Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Crystal and Molecular Structure of 3,5,6-Trichloro-2-Pyridinol Complexes

M. A. Sridhar [a] , N. K. Lokanath [a] , J. Shashidhara Prasad [a] & Akmal Pasha [b]

[a] Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, 570006, India

[b] Central Food Technology Research Institute, Mysore, 570020, India

Version of record first published: 24 Sep 2006

To cite this article: M. A. Sridhar, N. K. Lokanath, J. Shashidhara Prasad & Akmal Pasha (2001): Crystal and Molecular Structure of 3,5,6-Trichloro-2-Pyridinol Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 369:1, 153-165

To link to this article: http://dx.doi.org/10.1080/10587250108030018

Mol. Cryst. Liq. Cryst., Vol. 369, pp. 153-165
Reprints available directly from the publisher
Photocopying permitted by license only

Crystal and Molecular Structure of 3,5,6-Trichloro-2-Pyridinol Complexes

M.A. SRIDHAR[a*], N.K. LOKANATH[a], J. SHASHIDHARA PRASAD[a] and AKMAL PASHA[b]

[a]*Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore 570006, India and* [b]*Central Food Technology Research Institute, Mysore 570020, India*

(Received June 14, 2000; In final form January 15, 2001)

The complex (**A**), 3,5,6-trichloro-2-pyridinol-piperazine, $C_9H_{12}N_3OCl_3$, crystallizes in the monoclinic space group $P2_1/n$ with the parameters $a = 8.915(4)$ Å, $b = 7.062(3)$ Å, $c = 19.039(5)$ Å, $\beta = 102.79(3)°$, $V = 1168.9(8)$ Å^3, $Z = 4$. The structure was solved by direct methods using SHELXS-86 (Sheldrick, 1990) and refined using SHELXL-93 (Sheldrick, 1993). The final residual factor is $R1 = 0.0662$ for 1273 reflections with $I > 2\sigma(I)$. The structure has intermolecular hydrogen bonds. The molecules which are stacked in layers are interconnected through the hydrogen bonds.

The complex **B**, 3,5,6-trichloro-2-pyridinol-piperdine, $C_{10}H_{13}N_2OCl_3$, crystallizes in the monoclinic space group $P2_1/c$ with the parameters $a = 12.514(4)$ Å, $b = 22.464(2)$ Å, $c = 13.765(3)$ Å, $\beta = 98.02(2)°$, $V = 3831.9(2)$ Å^3, $Z = 12$. The structure was solved by direct methods using SHELXS-86 and refined using SHELXL-93. The final residual factor is $R1 = 0.072$ for 2662 reflections with $I > 2\sigma(I)$. The structure has both intra and intermolecular hydrogen bonds.

Keywords: Crystal structure; pyridinol complexes

INTRODUCTION

3,5,6-Trichloro-2-pyridinol (**I**) is the precursor to *o*-pyridylthiophosphate insecticides such as chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate, IIa) and chlorpyrifosmethyl (O,O-dimethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate, IIb). It is also used to prepare triclopyr (3,5,6-trichloro-2-pyridyloxyacetic acid, III), a herbicide [1] (see Figure 1).

3,5,6-Trichloro-2-pyridinol has also been reported to be the toxic metabolite formed in technical formulations of chlorpyrifos that were stored at high temper-

* Corresponding author: E-mail: mas@uomphysics.net, Tel: +91–821–516133, Fax: +91–821–516133.

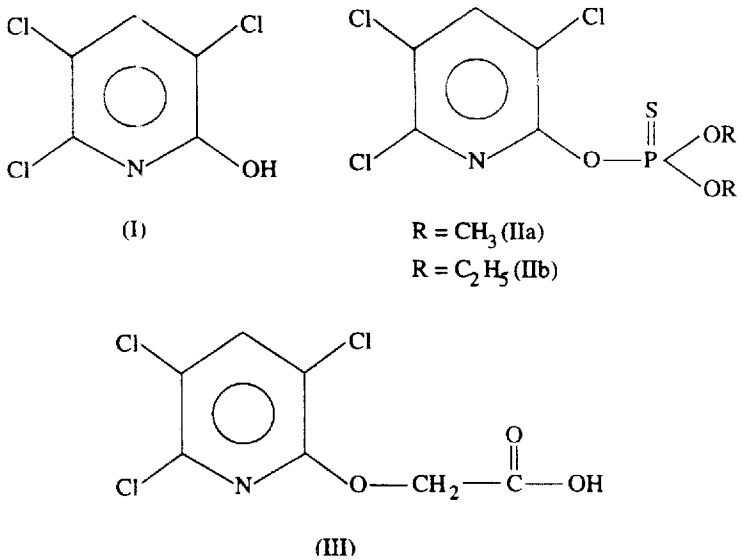

FIGURE 1 Chemical Scheme

atures and/or over long periods of time. Application of formulations containing 3,5,6-trichloro-2-pyridinol at or above 14% on to livestock for the control of ectoparasites resulted in cattle deaths [2].

A process has been developed by one of the authors for the isolation of toxic 3,5,6-trichloro-2-pyridinol from the technical material and formulations of chlorpyrifos and chlorpyrifosmethyl by complexation [3].

3,5,6-Trichloro-2-pyridinol therefore forms stable H-bonded complexes with cyclic amines. The present paper describes the crystal structure of these important complexes formed by the pyridinol that is a toxic metabolite of chlorpyrifos as well as the precursor.

EXPERIMENTAL

Synthesis of the complexes

3,5,6-Trichloro-2-pyridinol was dissolved in a solvent and excess of cyclic amine dissolved in a solvent was added to the solution. The mixture was allowed to stand overnight and the solvent was distilled off. The complex was washed with

a suitable solvent to remove the excess cyclic amine to obtain the pure complex. 3,5,6-Trichloro-2-pyridinol-piperazine melted at 178–180° C and 3,5,6-trichloro-2-pyridinol-piperdine had a melting point between 117–120° C.

XRD Data collection

X-ray diffraction data were collected on a AFC7S diffractometer with graphite monochromated MoK_α radiation. The data were reduced using teXsan [4]. Structures were solved by direct methods using SHELXS86 [5] and refined using SHELXL93 [6] by full-matrix least squares method. Data collection and solution details are given in Table I.

TABLE I Data Collection Details

	A	*B*
Molecular formula	$C_9H_{12}N_3OCl_3$	$C_{10}H_{13}N_2OCl_3$
Formula Weight	284.57	283.57
Crystal colour	colourless	yellow
Crystal size (mm)	0.15 × 0.15 × 0.2	0.1 × 0.1 × 0.1
Radiation/Wavelength (Å)	– MoK_α (0.71069) –	
F_{000}	584	1752
μ (mm^{-1})	0.765	0.698
Reflections for cell determination	21	25
0 range for above (°)	7.9 – 8.9	6.9 – 9.0
Scan type	– ω-2θ –	
$2\theta_{max}$	50°	50°
Indices range	$0 \le h \le 10$	$0 \le h \le 14$
	$0 \le k \le 8$	$0 \le k \le 26$
	$-22 \le l \le 22$	$-16 \le l \le 16$
Reflections (Total/Unique)	2069/2069	7081/6754
R_{int}	0.0000	0.0326
Corrections applied	– Lorentz and polarisation –	
Data reduction	– teXsan [4] –	
Structure solution	– SHELXS-86 [5] –	
Structure refinement	– SHELXL-93 [6] –	
Refinement method	Full matrix least squares on F^2	
Reflections/parameters	2069/159	6754/455
Extinction coefficient	0.003(3)	0.0002(3)
*R*1	0.0662	0.0720
Reflections	1673	2662
Observed criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Max. peak/hole ($e.Å^{-3}$)	0.935/0.788	0.519/0.540

RESULTS AND DISCUSSION

Tables II to V list the coordinates, equivalent thermal parameters, anisotropic thermal parameters, bond lengths and angles of **A**. Tables VI to IX list the coordinates, equivalent thermal parameters, anisotropic thermal parameters, bond lengths and angles of **B**. The bond distances and angles do not show any large deviations.

TABLE II Atomic coordinates and equivalent thermal parametersof the non-hydrogen atoms (**A**)

Atom	*x*	*y*	*z*	U_{eq}
Cl1	0.90352(12)	0.13391(17)	0.24689(6)	0.0499(4)
Cl2	0.33256(11)	0.24327(15)	0.08835(6)	0.0453(4)
Cl3	0.47555(13)	0.26839(17)	−0.05085(6)	0.0482(4)
N10	0.9587(4)	0.4021(5)	−0.2027(2)	0.0443(9)
N4	0.7420(4)	0.2077(5)	0.03632(18)	0.0367(8)
O1	0.9860(3)	0.1637(4)	0.10242(18)	0.0492(8)
C1	0.6251(4)	0.1867(6)	0.1600(2)	0.0341(8)
C6	0.5285(4)	0.2196(5)	0.0935(2)	0.0342(9)
C2	0.7803(4)	0.1688(5)	0.1638(2)	0.0352(9)
N7	0.8804(4)	0.1831(5)	−0.08701(19)	0.0402(9)
C9	1.0747(5)	0.3433(6)	−0.1404(2)	0.0428(10)
C11	0.8291(5)	0.2706(6)	−0.2160(2)	0.0388(9)
C8	1.0115(5)	0.3182(7)	−0.0732(2)	0.0476(10)
C5	0.5922(5)	0.2293(5)	0.0341(2)	0.0340(9)
C3	0.8423(4)	0.1779(5)	0.1004(2)	0.0376(9)
C12	0.7596(5)	0.2387(6)	−0.1502(2)	0.0397(10)

TABLE III Anisotropic thermal parameters of the non-hydrogen atoms (**A**)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl1	0.0344(6)	0.0708(8)	0.0458(7)	0.0030(5)	0.0117(5)	0.0027(5)
Cl2	0.0256(6)	0.0662(8)	0.0495(7)	0.0048(4)	0.0198(5)	0.0022(4)
Cl3	0.0440(7)	0.0649(8)	0.0393(6)	0.0029(4)	0.0170(5)	0.0028(4)
N10	0.046(2)	0.0444(19)	0.051(2)	−0.0009(16)	0.0274(17)	0.0055(16)
N4	0.0342(18)	0.0437(18)	0.0402(18)	0.0021(14)	0.0254(15)	0.0025(14)
O1	0.0294(15)	0.0524(17)	0.076(2)	0.0066(13)	0.0338(15)	0.0096(15)
C1	0.0250(18)	0.045(2)	0.039(2)	0.0008(16)	0.0209(16)	−0.0019(17)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C6	0.0239(19)	0.039(2)	0.047(2)	0.0022(14)	0.0231(17)	−0.0017(16)
C2	0.034(2)	0.0370(19)	0.040(2)	0.0022(15)	0.0201(17)	0.0027(16)
N7	0.0374(19)	0.049(2)	0.0403(19)	0.0049(17)	0.0219(15)	0.0051(17)
C9	0.034(2)	0.045(2)	0.054(2)	−0.0052(17)	0.0191(18)	−0.0066(18)
C11	0.036(2)	0.051(2)	0.034(2)	0.0043(17)	0.0167(17)	0.0017(16)
C8	0.045(2)	0.057(3)	0.041(2)	−0.003(2)	0.0105(19)	−0.006(2)
C5	0.035(2)	0.0354(19)	0.037(2)	0.0008(15)	0.0186(16)	0.0002(15)
C3	0.031(2)	0.0357(19)	0.057(2)	0.0041(15)	0.0319(19)	0.0036(17)
C12	0.033(2)	0.048(2)	0.047(2)	0.0030(16)	0.0259(19)	0.0027(17)

TABLE IV Bond Lengths of A (Å)

Atoms	*Length*	*Atoms*	*Length*
Cl1-C2	1.732(4)	C1-C2	1.375(5)
Cl2-C6	1.735(4)	C1-C6	1.384(6)
Cl3-C5	1.741(4)	C6-C5	1.376(5)
N10-C9	1.451(6)	C2-C3	1.437(5)
N10-C11	1.460(6)	N7-C12	1.479(6)
N4-C5	1.335(5)	N7-C8	1.487(6)
N4-C3	1.359(5)	C9-C8	1.519(6)
O1-C3	1.277(5)	C11-C12	1.533(5)

TABLE V Bond Angles of A (°)

Atoms	*Angle*	*Atoms*	*Angle*
C9-N10-C11	110.7(3)	N10-C9-C8	113.1(3)
C5-N4-C3	120.0(3)	N10-C11-C12	113.5(3)
C2-C1-C6	118.6(3)	N7-C8-C9	110.4(3)
C5-C6-C1	118.3(3)	N4-C5-C6	124.1(4)
C5-C6-Cl2	122.8(3)	N4-C5-Cl3	115.8(3)
C1-C6-Cl2	118.9(3)	C6-C5-Cl3	120.1(3)
C1-C2-C3	121.4(4)	O1-C3-N4	119.7(3)
C1-C2-Cl1	119.2(3)	O1-C3-C2	122.7(4)
C3-C2-Cl1	119.3(3)	N4-C3-C2	117.5(3)
C12-N7-C8	112.1(3)	N7-C12-C11	110.5(3)

TABLE VI Atomic coordinates and equivalent thermal parameters of the non-hydrogen atoms (B)

Atom	*x*	*y*	*z*	U_{eq}
C1A	0.5892(5)	0.1947(3)	0.8424(5)	0.0590(17)
C2A	0.5007(5)	0.1612(3)	0.8154(5)	0.0547(17)
C3A	0.5042(5)	0.0979(3)	0.8253(5)	0.0538(16)
N4A	0.6010(4)	0.0727(2)	0.8591(4)	0.0562(14)
C5A	0.6859(5)	0.1069(3)	0.8835(5)	0.0568(17)
C6A	0.6865(5)	0.1676(3)	0.8780(5)	0.0582(18)
Cl1A	0.37751(14)	0.19441(8)	0.77453(17)	0.0887(7)
O8A	0.4225(3)	0.06459(18)	0.8042(4)	0.0728(14)
Cl2A	0.80443(15)	0.06819(8)	0.92581(17)	0.0853(7)
Cl3A	0.80163(15)	0.20916(8)	0.90959(17)	0.0871(7)
C1B	0.2519(5)	0.1996(3)	0.4768(5)	0.0606(17)
C2B	0.3457(5)	0.1678(3)	0.4893(5)	0.0541(16)
C3B	0.3431(5)	0.1037(3)	0.4835(5)	0.0543(17)
N4B	0.2452(4)	0.0769(2)	0.4696(4)	0.0554(14)
C5B	0.1559(5)	0.1086(3)	0.4581(4)	0.0506(15)
C6B	0.1532(5)	0.1699(3)	0.4616(5)	0.0576(7)
Cl1B	0.46853(13)	0.20283(8)	0.50796(7)	0.0816(6)
O8B	0.4268(3)	0.07176(18)	0.4900(4)	0.0704(13)
Cl2B	0.03703(13)	0.06782(8)	0.44166(15)	0.0761(6)
Cl3B	0.03382(13)	0.20974(8)	0.44787(15)	0.0795(6)
C1C	-0.0915(5)	0.1996(3)	0.1830(5)	0.0604(18)
C2C	-0.1849(5)	0.1687(3)	0.1839(5)	0.0514(16)
C3C	-0.1851(5)	0.1053(3)	0.1873(5)	0.0528(16)
N4C	-0.0889(4)	0.0773(2)	0.1871(4)	0.0545(13)
C5C	0.0000(5)	0.1084(3)	0.1877(5)	0.0549(17)
C6C	0.0056(5)	0.1698(3)	0.1857(5)	0.0559(17)
Cl1C	-0.30652(13)	0.20598(7)	0.17577(16)	0.0809(6)
O8C	-0.2690(3)	0.07390(18)	0.1914(4)	0.0669(13)
Cl2C	0.11662(14)	0.06570(8)	0.18762(18)	0.0881(7)
Cl3C	0.12558(13)	0.20793(8)	0.18965(17)	0.0830(6)
N7A	0.0992(6)	0.1224(3)	0.7113(6)	0.105(2)
C8A	0.1343(6)	0.0576(3)	0.7138(5)	0.073(2)
C9A	0.2058(4)	0.0443(2)	0.8067(4)	0.0414(14)
C10A	0.1584(6)	0.0605(3)	0.8936(6)	0.075(2)
C11A	0.1219(7)	0.1244(3)	0.8944(6)	0.082(2)
C12A	0.0478(6)	0.1389(3)	0.8018(6)	0.076(2)
N7B	0.7093(5)	0.0611(3)	0.4465(5)	0.097(2)

Atom	*x*	*y*	*z*	U_{eq}
C8B	0.7396(6)	0.1271(3)	0.4517(5)	0.071(2)
C9B	0.7964(6)	0.1425(3)	0.5522(5)	0.074(2)
C10B	0.7299(5)	0.1249(3)	0.6302(5)	0.0671(19)
C11B	0.6964(6)	0.0592(3)	0.6233(5)	0.071(2)
C12B	0.6416(4)	0.0458(2)	0.5253(4)	0.0368(13)
N7C	0.4671(5)	0.0663(3)	0.0676(5)	0.091(2)
C8C	0.5151(4)	0.0535(2)	0.1700(4)	0.0344(13)
C9C	0.4433(5)	0.0714(3)	0.2407(5)	0.0659(19)
C10C	0.4169(5)	0.1370(3)	0.2332(5)	0.0661(19)
C11C	0.3693(5)	0.1523(3)	0.1288(5)	0.0665(19)
C12C	0.4397(5)	0.1317(2)	0.0556(5)	0.0598(18)

TABLE VII Anisotropic thermal parameters of the non-hydrogen atoms (**B**)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1A	0.069(4)	0.037(3)	0.073(5)	−0.009(3)	0.018(4)	−0.002(3)
C2A	0.052(4)	0.040(3)	0.072(5)	−0.001(3)	0.009(3)	0.011(3)
C3A	0.054(4)	0.044(4)	0.064(4)	−0.010(3)	0.014(3)	0.003(3)
N4A	0.060(4)	0.034(3)	0.074(4)	0.000(3)	0.007(3)	0.002(3)
C5A	0.051(4)	0.046(4)	0.075(5)	0.000(3)	0.017(3)	0.007(3)
C6A	0.053(4)	0.039(4)	0.082(5)	−0.003(3)	0.010(4)	−0.003(3)
Cl1A	0.0628(11)	0.0637(12)	0.1352(19)	0.0030(9)	−0.0019(11)	0.0298(12)
O8A	0.065(3)	0.046(3)	0.107(4)	−0.012(2)	0.009(3)	0.016(3)
Cl2A	0.0640(11)	0.0638(12)	0.1241(18)	0.0089(9)	−0.0008(11)	0.0142(11)
Cl3A	0.0669(12)	0.0620(12)	0.1285(18)	−0.0170(9)	−0.0007(11)	−0.0123(11)
C1B	0.063(4)	0.036(3)	0.083(5)	0.004(3)	0.009(4)	0.004(3)
C2B	0.051(4)	0.040(4)	0.069(5)	−0.002(3)	0.003(3)	−0.010(3)
C3B	0.046(4)	0.037(4)	0.079(5)	0.005(3)	0.004(3)	−0.006(3)
N4B	0.048(3)	0.038(3)	0.077(4)	0.002(3)	−0.002(3)	−0.002(3)
C5B	0.047(4)	0.047(4)	0.056(4)	0.002(3)	0.002(3)	−0.004(3)
C6B	0.046(4)	0.045(4)	0.079(5)	0.007(3)	0.001(3)	0.010(3)
Cl1B	0.0518(10)	0.0529(11)	0.1391(18)	−0.0094(8)	0.0098(10)	−0.0134(11)
O8B	0.051(3)	0.045(2)	0.113(4)	0.011(2)	0.002(2)	−0.008(3)
Cl2B	0.0515(10)	0.0634(11)	0.1090(16)	−0.0117(8)	−0.0037(9)	−0.0052(10)
Cl3B	0.0549(10)	0.0625(11)	0.1168(16)	0.0191(9)	−0.0036(10)	0.0085(10)
C1C	0.060(4)	0.030(3)	0.087(5)	0.000(3)	−0.004(4)	−0.012(3)
C2C	0.047(4)	0.040(3)	0.066(4)	0.007(3)	0.001(3)	−0.007(3)
C3C	0.051(4)	0.036(4)	0.068(4)	−0.005(3)	−0.003(3)	−0.002(3)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N4C	0.051(3)	0.037(3)	0.074(4)	0.003(3)	0.001(3)	0.002(3)
C5C	0.044(4)	0.045(4)	0.074(5)	0.002(3)	−0.002(3)	−0.001(3)
C6C	0.043(4)	0.044(4)	0.079(5)	0.001(3)	0.002(3)	0.001(3)
Cl1C	0.0507(10)	0.0505(10)	0.1385(18)	0.0110(8)	0.0021(10)	0.0055(11)
O8C	0.047(2)	0.042(2)	0.109(4)	−0.009(2)	−0.002(2)	−0.002(2)
Cl2C	0.0546(11)	0.0557(11)	0.156(2)	0.0136(9)	0.0200(11)	0.0041(12)
Cl3C	0.0521(10)	0.0549(11)	0.1410(18)	−0.0106(8)	0.0092(11)	−0.0001(11)
N7A	0.126(6)	0.078(5)	0.109(6)	0.025(4)	0.015(5)	0.022(4)
C8A	0.087(5)	0.054(4)	0.074(5)	0.003(4)	−0.006(4)	−0.004(4)
C9A	0.040(3)	0.022(3)	0.060(4)	0.003(2)	−0.003(3)	0.000(3)
C10A	0.085(5)	0.049(4)	0.082(5)	0.000(4)	−0.016(4)	0.002(4)
C11A	0.116(7)	0.052(5)	0.075(5)	0.011(4)	0.000(5)	−0.005(4)
C12A	0.080(5)	0.054(4)	0.099(6)	0.023(4)	0.027(5)	0.010(4)
N7B	0.108(5)	0.067(4)	0.110(6)	0.005(4)	−0.003(4)	−0.016(4)
C8B	0.083(5)	0.052(4)	0.079(5)	−0.003(4)	0.016(4)	0.013(4)
C9B	0.073(5)	0.060(5)	0.084(6)	−0.018(4)	−0.002(4)	−0.008(4)
C10B	0.072(5)	0.052(4)	0.075(5)	−0.005(3)	0.001(4)	−0.011(4)
C11B	0.084(5)	0.049(4)	0.079(5)	0.009(4)	0.013(4)	0.001(4)
C12B	0.037(3)	0.025(3)	0.047(4)	−0.002(2)	0.003(3)	0.003(2)
N7C	0.120(5)	0.054(4)	0.095(5)	0.009(4)	0.003(4)	−0.005(3)
C8C	0.029(3)	0.021(3)	0.052(4)	0.003(2)	−0.001(3)	0.003(2)
C9C	0.067(4)	0.051(4)	0.074(5)	0.002(3)	−0.011(4)	0.010(4)
C10C	0.074(5)	0.055(4)	0.070(5)	0.005(4)	0.014(4)	−0.006(4)
C11C	0.066(4)	0.046(4)	0.087(6)	0.015(3)	0.008(4)	0.004(4)
C12C	0.061(4)	0.039(4)	0.076(5)	0.003(3)	−0.002(4)	0.005(3)

TABLE VIII Bond Lengths of **B** (Å)

Atoms	*Length*	*Atoms*	*Length*
C1A-C2A	1.347(8)	C3C-O8C	1.273(7)
C1A-C6A	1.387(8)	C3C-N4C	1.359(7)
C2A-C3A	1.427(8)	N4C-C5C	1.312(7)
C2A-Cl1A	1.735(6)	C5C-C6C	1.381(8)
C3A-O8A	1.269(7)	C5C-Cl2C	1.746(6)
C3A-N4A	1.359(7)	C6C-Cl3C	1.724(6)
N4A C5A	1.317(7)	N7A-C8A	1.519(8)
C5A-C6A	1.366(8)	N7A-C12A	1.526(9)
C5A-Cl2A	1.747(6)	C8A-C9A	1.486(8)

Atoms	*Length*	*Atoms*	*Length*
C6A-Cl3A	1.721(6)	C9A-C10A	1.454(9)
C1B-C2B	1.365(8)	C10A-C11A	1.506(9)
C1B-C6B	1.393(8)	C11A-C12A	1.503(10)
C2B-C3B	1.443(8)	N7B-C12B	1.507(9)
C2B-Cl1B	1.715(6)	N7B-C8B	1.530(8)
C3B-O8B	1.262(6)	C8R-C9B	1.505(9)
C3H-N4B	1.353(7)	C9B-C10B	1.501(9)
N4B-C5B	1.316(7)	C10B-C11B	1.533(8)
C5B-C6B	1.379(8)	C11B-C12B	1.457(8)
C5B-Cl2B	1.735(6)	N7C-C8C	1.482(8)
C6B-Cl3H	1.729(6)	N7C-C12C	1.512(7)
C1C-C2C	1.361(8)	C8C-C9C	1.469(8)
C1C-C6C	1.383(8)	C9C-C10C	1.510(8)
C2C-C3C	1.424(8)	C10C-C11C	1.516(9)
C2C-Cl1C	1.728(6)	C11C-C12C	1.502(9)

TABLE IX Bond Angles of **B** (°)

Atoms	*Angle*	*Atoms*	*Angle*
C2A-C1A-C6A	120.0(6)	C1C-C2C-Cl1C	120.1(5)
C1A-C2A-C3A	121.1(6)	C3C-C2C-Cl1C	118.7(5)
C1A-C2A-Cl1A	120.6(5)	08C-C3C-N4C	118.7(5)
C3A-C2A-Cl1A	118.2(5)	08C-C3C-C2C	124.2(6)
O8A-C3A-N4A	118.9(5)	N4C-C3C-C2C	117.1(5)
O8A-C3A-C2A	123.6(6)	C5C-N4C-C3C	120.4(5)
N4A-C3A-C2A	117.5(5)	N4C-C5C-C6C	125.1(5)
C5A-N4A C3A	119.5(5)	N4C-C5C-Cl2C	114.6(5)
N4A-C5A-C6A	125.4(6)	C6C-C5C-Cl2C	120.3(5)
N4A-C5A-Cl2A	114.3(5)	C5C-C6C-C1C	116.0(5)
C6A-C5A-C12A	120.3(5)	C5C-C6C-Cl3C	122.8(5)
C5A-C6A-C1A	116.5(6)	C1C-C6C-Cl3C	121.2(5)
C5A-C6A-Cl3A	122.6(5)	C8A-N7A-C12A	111.5(6)
C1A-C6A-Cl3A	120.9(5)	C9A-C8A-N7A	110.5(5)
C2B-C1B-C6B	119.7(6)	C10A-C9A-C8A	113.1(5)
C1B-C2B-C3B	120.3(6)	C9A-C10A-C11A	113.8(6)
C1B-C2B-Cl1B	121.0(5)	C12A-C11A-C10A	110.6(6)
C3B-C2B-Cl1B	118.7(5)	C11A-C12A-N7A	111.1(6)
O8B-C3B-N4B	118.9(5)	C12B-N7B-C8B	110.4(5)

Atoms	*Angle*	*Atoms*	*Angle*
O8B-C3B-C2B	123.4(6)	C9B-C8B-N7B	110.3(6)
N4B-C3B-C2B	117.7(5)	C10B-C9B-C8B	111.0(6)
C5B-N4B-C3B	120.9(5)	C9B-C10B-C11B	112.6(6)
N4B-C5B-C6B	124.1(6)	C12B-C11B-C10B	110.2(5)
N4B-C5B-C12B	115.4(5)	C11B-C12B-N7B	112.3(5)
C6B-C5B-C12B	120.5(5)	C8C-N7C-C12C	110.4(5)
C5B-C6B-C1B	117.3(5)	C9C-C8C-N7C	111.9(5)
C5B-C6B-C3B	122.5(5)	C8C-C9C-C10C	111.7(6)
C1B-C6B-C3B	120.2(5)	C9C-C10C-C11C	109.9(6)
C2C-C1C-C6C	120.2(6)	C12C-C11C-C10C	112.1(5)
C1C-C2C-C3C	121.1(5)	C11C-C12C-N7C	111.9(5)

TABLE X Hydrogen Bonds

Atoms	*Length(Å)*	*Angle*	*Symmetry Code*
Compound **A**			
O1-H1···N7	2.767(5)	157.6(3)	2-*x*, -*y*, -*z*
N7-H7···O1	2.767(5)	157.1(6)	2-*x*, -*y*, -*z*
C1-H1A···N10	3.338(5)	169.3(4)	−1/2 + *x*, 1/2 − *y*, 1/2 + *z*
C8-H8A···Cl2	3.746(5)	163.8(2)	1 + *x*, *y*, *z*
Compound **B**			
C12B-H12C···O8B	2.727(6)	151.8(4)	
C9A-H92A···O8A	2.755(6)	149.4(3)	
C12B-H12D···O8B	2.775(6)	172.5(1)	1 − *x*, -*y*, 1 − *z*
C8C-H81C···O8A	2.774(6)	171.7(5)	1 − *x*, − *y*, 1 − *z*
C8C-H82C···O8C	2.716(6)	148.5(6)	1 + *x*, *y*, *z*
C9A-H91A···O8C	2.770(6)	172.5(2)	-*x*, -*y*, 1 − *z*

The thermal ellipsoid plot of the molecule **A** is shown in Figure 2 [7]. The structure of **A** has intermolecular hydrogen bonds of the type CH···N, CH···Cl, NH···O and OH···N. The lengths and angles along with the symmetry code are given in Table X. The molecules appear stacked when viewed along *a* and *c* axes (Figures 3 and 4). The molecules in one layer are connected with those in the neighbouring layer through hydrogen bonds shown as dashed lines in the Figures 3 and 4 [7]. The atoms C1 to C6, C11, C12, C13 and O1 are planar with maximum deviation being 0.019Å for the C12 atom. The atoms N7, C8, C9, N10, C11 and C12 are in chair conformation.

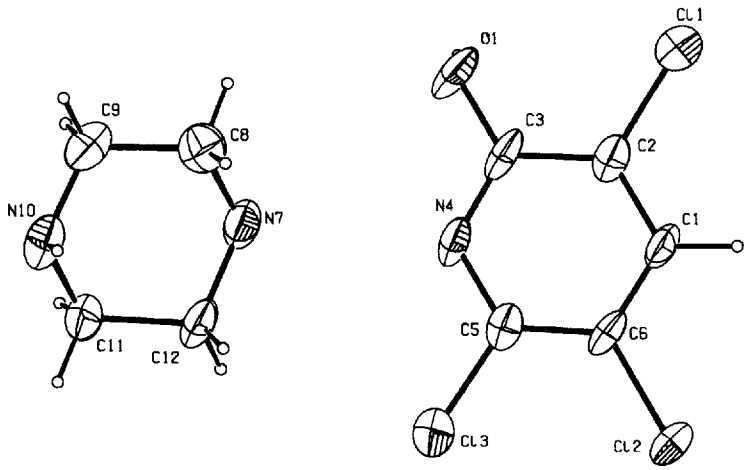

FIGURE 2 ORTEP of **A** at 50% probability

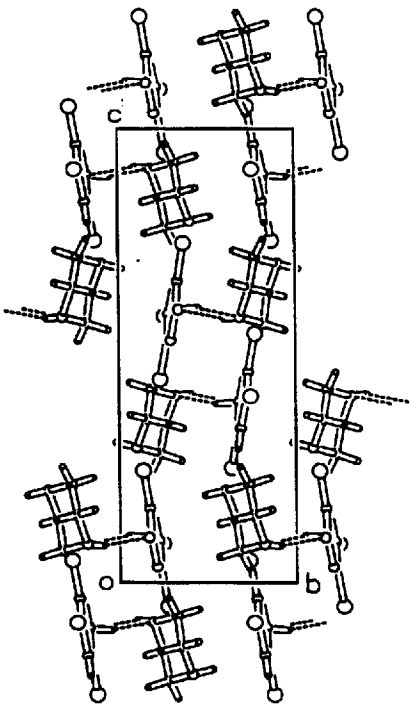

FIGURE 3 Packing of the molecules of **A** down *a* axis

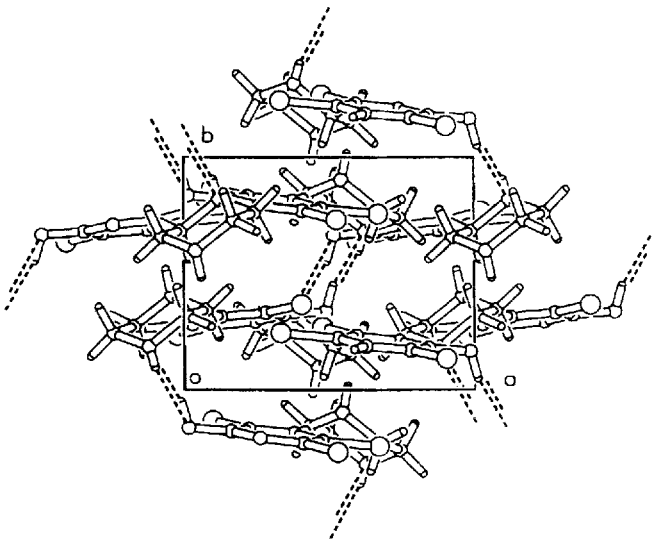

FIGURE 4 Packing of the molecules of **A** down **c** axis

The thermal ellipsoid plot of the molecule **B** is shown in Figure 5. The structure has both intra and intermolecular hydrogen bonds of the type CH···O and CH···N.

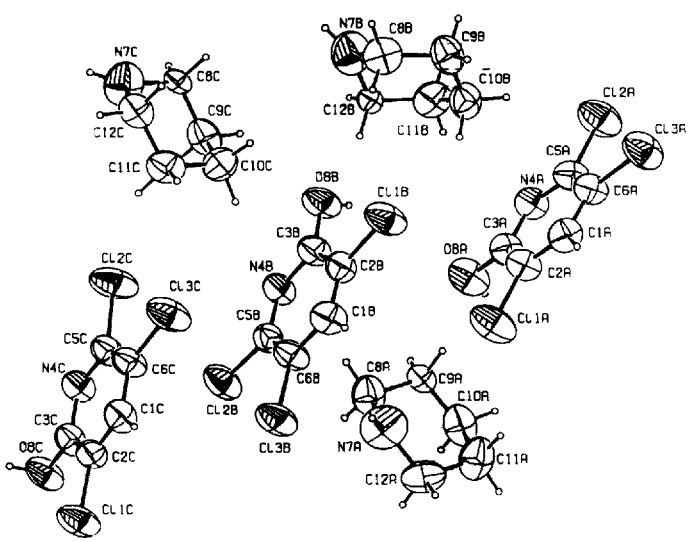

FIGURE 5 Thermal ellipsoid plot of **B** at 50% probability

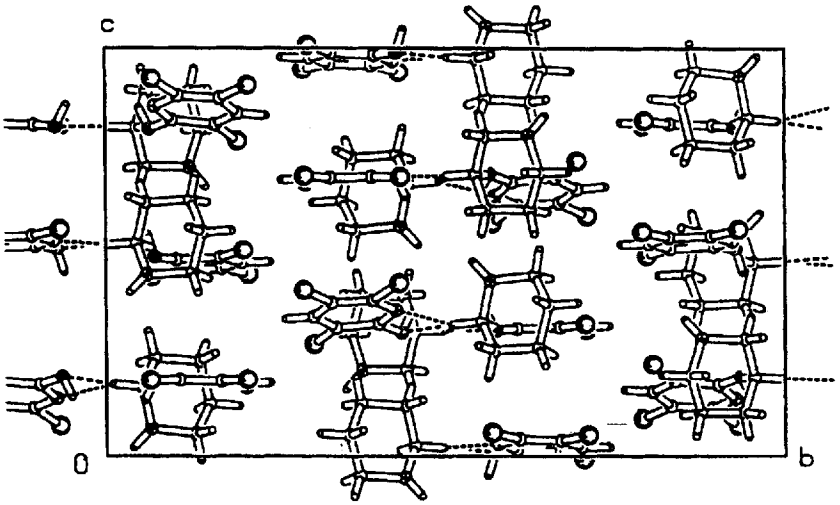

FIGURE 6 Packing of the molecules of **B** down *a* axis

Acknowledgements

The authors would like to express their thanks to DST, Government of India for financial assistance under the project SP/I2/FOO/93.

References

[1] *The Pesticide Manual*, Tenth Edition (Ed. C. Tomlin), The British Crop Protection Council and the Royal Society of Chemistry, U.K., p. 200–203; 1015–1017 (1994).
[2] W.J. Allender and Keegan, *Bull. Environ. Contain. Toxicol.*, **46**, 313 (1991).
[3] A. Pasha, *Ind. Pat.* NF-86/2000 Appl. 2000, A process for the preparation of o-pyridyl thiophosphate insecticides free of 3,5,6-trichloropyridin-2-ol toxin.
[4] Molecular Structure Corporation. (1995). teXsan. Single Crystal Structure Analysis Software. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
[5] G.M. Sheldrick, *Acta Crystallogr.*, **A46**, 467 (1990).
[6] G.M. Sheldrick, *SHELXL93-Crystal structure refinement program*, University of Göttingen, Germany (1993).
[7] A.L. Spek, *Acta Crystallogr.*, **A46**, C-34 (1990).