the 2-pyridone in the 2-pyridone-6-chloro-2-hydroxypyridine complex reflect an increase in π-delocalization over that in (I); the difference may result from intermolecular H bonding in the N-hydro-2-pyridones (see above).

Molecular packing

The molecular packing of (I) is illustrated in Fig. 3. The oxygen is involved in two weak interactions with H(7B): one 2·30 Å and one 2·41 Å intermolecular contact. While the contacts are less than the 2·6 Å H···O van der Waals distance (Pauling, 1960), they are considerably larger than the H···O distances observed in strong H bonds. The shortest Cl···H contact is 2·81 Å, between Cl (6A) at x,y,z and H(3) at $2-x, -y, 2-z$.

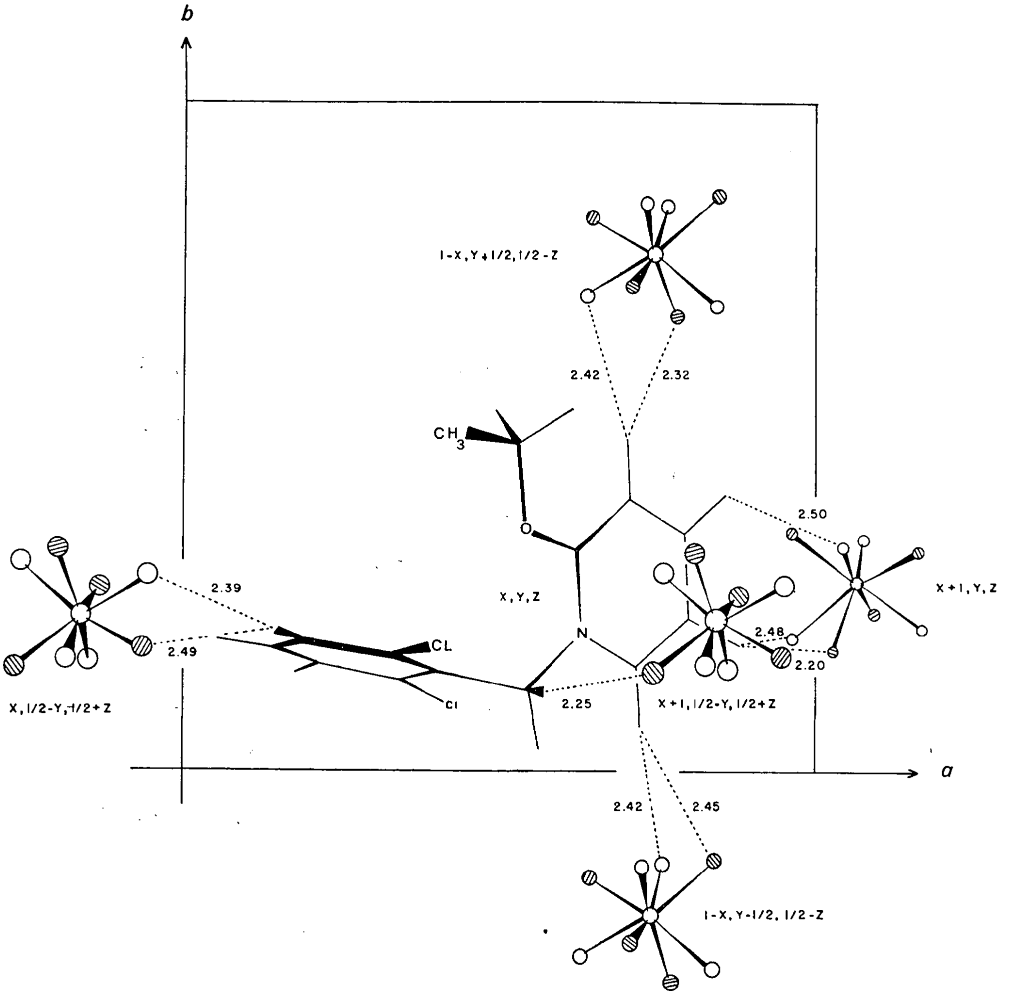


Fig. 4. Intermolecular contact diagram for 1-(2′,6′-dichlorobenzyl)-2-ethoxypyridinium fluoroborate showing the anion···cation interactions. Distances (Å) are given. The unshaded circles in the BF_8 moieties represent 0·64F, the shaded circles 0·36F.

A packing diagram for (II), which illustrates the $BF_4^-\cdots$ cation approaches, is shown in Fig. 4. The only intermolecular contacts less than the van der Waals limit are $F\cdots H$ (2·55 Å; Pauling, 1960) interactions, ranging from 2·20–2·50 Å. Many of the $F\cdots H$ contacts occur in pairs, involving F atoms from both tetrahedra in the disordered BF_8 moieties. The similarities between the two sets of contacts probably favor the BF_4 disorder.

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The Crystal Structure of a Hofmann-type Clathrate, $Mn(NH_3)_2Ni(CN)_4.2C_6H_6$

BY R. KURODA* AND Y. SASAKI

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, 113 *Japan*

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The crystal structure of a clathrate compound, $Mn(NH_3)_2Ni(CN)_4.2C_6H_6$, has been determined from three-dimensional X-ray data collected by diffractometry. The crystals are tetragonal, space group $P4/m$, $Z=1$, with the cell constants: $a=7·432$ (6) and $c=8·335$ (5) Å. The structure was refined by the block-diagonal least-squares method to give an R value of 0·060 for 824 observed reflexions. The host lattice is isostructural with other Hofmann-type clathrates; however, the benzene molecules are disordered, taking two alternative orientations. The population of the two orientations depends on the conditions of crystal growing, taking different values from crystal to crystal.

Introduction

Among a series of Hofmann-type clathrates $M(NH_3)_2Ni(CN)_4.2C_6H_6$, hereafter abbreviated to M–Ni–Bz, crystal structures of Ni–Ni–Bz, Cd–Ni–Bz and Cu–Ni–Bz have been determined by single-crystal X-ray diffraction (Rayner & Powell, 1952; Miyoshi, Iwamoto & Sasaki, 1973; Sasaki, 1969). The three compounds have isostructural host lattices. The last compound possesses a superstructure and the c axis is doubled owing to the different arrangement of the guest molecules. The present compound, Mn–Ni–Bz, has been subjected to X-ray crystal analysis in order to study the effect of the replacement of the atom M by Mn on the mode of clathration.

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* Present address: The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan.