CHAPTER-2

MOLECULAR AND CRYSTAL STRUCTURE OF COMPOUND "6α ACETOXY AZADIRONE" FROM *CHISOCHETON PANICULATUS* [$C_{30}H_{38}O_6$]

2.1 INTRODUCTION

6α acetoxy azadirone (MK-001) one of the most important limonoid found in the plant *Chisocheton paniculatus*[1] Hiren of Maliaceae family[2].Some of its derivatives and itself are great importance largely because of their potent antifungal[3] and antifeedant properties. The biological activity of the molecule is found to be due to two main functionalities, one is a furan ring in position 17 and the other is the α, β-unsaturated carbonyl group in position 1, 2 and 3. Due to the absence of these two functionalities the molecule is found to loss its activity to a greater extent. The crystal structure of the β isomar[4,5,6,7,8,9] of the title compound has already been explored.So,here we will only explain the single crystal structural elucidation of its α-isomar.The analysis of this structure is undertaken in order to get accurate bond angles and bond distances of this compound.The study of the title compound will help to understand the nature of molecular packing in crystalline space. It is also aimed at finding the molecular geometry and molecular conformations of the crystal.

2.2 CRYSTAL GROWTH

For the growth of the single crystal of the compound (MK-001) toluene is used as a solvent. Glass tubes are used for growing of crystals. A glass tube stand is used to keep the tube undisturbed for growing the crystals. The 6α-acetoxy azadirone ($C_{30}H_{38}O_6$) powder is dissolved in minimum volume of toluene until the solution becomes saturated. The mouth of the tube is covered by a piece of alumunium foil to slow down the rate of evaporation. Precaution is taken so that no foreign particles could enter into the solution. During the entire seeding period, solution is kept undisturbed. After two weeks some white crystalline solid of size 0.48×0.34×0.22 mm3 are obtained. The crystals are taken out of the solution carfully and allowed to dry in a glass plate inside a vacuum dessicator. The crystal growth took place at room temperature (29+3°c)

2.3 SELECTION OF THE CRYSTAL

A good crystal is selected by observing it under a polarizing microscope. Deformed or twinned crystals were rejected. The cross section of the instance region of x-ray is ordinarily about 1mm in diameter, care have been taken to select a crystal of this range. Stress is given on the surface morphology of the crystal so that it can be oriented about the desired axis.

2.4 EXPERIMENTAL

Compound (MK-001) have been isolated by chromatographic method in the laboratory of Institute of Advanced Studies in Science & Techonology (IASST) Guwahati, Assam, India. Again the isolated pure compound from the fruits of *Chisocheton paniculatus* colourless needle like crystal are grown in toluene for our further study.

Preliminary crystal data are obtained from oscillation and Weissenberg Photographs using CuKα radiation. The crystals are found to be orthorhombic. The zero layer line Weissenberg photographs about different axes revealed that the hkl reflections have no systematic absence. But reflections, h00 for h=2n; 0k0 for k=2n; 00l for l=2n are absent. This uniquely establishes that the space group is $P2_12_12_1$ with the general equivalent positions ±(x,y,z ;·5-x ,-y ,·5+z ;-x , ·5+y,-z ;·5+x ,·5-y ,-z)

The density is determined by floatation method in water and ethanol. The number of molecules per unit cell is found to be 4; hence the asymmetric unit must consist of 2 molecules

A single crystal of title compound (MK-001) is grown from toluene by slow evaporation of the solvent. Single crystals of size 0.40 × 0.34 × 0.22 mm^3 are taken and XRD data are collected at 296K temperature with a Bruker 3-circle diffractometer (Bruker Nonius SMART APEX 2) equipped with CCD area detector, and using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) from 60W microfocus Siemens Microsource with glass polycapillary optics in Chemistry Department, Indian Institute of Technology Guwahati (IITG). Bruker SMART software[10] is used for data collection and also for indexing the reflections and the unit cell parameters. The collected data are integrated using SAINT software[11]. The structures are solved by direct method and refined by full-matrix least squares calculation using SHELXTL software[12-13]. Lattice parameters are determined from θ values in the range $3.81 < \theta < 28.40$. A total of 20488 reflections are recorded for the values of θ up to 28.40, out of which 6681 reflections are unique. Absorption (μ = 0.082 mm^{-1}) and absorption corrections are not applied. The accurate cell parameters are refined by least squares method of the setting angles of 28 reflections lying in the range 3.81 to 28.40°.on the basis of 6681 independent reflections

are recorded up to 80°in 2θ with I>2δ (I) are measured by w/2θ scan technique, with scan speed of 2.5°min^{-1}.The hkl range of measured reflections are -11<=h<=14, -20<=k<=20, -22<=l<=21

The intensities are corrected for the Lortentz and polarization factors but absorption correction is ignored as structure contained only light atoms.

All the non-H atoms are refined in the anisotropic approximation against F^2 of all reflections. The H-atoms except those attached to N, O and F are placed at their calculated positions and refined in the isotopic approximations, those attached to heteroatoms (N, O and F) are located in the difference Fourier maps, and refined with

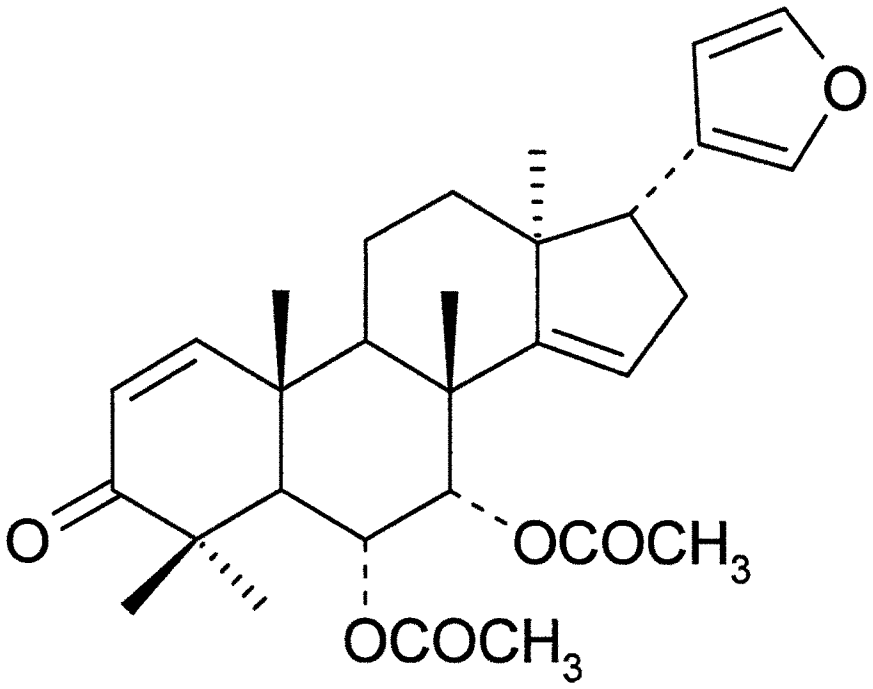

Figure 2.1: Structure of 6α-acetoxy azadirone (MK-001)

isotopic displacement co-efficients. The final refinement cycle converged R= 0.0501 and wR (F^2) = 0.1464. Final cycle of refinement resulted in the residual electron density in the range 0.174 and -0.180e $Å^{-3}$. Atomic scattering factors are taken from International Tables for X-ray crystallography[14].

The covalent structure of (MK-001) is given in the figure 2.1.Crystal data and other experimental details are given in the table 2.1.

2.5 RESULT AND DISCUSSION

In the analysis of the crystal structure of 6α acetoxy azadirone, it has been observed that the values obtained for bond lengths and bond angles are on the average; satisfy the requirement of the molecular valancy structure. The results of investigation reveal that the crystal structure comprises two molecules per asymmetric unit.

The ORTEP diagram[15] of (MK-001) with the atomic numbering scheme is shown in the figure.2.2. table 2.2 anisotropic displacement parameters ($Å^2$x 10^3) for (MK-001) .The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$.The co-ordinates of hydrogen atoms with the corresponding isotropic displacement parameters are listed in table 2.3. The least of atomic co-ordinate and equivalent isotropic displacement parameters ($Å^2$x 10^3) for MK-001. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor are given in the table 2.4. The list of structure factors are also given in Appendix-1.

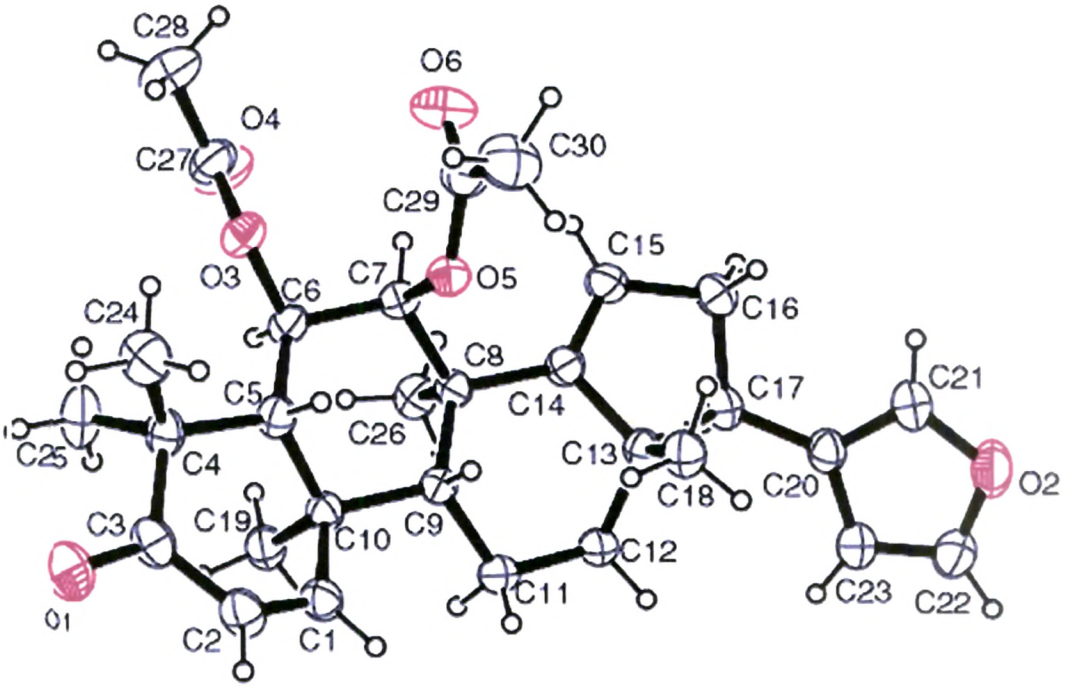

Figure 2.2: An ORTEP view of (MK-001) in 30% probability with atomic numbering scheme.

Table 2.1: Crystal data and structure refinement for (MK-001)

Empirical formula	: $C_{30}H_{38}O_6$
Formula weight	: 494.60
Temperature	: 296(2) K
Wavelength	: 0.71073 Å
Crystal system	: Orthorhombic
Space group	: $P2_12_12_1$
Unit cell dimensions	: a = 10.699(3) Å α=90°
b = 15.510(4) Å	β=90°
c = 16.626(4) Å	γ= 90°
Volume	: 2759.0(12) $Å^3$
Z	: 4
Density (calculated)	: 1.191 Mg/m^3
Absorption coefficient	: 0.082 mm^{-1}
F(000)	: 1064
Crystal size	: 0.48 x 0.34 x 0.22 mm^3
Theta range for data collection	: 3.81 to 28.40°.
Index ranges	: -11<=h<=14, -20<=k<=20,
-22<=l<=21	
Reflections collected	: 20488
Independent reflections	: 6681 [R(int) = 0.0585]
Completeness to theta = 28.40°	: 98.1 %

Absorption correction	: None
Refinement method	: Full-matrix least-squares on F^2
Data / restraints / parameters	: 6681 / 0 / 332
Goodness-of-fit on F^2	: 0.998
Final R indices [I>2sigma (I)]	: R1 = 0.0501, wR2 = 0.1200
R indices (all data)	: R1 = 0.0876, wR2 = 0.1464
Absolute structure parameter	: 0.0(11)
Largest diff. peak and hole	: 0.174 and -0.180 e.$Å^{-3}$

2.6 EVALUTION OF SYMMETRY ELEMENTS

Specimen-Single crystal of 6α-acetoxy azadiron ($C_{30}H_{38}O_6$)

X-ray target material = Mo

Applied voltage =50 KV

Applied current =30 mA

Exposure time =8(eight) hours

Wavelength of MoKα = 0.71073Å

Space group =Orthorhombic P2 (1)2(1)2(1)

Cell contstants: a=10.699(3)Å

b =15.510(4)Å

c=16.626(4)Å

α = 90°, β = 90°, γ =90°

Volume =2759.0(2)$Å^3$ Z = 4

Instrument used for data collection: Bruker Nonius SMART CCD 3-circle diffractometer.Equipped with graphite monochromator

Number of reflections measured: 20488

Temperature of crystal during data collection: 296K

Crystal dimention =0·48×0·34×0·22 mm^3

Density calculated: 1·191 Mg/ m^3

Absorption coefficient: 0·082mm^{-1}

F(000) : 1064

Theta range : 3·81 to 28·40°

Index ranges :–11<= h <= 14,

–20<= k <= 20

– 22 <= I <=21

Independent reflection: 6681[R (int) = ·0585]

Completeness to theta =28·40° 98·1 %

Goodness of fit on F2 = 0·998

Absolute structure parameter: 0·0(11)

Refinement method: Full Matrix least- squares on F2

Largest diff.peak and hole: 0·174 and– 0·180°e$Å^{-3}$

2.7 DATA COLLECTION AND REDUCTION

The size of the crystal 0·48×0·34×0·22 mm^3, Symmetry $P2_12_12_1$ is determine using a Bruker Nonius SMART CCD diffractometer. Three dimentional intensity data are collected on a bruker Nonius SMART CCD 3circle diffractometer with MoK_α radiation(λ=·71073Å) equipped with graphite monocromator. The Bruker SMART software[10] is used for data collection and also for indexing the reflections and

determining the unit cell. The cell parameter are refined by least squares method on the basis of 6681 independent reflections with I>2δ (I)(<–11<=h<14,–20<=k<=20,–<=l<=21) are measured up to 80° in 2θ by the w/2θ scan technique, with scan speed of 2·5°min^{-1}. Lortentz and polarization correction applied but absorption correction is ignored as structure contained only light atoms.

2.8 STRUCTURE DETERMINATION

The structure is solved by direct method refined by full-matrix least-squares calculations using SHELXTL-97 software[12-13].In this program,E-values are calculated by a modified k-curve method (Karle, Hauptmann and Christ,1958)[16].The atoms are refined by full matrix least squres method first isotropically and then anisotropically using the program SHELX-97.H-atoms are not refined .Altogether 332 parameters are refined. The E-statistics $<|E^2-1|> = 0.773$ imply that the crystal is chiral. The values of R(int) = 0.0585 and R(sigma) = 0.0640 show that the quality of the data is satisfactory

The final R value is 0.0727.The function is minimized with weight = 1 / [$sigma^2(Fo^2)$ + (0.0750 * P)^2 + 0.00 * P] where P = (Max (Fo^2, 0) + 2 * Fc^2) / 3

The final R=0·079 for 6681 reflection and goodness of fit=0·998 The final R indices[I>2 sigma(I)] =R=0·0501,wR_2 =0·1200. R indices (all data), R1=0·0876, wR2=0·1464.A final difference fourier synthesis revealed the maximum and minimum electron density peaks of 0·174 $eÅ^{-3}$and–0·40$eÅ^{-3}$ respectively.

2.9 BOND ANGLES AND BOND LENGTHS (Å)

Selected bond lengths and bond angles of the molecule (MK-001) involving non-hydrogen atoms are given in table 2.6 and table 2.7 and those involving hydrogen atoms are in table 2.8 and table 2.9.The furan[18-19] ring in the molecule at the position 17 shows normal geometry and lies in the same plane with those of the two-acetyl groups in

positions 6 and 7. Both the acetyl groups lying in the same side represent a specific geometry to the molecule (α –isomer). The furan ring at the position 17 is found to be twisted with respect to the D ring of the steroidal structure. The existence of the two acetyl groups at positions 6 & 7 in the molecule is expected to stabilize the three dimensional assembly of the molecules in the solid state through C-H···O weak interaction involving C_{28}-H···O_5, C_{26}-H···O_6 and C_1-H···O_6 interactions ($d_{C28\cdots O5}$ 3.40, $d_{C26\cdots O6}$ 3.42 Å and $d_{C1\cdots O6}$ 3.42 Å) respectively and Van der Waals interactions as shown in the Figure 2.3. These distances are well within the reported range for C-H···O interaction[20]. The length of the double bond C_3=O_4 is slightly larger (1.217Å) than the normal C=O double (1.20 Å) bond that could be attributed to the resonance made by the, β- unsaturated system present in the molecule.

2.10 CONFORMATION OF THE MOLECULE

The molecular conformation can be described by the torsion angles about the various bonds; and the calculations of the least squares planes for various sets of atom in the molecule, together with their e.s.d's from the respective planes.

The torsion angles for the molecule 6α acitoxy azadiron are listed in the Table10.Furan ring deviates from the planes containing C16–C17–C20 and C21–C20–C21 with a dihedral angle at -165.46(24) along with C16–C17–C20 & C23–C20–C17 having 12.70(0.37).Similarly in the other side the plane having C13–C17–C20 and C23–C20–C17 showed a torsional angle of 71.76(32) with C17–C19–C20–C21 torsion by -110.08(29)°.

2.11 MOLECULAR PACKING

The crystal structure is stabilized by a network of intermolecular hydrogen bonds and normal van der Waals contacts. The packing of the molecules of mercury[21] diagram in the crystalline space as viewed down the a-axis, b-axis and c-axis of the unit cell is depicted in figure 2.4., figure 2.5 and figure 2.6. All the intermolecular contacts less than 4.00(Å) involving the non hydrogen atoms are listed in the table2.10.

The molecule of the asymmetric is held by C–H....O hydrogen bonds and they are related by a center of inversion.

Details of hydrogen bond geometry of the present structure **6α acetoxy azadirone.**

D-H....A	D–H	D...A	H...A	D–H...A
C7 -H7...O6$^{(i)}$	0.980(2)	2.714(3)	2.320(2)	103.03(14)
C5 -H5...O5$^{(i)}$	0.980(3)	2.888(3)	2.429(1)	108.10(13)
C9 -H9...O5$^{(i)}$	0.980(2)	2.950(3)	2.559(2)	103.77(14)
C6 -H6...O4$^{(i)}$	0.980(3)	2.668(3)	2.384(2)	95.83(13)
C25 -H25...O1$^{(i)}$	0.960(2)	2.870(4)	2.559(2)	99.00(17)
C24 -H24...O1$^{(i)}$	0.960(3)	2.854(4)	2.565(2)	97.47(18)
C24 -H24...O3$^{(i)}$	0.960(3)	2.900(3)	2.241(2)	124.96(18)

Symmetry codes: (i) x,y,z

The molecule contains seven strong C–H····O interactions of, C7–H7····O6= 2.714(3), C5–H5·····O5 = 2.888(3), C9–H9·····O5 = 2.950(3), C6–H6·····O4 = 2.668(3), C25–H25·····O1= 2.870(4), C24–H25·····O1=2.854(4) and C24–H25·····O1= 2.854(4).But there is no any intermolecular D·····A interactions in the molecule.

Moreover, it can be concluded that the structural features of the compound investigated fit into general pattern observed in all other steroids derivatives[22-26]. The

approximate correlations between the bond distances are indicative of extensive electron delocalization in the molecule. The structural activity of the compound may be estimated from the atomic charge density distribution using the three dimensional crystallographic parameters of the molecule.

The stereo mercury[21] diagram of molecular packing structure with C--H···O interaction are shown in figure-3.3. The unit cell contains four molecules related by 2-fold screw operation.

2.12 CONCLUSION

The single crystal of 6α acetoxy azadirone has a orthorhombic cell with lattice parameters a = 10·699(3)Å b = 15·5100(4)Å c = 16·626(4)Å α =90° β =90° γ= 90° with space group $P2_12_12_1$.

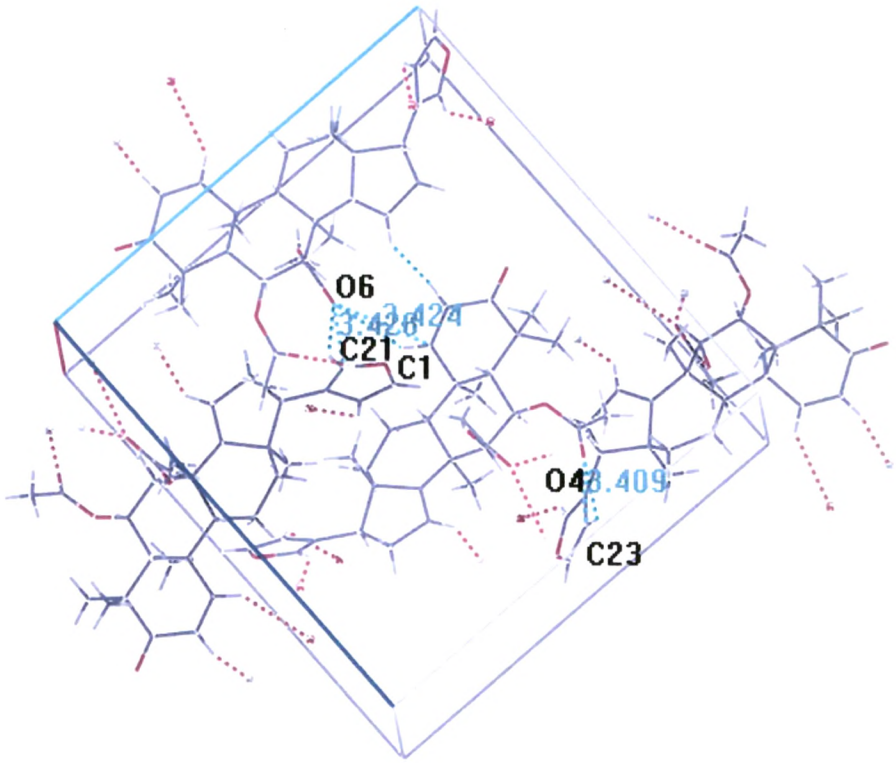

Figure 2.3: Packing structure with C-H···O Interactions

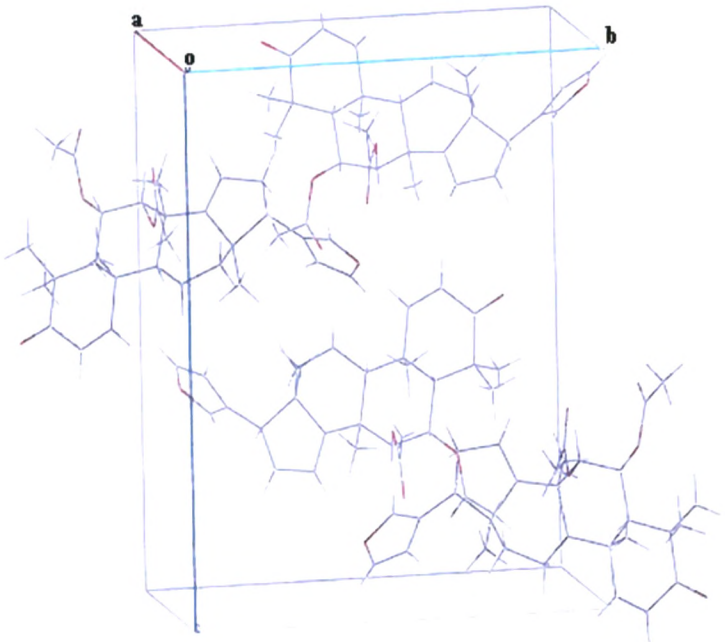

Figure 2.4: The packing of the molecules in the crystalline space as viewed down the a-axis of the unit cell.

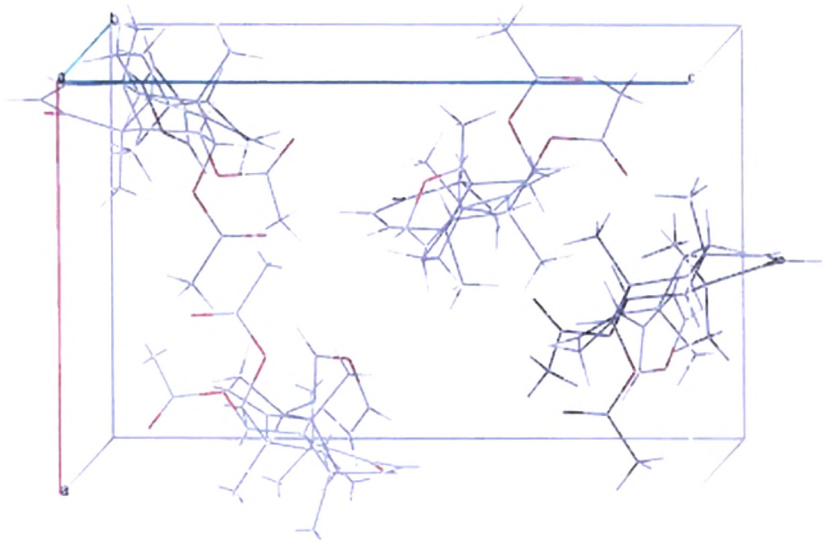

Figure 2.5: The packing of the molecules in the crystalline space as viewed down the b-axis of the unit cell.

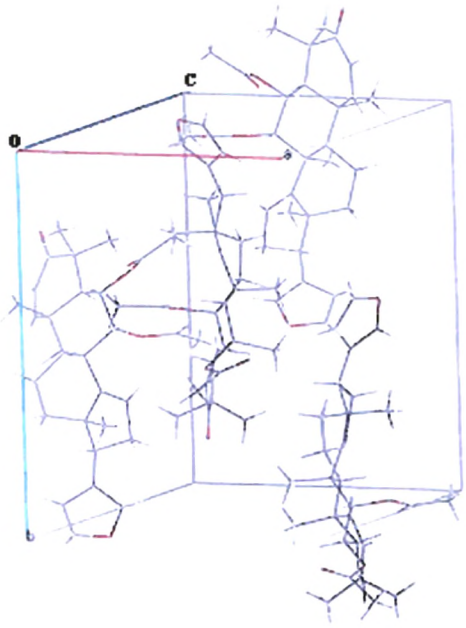

Figure 2.6: The packing of the molecules in the crystalline space as viewed down the c-axis of the unit cell.

Table 2.2: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for(MK-001) Theanisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	48(1)	52(1)	45(1)	0(1)	-1(1)	1(1)
O(1)	63(1)	49(1)	52(1)	5(1)	3(1)	11(1)
O(3)	104(2)	57(1)	91(1)	7(1)	5(1)	-22(1)
O(4)	126(2)	59(1)	87(1)	-28(1)	-11(1)	4(1)
O(5)	83(2)	117(2)	57(1)	23(1)	15(1)	23(1)
O(6)	65(1)	124(2)	62(1)	-6(1)	-15(1)	11(1)
C(11)	51(2)	44(1)	42(1)	-1(1)	1(1)	-5(1)
C(7)	43(1)	47(1)	38(1)	0(1)	3(1)	5(1)
C(8)	42(1)	42(1)	44(1)	-3(1)	-1(1)	2(1)
C(5)	57(2)	42(1)	43(1)	-2(1)	6(1)	-1(1)
C(20)	50(2)	42(1)	46(1)	-4(1)	2(1)	0(1)
C(19)	53(2)	43(1)	53(1)	-4(1)	4(1)	-3(1)
C(21)	57(2)	43(1)	44(1)	-5(1)	-1(1)	5(1)
C(10)	51(2)	42(1)	43(1)	1(1)	-4(1)	-2(1)
C(1)	68(2)	56(1)	44(1)	-1(1)	-2(1)	-13(1)
C(24)	74(2)	49(1)	62(1)	1(1)	-23(1)	0(1)

C(3)	57(2)	56(1)	60(1)	-16(1)	10(1)	-4(1)
C(6)	57(2)	42(1)	44(1)	3(1)	1(1)	8(1)
C(15)	60(2)	59(1)	59(1)	-5(1)	-10(1)	4(1)
C(23)	52(2)	48(1)	60(1)	3(1)	-14(1)	0(1)
C(17)	66(2)	53(1)	53(1)	-6(1)	-12(1)	1(1)
C(4)	62(2)	42(1)	54(1)	-6(1)	8(1)	2(1)
C(13)	82(2)	60(1)	55(1)	14(1)	-5(2)	7(1)
C(9)	63(2)	53(1)	53(1)	-4(1)	6(1)	7(1)
C(28)	81(2)	49(1)	76(2)	3(1)	-11(2)	-7(1)
C(25)	64(2)	43(1)	55(1)	-5(1)	2(1)	-3(1)
C(22)	65(2)	56(1)	54(1)	-5(1)	7(1)	-3(1)
C(2)	78(2)	64(1)	43(1)	-10(1)	9(1)	-14(1)
C(12)	60(2)	51(1)	59(1)	-1(1)	2(1)	-7(1)
C(18)	69(2)	52(1)	57(1)	-10(1)	-6(1)	-4(1)
C(27)	93(3)	54(1)	73(2)	7(1)	-7(2)	-2(2)
C(16)	53(2)	121(3)	94(2)	2(2)	6(2)	-4(2)
C(26)	78(2)	54(1)	82(2)	1(1)	-6(2)	-14(1)
C(14)	100(3)	99(2)	84(2)	26(2)	-11(2)	32(2)
C(29)	100(2)	47(1)	78(2)	-5(1)	28(2)	-9(1)
C(30)	65(2)	62(1)	89(2)	-20(1)	4(2)	18(1)

Table 2.3: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for MK-001.

	x	y	z	U(eq)
H(7)	2243	4924	2677	51
H(5)	2460	3949	790	57
H(19)	751	7961	1958	60
H(10)	1850	5378	601	54
H(1)	534	4688	-575	68
H(24A)	371	5986	-130	74
H(24B)	-678	5809	505	74
H(6)	971	3793	2181	57
H(23A)	241	7309	316	64
H(23B)	-349	7025	1136	64
H(17)	2535	6444	2923	69
H(9A)	-250	4891	2315	85
H(9B)	-592	5824	2027	85
H(9C)	227	5693	2799	85
H(28)	123	8985	620	82
H(22A)	3432	7145	876	87
H(22B)	2573	7573	225	87

H(22C)	2669	6566	280	87
H(2)	926	3410	-1124	74
H(12A)	-1267	4551	731	85
H(12B)	-744	4068	1488	85
H(12C)	-927	3569	677	85
H(18A)	3358	7841	2207	71
H(18B)	2315	8023	2860	71
H(27)	1073	10313	172	88
H(16A)	6228	5253	2010	134
H(16B)	5416	5375	1234	134
H(16C)	5815	4448	1507	134
H(26)	3515	9165	1586	85
H(14A)	4290	2954	3605	141
H(14B)	4109	2379	2839	141
H(14C)	3388	2158	3634	141
H(29A)	-112	2488	1300	112
H(29B)	1019	2232	1849	112
H(29C)	671	1659	1105	112
H(30A)	2848	1773	605	108
H(30B)	3242	2378	1317	108
H(30C)	3439	2677	425	108

Table 2.4 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for MK-001. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O (5)	3378(2)	4974(1)	1724(1)	49(1)
O (3)	2742(2)	3354(1)	2256(1)	55(1)
O (2)	2622(2)	9988(1)	823(1)	84(1)
O (1)	1035(2)	1974(1)	-388(1)	91(1)
O (4)	1831(2)	3445(1)	3464(1)	86(1)
O (6)	4381(2)	4849(1)	2894(1)	84(1)
C (10)	642(2)	4349(1)	661(1)	46(1)
C (7)	2170(2)	4842(1)	2095(1)	43(1)
C (8)	1234(2)	5499(1)	1752(1)	43(1)
C (5)	1669(3)	3746(1)	1020(1)	48(1)
C (13)	1558(2)	7079(1)	1180(1)	46(1)
C (17)	1574(2)	7921(1)	1701(1)	50(1)
C (14)	1767(2)	6409(1)	1834(1)	48(1)
C (9)	1026(2)	5306(1)	850(1)	45(1)
C (1)	680(3)	4219(2)	-240(1)	57(1)
C (11)	187(3)	5984(1)	442(2)	62(1)

C (3)	1157(2)	2686(2)	-91(2)	58(1)
C (6)	1774(3)	3914(1)	1920(1)	48(1)
C (26)	4418(3)	4939(2)	2179(2)	60(1)
C (12)	326(2)	6910(1)	762(2)	54(1)
C (15)	2306(3)	6754(1)	2467(2)	58(1)
C (4)	1580(3)	2772(1)	781(1)	53(1)
C (24)	2651(3)	3174(2)	3042(2)	66(1)
C (30)	42(3)	5475(2)	2272(1)	57(1)
C (21)	917(3)	9180(1)	758(2)	69(1)
C (20)	1773(3)	8755(1)	1267(1)	54(1)
C (18)	2662(3)	7092(2)	584(1)	59(1)
C (2)	916(3)	3455(2)	-566(2)	62(1)
C (19)	-701(3)	4112(1)	913(1)	57(1)
C (16)	2508(3)	7712(1)	2369(2)	60(1)
C (22)	1449(3)	9912(2)	510(2)	74(1)
C (27)	5571(3)	5010(2)	1690(2)	90(1)
C (23)	2795(3)	9279(2)	1290(2)	72(1)
C (25)	3703(4)	2618(2)	3303(2)	95(1)
C (28)	708(3)	2238(2)	1308(2)	75(1)
C (29)	2903(3)	2361(2)	782(2)	72(1)

Table 2.5. Bond distances (Angstrom) for MK-001 involving non-hydrogen atoms with e.s.d's in parenthesis.

O5	- C7	1.4473(28)	C5	- C4	1.5642(28)
O5	- C29	1.3467(32)	C13	- C17	1.5677(28)
O3	- C6	1.4622(29)	C13	- C14	1.5209(28)
O3	- C27	1.3406(31)	C13	- C12	1.5128(35)
O2	- C22	1.3634(44)	C13	- C18	1.5424(35)
O2	- C21	1.3602(33)	C11	- C12	1.5387(31)
O1	- C3	1.2166(31)	C3	- C4	1.5248(34)
O4	- C27	1.1986(39)	C3	- C2	1.4540(34)
O6	- C29	1.1983(32)	C29	- C30	1.4819(44)
C10	- C5	1.5626(32)	C15	- C16	1.5105(31)
C10	- C9	1.5710(27)	C4	- C25	1.5233(38)
C10	- C1	1.5107(30)	C4	- C24	1.5536(39)
C10	- C19	1.5412(36)	C27	- C28	1.4831(48)
C7	- C8	1.5375(30)	C23	- C20	1.4096(38)
C7	- C6	1.5288(29)	C23	- C22	1.3360(37)
C8	- C14	1.5288(29)			
C8	- C9	1.5448(29)			
C8	- C26	1.5407(34)			
C5	- C6	1.5231(29)			

Table 2.6: Bond angles (deg) involving non-hydrogen atoms with e.s.d's in parenthesis for MK-001.

C7	- O5 - C29	119.51	0.19
C6	- O3 - C27	116.37	0.18
C22	- O2 - C21	105.88	0.23
C5	- C10 - C9	107.73	0.15
C5	- C10 - C1	106.24	0.17
C5	- C10 - C19	114.12	0.20
C9	- C10 - C1	108.56	0.16
C9	- C10 - C19	114.49	0.18
C1	- C10 - C19	105.25	0.18
O5	- C7 - C8	109.28	0.18
O5	- C7 - C6	107.45	0.17
C8	- C7 - C6	111.88	0.16
C7	- C8 - C14	109.58	0.16
C7	- C8 - C9	108.97	0.16
C7	- C8 - C26	108.35	0.18
C14	- C8 - C9	108.63	0.16
C14	- C8 - C26	106.29	0.18
C9	- C8 - C26	114.92	0.17
C10	- C5 - C6	108.96	0.17

C10 - C5 - C4	115.97	0.16
C6 - C5 - C4	114.77	0.16
C17 - C13 - C14	99.93	0.15
C17 - C13 - C12	114.04	0.17
C17 - C13 - C18	109.60	0.17
C14 - C13 - C12	109.80	0.18
C14 - C13 - C18	110.86	0.17
C12 - C13 - C18	112.01	0.21
C13 - C17 - C20	117.09	0.17
C13 - C17 - C16	103.43	0.17
C20 - C17 - C16	116.12	0.18
C8 - C14 - C13	120.79	0.17
C8 - C14 - C15	127.73	0.20
C13 - C14 - C15	111.03	0.19
C10 - C9 - C8	114.54	0.16
C10 - C9 - C11	113.82	0.16
C8 - C9 - C11	112.28	0.17
C10 - C1 - C2	121.97	0.20
C9 - C11 - C12	115.38	0.17
O1 - C3 - C4	119.88	0.22
O1 - C3 - C2	120.35	0.22
C4 - C3 - C2	119.76	0.21
O3 - C6 - C7	106.88	0.16

O3 - C6 - C5	108.98	0.17
C7 - C6 - C5	111.59	0.16
O5 - C29 - O6	122.39	0.24
O5 - C29 - C30	112.10	0.24
O6 - C29 - C30	125.50	0.27
C13 - C12 - C11	113.85	0.19
C14 - C15 - C16	112.19	0.20
C5 - C4 - C3	110.17	0.17
C5 - C4 - C25	114.62	0.18
C5 - C4 - C24	109.92	0.18
C3 - C4 - C25	108.46	0.19
C3 - C4 - C24	103.59	0.21
C25 - C4 - C24	109.51	0.23
O3 - C27 - O4	123.43	0.25
O3 - C27 - C28	110.55	0.24
O4 - C27 - C28	126.01	0.30
C20 - C23 - C22	107.78	0.22
C17 - C20 - C23	126.89	0.20
C17 - C20 - C21	127.97	0.21
C23 - C20 - C21	105.12	0.25
C1 - C2 - C3	123.01	0.22
C17 - C16 - C15	101.12	0.18

Table 2.7: Bond distances (Angstrom) for MK-001 involving hydrogen atoms with e.s.d's in parenthesis.

C7	- H7	0.9801(20)	C19	- H19B	0.9600(24)
C5	- H5	0.9800(25)	C19	- H19A	0.9599(23)
C17	- H17	0.9800(25)	C19	- H19C	0.9600(22)
C9	- H9	0.9801(24)	C16	- H16A	0.9700(29)
C1	- H1	0.9301(23)	C16	- H16B	0.9700(25)
C11	- H11B	0.9699(25)	C22	- H22	0.9300(29)
C11	- H11A	0.9700(28)	C30	- H30B	0.9600(34)
C6	- H6	0.9800(25)	C30	- H30A	0.9601(35)
C12	- H12A	0.9699(23)	C30	- H30C	0.9600(35)
C12	- H12B	0.9700(25)	C21	- H21	0.9301(32)
C15	- H15	0.9302(24)	C28	- H28A	0.9600(36)
C26	- H26C	0.9600(24)	C28	- H28B	0.9601(36)
C26	- H26B	0.9600(26)	C28	- H28C	0.9600(35)
C26	- H26A	0.9600(24)	C25	- H25C	0.9599(34)
C23	- H23	0.9299(32)	C25	- H25B	0.9600(29)
C18	- H18A	0.9600(27)	C25	- H25A	0.9599(24)
C18	- H18B	0.9600(23)	C24	- H24B	0.9599(27)
C18	- H18C	0.9601(23)	C24	- H24C	0.9601(31)
C2	- H2	0.9300(25)	C24	- H24A	0.9600(29)

Table 2.8: Bond angles (deg) involving hydrogen atoms with e.s.d's in parenthesis for MK-001

O5 - C7 - H7	109.39	0.18
H7 - C7 - C8	109.40	0.18
H7 - C7 - C6	109.39	0.18
H5 - C5 - C6	105.35	0.18
H5 - C5 - C4	105.36	0.18
C13 - C17 - H17	106.47	0.19
H17 - C17 - C20	106.47	0.20
H17 - C17 - C16	106.48	0.22
C10 - C9 - H9	105.00	0.18
C8 - C9 - H9	105.00	0.18
H9 - C9 - C11	105.00	0.21
C10 - C1 - H1	119.02	0.20
H1 - C1 - C2	119.01	0.24
C9 - C11 - H11B	108.43	0.21
C9 - C11 - H11A	108.43	0.24
H11B - C11 - H11A	107.48	0.25
H11B - C11 - C12	108.43	0.21
H11A - C11 - C12	108.43	0.21
O3 - C6 - H6	109.77	0.22
C7 - C6 - H6	109.78	0.20
C5 - C6 - H6	109.78	0.19

C13 - C12 - H12A	108.79	0.21
C13 - C12 - H12B	108.79	0.22
C11 - C12 - H12A	108.78	0.18
C11 - C12 - H12B	108.78	0.20
H12A - C12 - H12B	107.67	0.23
C14 - C15 - H15	123.90	0.25
H15 - C15 - C16	123.91	0.22
C8 - C26 - H26C	109.47	0.22
C8 - C26 - H26B	109.47	0.23
C8 - C26 - H26A	109.47	0.21
H26C - C26 - H26B	109.47	0.23
H26C - C26 - H26A	109.47	0.23
H26B - C26 - H26A	109.47	0.24
H23 - C23 - C20	126.11	0.31
H23 - C23 - C22	126.10	0.28
C13 - C18 - H18A	109.46	0.24
C13 - C18 - H18B	109.47	0.21
C13 - C18 - H18C	109.47	0.21
H18A - C18 - H18B	109.48	0.24
H18A - C18 - H18C	109.47	0.24
H18B - C18 - H18C	109.47	0.23
C1 - C2 - H2	118.49	0.24
C3 - C2 - H2	118.49	0.24
C10 - C19 - H19B	109.47	0.23

C10 - C19 - H19A	109.47	0.21
C10 - C19 - H19C	109.46	0.21
H19B - C19 - H19A	109.49	0.23
H19B - C19 - H19C	109.47	0.22
H19A - C19 - H19C	109.47	0.22
C17 - C16 - H16A	111.55	0.26
C17 - C16 - H16B	111.55	0.22
C15 - C16 - H16A	111.55	0.22
C15 - C16 - H16B	111.55	0.20
H16A - C16 - H16B	109.35	0.26
O2 - C22 - H22	124.82	0.31
C23 - C22 - H22	124.82	0.26
C29 - C30 - H30B	109.47	0.29
C29 - C30 - H30A	109.46	0.30
C29 - C30 - H30C	109.48	0.29
H30B - C30 - H30A	109.46	0.34
H30B - C30 - H30C	109.48	0.34
H30A - C30 - H30C	109.47	0.35
O2 - C21 - H21	124.58	0.27
C20 - C21 - H21	124.57	0.31
C27 - C28 - H28A	109.47	0.33
C27 - C28 - H28B	109.46	0.32
C27 - C28 - H28C	109.47	0.30
H28A - C28 - H28B	109.47	0.34

H28A - C28 - H28C	109.49	0.35
H28B - C28 - H28C	109.47	0.35
C4 - C25 - H25C	109.48	0.29
C4 - C25 - H25B	109.47	0.24
C4 - C25 - H25A	109.47	0.21
H25C - C25 - H25B	109.47	0.31
H25C - C25 - H25A	109.47	0.25
H25B - C25 - H25A	109.46	0.26
C4 - C24 - H24B	109.47	0.23
C4 - C24 - H24C	109.46	0.25
C4 - C24 - H24A	109.46	0.25
H24B - C24 - H24C	109.48	0.29
H24B - C24 - H24A	109.48	0.26
H24C - C24 - H24A	109.47	0.30

Table 2.9: Torsion angles (deg) for MK-001

C29 -O5 -C7 -C8	138.02	0.20
C29 -O5 -C7 -C6	-100.40	0.22
C7 -O5 -C29 -O6	-4.22	0.35
C7 -O5 -C29 -C30	174.82	0.21
C27 -O3 -C6 -C7	83.47	0.23
C27 -O3 -C6 -C5	-155.80	0.20
C6 -O3 -C27 -O4	0.17	0.38

C6	-O3	-C27	-C28	-178.88	0.22
C21	-O2	-C22	-C23	-1.08	0.33
C22	-O2	-C21	-C20	1.08	0.32
C9	-C10	-C5	-C6	58.04	0.22
C9	-C10	-C5	-C4	-170.65	0.18
C1	-C10	-C5	-C6	174.22	0.18
C1	-C10	-C5	-C4	-54.47	0.24
C19	-C10	-C5	-C6	-70.28	0.23
C19	-C10	-C5	-C4	61.03	0.25
C5	-C10	-C9	-C8	-56.14	0.22
C5	-C10	-C9	-C11	172.78	0.18
C1	-C10	-C9	-C8	-170.80	0.18
C1	-C10	-C9	-C11	58.12	0.24
C19	-C10	-C9	-C8	71.96	0.23
C19	-C10	-C9	-C11	-59.12	0.25
C5	-C10	-C1	-C2	35.86	0.30
C9	-C10	-C1	-C2	151.48	0.23
C19	-C10	-C1	-C2	-85.50	0.28
O5	-C7	-C8	-C14	-52.90	0.22
O5	-C7	-C8	-C9	65.84	0.21
O5	-C7	-C8	-C26	-168.47	0.17
C6	-C7	-C8	-C14	-171.77	0.18
C6	-C7	-C8	-C9	-53.03	0.22
C6	-C7	-C8	-C26	72.66	0.22

O5	-C7	-C6	-O3	58.77	0.21
O5	-C7	-C6	-C5	-60.29	0.22
C8	-C7	-C6	-O3	178.72	0.16
C8	-C7	-C6	-C5	59.66	0.23
C7	-C8	-C14	-C13	142.44	0.20
C7	-C8	-C14	-C15	-45.98	0.31
C9	-C8	-C14	-C13	23.50	0.26
C9	-C8	-C14	-C15	-164.92	0.24
C26	-C8	-C14	-C13	-100.68	0.22
C26	-C8	-C14	-C15	70.90	0.29
C7	-C8	-C9	-C10	53.22	0.23
C7	-C8	-C9	-C11	-174.96	0.18
C14	-C8	-C9	-C10	172.55	0.17
C14	-C8	-C9	-C11	-55.63	0.23
C26	-C8	-C9	-C10	-68.57	0.24
C26	-C8	-C9	-C11	63.25	0.24
C10	-C5	-C6	-O3	-179.55	0.16
C10	-C5	-C6	-C7	-61.75	0.23
C4	-C5	-C6	-O3	48.49	0.24
C4	-C5	-C6	-C7	166.29	0.18
C10	-C5	-C4	-C3	37.38	0.26
C10	-C5	-C4	-C25	-85.25	0.25
C10	-C5	-C4	-C24	150.92	0.20
C6	-C5	-C4	-C3	165.91	0.19

C6	-C5	-C4	-C25	43.27	0.28
C6	-C5	-C4	-C24	-80.56	0.24
C14	-C13	-C17	-C20	162.42	0.19
C14	-C13	-C17	-C16	33.33	0.21
C12	-C13	-C17	-C20	-80.53	0.25
C12	-C13	-C17	-C16	150.37	0.19
C18	-C13	-C17	-C20	45.94	0.26
C18	-C13	-C17	-C16	-83.16	0.22
C17	-C13	-C14	-C8	150.29	0.19
C17	-C13	-C14	-C15	-22.59	0.24
C12	-C13	-C14	-C8	30.12	0.27
C12	-C13	-C14	-C15	-142.75	0.21
C18	-C13	-C14	-C8	-94.18	0.24
C18	-C13	-C14	-C15	92.95	0.24
C17	-C13	-C12	-C11	-164.60	0.19
C14	-C13	-C12	-C11	-53.43	0.25
C18	-C13	-C12	-C11	70.20	0.25
C13	-C17	-C20	-C23	71.76	0.32

Table 2.10: Intermolecular contacts less than 4.00Å for the non-hydrogen atoms for MK-001.

Atoms		Symmetry code	Distance (Å)
O2	...O6	-x+1,+y+1/2,-z+1/2	3.8570 0.0033
O2	...C1	x+1/2,-y+1/2+1,-z	3.6273 0.0038
O2	...C11	x+1/2,-y+1/2+1,-z	3.7711 0.0036
O2	...C19	x+1/2,-y+1/2+1,-z	3.6736 0.0033
O2	...C24	x,+y+1,+z	3.6929 0.0033
O1	...C19	x+1/2,-y+1/2,-z	3.9748 0.0036
O1	...C22	x,+y-1,+z	3.5567 0.0033
O1	...C30	x-1/2,-y+1/2,-z	3.7942 0.0041
O1	...C24	x-1/2,-y+1/2,-z	3.5661 0.0039
O4	...C17	-x,+y-1/2,-z+1/2	3.7420 0.0037
O4	...C12	-x,+y-1/2,-z+1/2	3.5561 0.0033
O4	...C23	-x,+y-1/2,-z+1/2	3.4086 0.0040
O4	...C20	-x,+y-1/2,-z+1/2	3.9117 0.0038
O4	...C18	-x+1/2,-y+1,+z+1/2	3.6622 0.0032
O6	...O2	-x+1,+y-1/2,-z+1/2	3.8570 0.0033
O6	...C1	-x+1/2,-y+1,+z+1/2	3.4237 0.0030
O6	...C2	-x+1/2,-y+1,+z+1/2	3.6848 0.0032
O6	...C21	-x+1,+y-1/2,-z+1/2	3.4272 0.0040
C17	...O4	-x,+y+1/2,-z+1/2	3.7420 0.0037
C1	...O2	x-1/2,-y+1/2+1,-z	3.6273 0.0038
C1	...O6	-x+1/2,-y+1,+z-1/2	3.4237 0.0030

C1	...C24	x-1/2,-y+1/2,-z	3.9547	0.0039
C11	...O2	x-1/2,-y+1/2+1,-z	3.7711	0.0036
C11	...C21	x-1/2,-y+1/2+1,-z	3.8735	0.0042
C12	...O4	-x,+y+1/2,-z+1/2	3.5561	0.0033
C12	...C18	x-1/2,-y+1/2+1,-z	3.9399	0.0036
C15	...C2	-x+1/2,-y+1,+z+1/2	3.7983	0.0038
C15	...C25	-x,+y+1/2,-z+1/2	3.8876	0.0044
C26	...C23	-x,+y-1/2,-z+1/2	3.9768	0.0037
C26	...C25	-x,+y+1/2,-z+1/2	3.7021	0.0036
C23	...O4	-x,+y+1/2,-z+1/2	3.4086	0.0040
C23	...C26	-x,+y+1/2,-z+1/2	3.9768	0.0037
C20	...O4	-x,+y+1/2,-z+1/2	3.9117	0.0038
C18	...O4	-x+1/2,-y+1,+z-1/2	3.6622	0.0032
C18	...C12	x+1/2,-y+1/2+1,-z	3.9399	0.0036
C2	...O6	-x+1/2,-y+1,+z-1/2	3.6848	0.0032
C2	...C15	-x+1/2,-y+1,+z-1/2	3.7983	0.0038
C2	...C24	x-1/2,-y+1/2,-z	3.4807	0.0041
C19	...O2	x-1/2,-y+1/2+1,-z	3.6736	0.0033
C19	...O1	x-1/2,-y+1/2,-z	3.9748	0.0036
C19	...C24	x-1/2,-y+1/2,-z	3.9232	0.0038
C22	...O1	x,+y+1,+z	3.5567	0.0033
C22	...C30	x-1/2,-y+1/2+1,-z	3.7773	0.0047
C22	...C25	x,+y+1,+z	3.9253	0.0037
C30	...O1	x+1/2,-y+1/2,-z	3.7942	0.0041

C30	...C22	x+1/2,-y+1/2+1,-z	3.7773	0.0047
C21	...O6	-x+1,+y+1/2,-z+1/2	3.4272	0.0040
C21	...C11	x+1/2,-y+1/2+1,-z	3.8735	0.0042
C21	...C30	-x+1,+y+1/2,-z+1/2	3.9526	0.0047
C25	...C15	-x,+y-1/2,-z+1/2	3.8876	0.0044
C25	...C26	-x,+y-1/2,-z+1/2	3.7021	0.0036
C25	...C22	x,+y-1,+z	3.9253	0.0037
C24	...O2	x,+y-1,+z	3.6929	0.0033
C24	...O1	x+1/2,-y+1/2,-z	3.5661	0.0039
C24	...C1	x+1/2,-y+1/2,-z	3.9547	0.0039
C24	...C3	x+1/2,-y+1/2,-z	3.6664	0.0040
C24	...C19	x+1/2,-y+1/2,-z	3.9232	0.0038

REFERENCES: 2

1. Kanjilal U N, Kanjilal P C & Das A; "*Flora of Assam*", 2nd Edition, Vol I (Part 1); pp 234, published by under the Authority of the Government of Assam, 1992.
2. Saikia B, Kataky J C S, Mathur R K & Baruah J N, *Ind J Chem* 16 (B), 1978,1042
3. Sarmah G K, Bhattacharyya N K, Goswami B N, Borthakur N, Baruah P, Kataky J C S, *Chemistry: An Indian Journal*, 1, 42-46. 2003
4. Sarkhel S, Jain G K, Singh H, Subramanya S & Maulik P R, *Acta Cryst* C56, 253-254, 2000
5. Glidewell C., Low J. N., Melguizo M and Quesada A. *Acta Cryst.*. C59, 14-18, 2003
6. Glidewell C., Low J. N., Melguizo M.and Quesada A. *Acta Cryst.*C59, 19-21, 2003
7. Jones N. A., Jenkinson S. F., Soengas R., Izumori K., Fleet G. W. J and Watkin D. J. *Acta Cryst.* C63, 7-10, 2007.
8. Chandan Tamuly, Rupam S.Sarma, Anderei S.Batsnov, Andres E.Goeta and Jubaraj B.Baruah. *Acta Cryst.* C61, 0324-0327,2005.
9. Simone M., Fleet G. W. J., Bream R and Watkin D. J. *Acta Cryst.* E63, 1409-1411, 2007
10. SMART-*NT, Data Collection Software, version 5.0*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1999.
11. *SAINT-NT, Data Reduction Software, version 5.0*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1999.
12. Sheldrick G M SHELX97, Program for the solution of crystal structure, University of Göttingen, Germany, 1997.

13. Sheldrick G M SHELXL97, Program for the refinement of crystal structure, University of Göttingen, Germany, 1997.

14. International TableforXraycrystallography,Vol.1V.KynochPress,Biraingham (present distributor:Kluwer Academic Publishers:Dordrecht).

15. Johnson C K, *ORTEP32, Report ORNL-5138*, Oak Ridge National Laboratory, Tennessee, USA, 1976.

16. Karle, J., Hauptman, H.and Christ, C.L *Acta Cryst.* 11,757–761,1958

17. Nardelli.M.*Comput.Chem.* **7,** 95–98,1983

18. Devi S. S., Malathi R., Rajan S. S., Aravind S. Krishnakumari G. N. and Ravikumar K. *Acta Cryst.* C59, 530-532, 2003

19. Malathi R., Rajan S. S., Gopalakrishnan G. and Suresh G. *Acta Cryst.* C58, 681-682, 2002

20. Desiraju G R, *Acc Chem Res*, 24, 1991, 290-296.

21. CCDC Mercury 1.4.1, 2005.

22. Parvez M., Edwards O. E. and Paryzek Z. *Acta Cryst.* C63, 249-251, 2007

23. Andrade L. C. R., Paixão J. A., de Almeida M. J. M., Tavares da Silva E. J. and Fernandes Roleira F. M. *Acta Cryst.* E61, 1144-1146, 2005

24. Andrade. L. C. R., Paixão J. A., de Almeida M. J. M., Fernandes Roleira F. M. and Tavares da Silva E.J.*Acta Cryst*C63, 330-331, 2007

25. Andrade L. C. R., Paixão J. A., de Almeida M. J. M., Tavares da Silva E. J. and Fernandes Roleira F. M. *Acta Cryst.* E62, 1856-1858, 2006

26. Andrade L. C. R., Paixão J. A., de Almeida M. J. M., Fernandes Roleira F. M. and Tavares da Silva E. J. *Acta Cryst.* C61, 131-133, 2005

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