CHAPTER-4

MOLECULAR AND CRYSTAL STRUCTURE OF COMPOUND. {5-HYDROXY-3-(3-HYDROXYPHENYL)-8,8-DIMETHYL-6-(3-METHYLBUT-2-ENYL)-4H.8H-PYRANO [2,3-H]CHROMEN-4-ONE],}(MN-01) [$C_{25}H_{24}O_4$]

4.1 INTRODUCTION

The title compound (MN-01) one of the most important isoflavonoids found in the plant fruits *Cudrania javanensis*[1-2] of Moraceae family. The cardioprotective effects of the isoflavonoids of the title compound against ischemia-reperfusion induced injury are studied[3,4]

The absolute configuration of this important phyto-constituent has been studied and the single crystal structure elucidation[5-11]of this compound (MN-01) has been elaborated in details in the following heading.

The analysis of this structure is undertaken in order to get accurate bond distances of this compound. The study of the title compound will help to understand the nature of molecular packing in crystalline space, the molecular geometry and molecular conformations of the crystal.

4.2 CRYSTAL GROWTH

For the growth of the single crystal of the compound (MN-01) toluene and ethyl acetate (98:02) as solvent. A glass tube stand is used to keep the tube undisturbed for growing the crystals. The Osajin ($C_{25}H_{24}O_4$) powder is dissolved in minimum volume of toluene until the solution becomes saturated and add a few drops of ethyl acetated in

the ratio 98:02.The mouth of the tube is covered by a piece of alumunium foil to slow down the rate of evaporation. Precation is taken so that no foreign particules could enter into the solution. During the entire seeding period, solution is kept undisturbed. After a week some pale yellow crystalline solid of size $0{\cdot}46\times0{\cdot}13\times0{\cdot}07mm^3$ are obtained. The crystals are taken out of the solution carefully and allowed to dry in a glass plate inside a vacuum dessicator. The crystal growth took place at room temperature ($29+2^{\circ}c$)

4.3 SELECTION OF THE CRYSTAL

A good crystal is selected by observing it under a polarizing microscope. Deformed or twinned crystals are 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.

4.4 EXPERIMENTAL

Compound (MN-01) have been isolated by chromatographic method in the laboratory of Institute of Advanced Studies in Science & Technology (IASST) Guwahati, Assam, India. from the fruits extract of *Cudrania javanensis*, colourless needle like crystal are grown in toluene for our further study.

Applying oscillation and Weissenberg technique the preliminary crystal data are determined using CuKα radiation. The crystals are found to be triclinic. The zero layer line Weissenberg photographs about different axes revealed that hkl have no systematic absences. But reflections, h+k+l=2n; h = k = l=2n; hol; 2n+k+2l; h00 are absent. This

uniquely establishes that the space group is P-1 with the general equivalent positions ±(x, y, z; -x,-y,-z)

The number of molecules per unit cell is found to be 2 and hence in the asymmetry unit there are two molecules.

For the collection of intensity data, a single crystal of size 0.46 × 0.13 × 0.07 mm^3 is selected. Three dimensional intensity data are collected at 296K temperature with Bruker 3-circle diffractometer (Bruker Nonius SMART APEX 2) equipped with CCD area detector, and using graphite monochromated MoK_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[12] is used for data collection and also for indexing the reflections and the unit cell parameters. The collected data are integrated using SAINT software[13]. The structures are solved by direct methods and refined by full-matrix least squares calculation using SHELXTL software[14, 15]. Lattice parameters are determined from θ values in the range 2.5< θ <24·74. A total of 12909 reflections are recorded for the values of θ up to 24·74, out of which 3463 reflections are unique. 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 2.5≤θ≤24.74 on the basis of 3463 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 -7<=h<=7, -9<=k<=9, -24<=l<=24.

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 heteroatom (N, O and F) are located from the difference Fourier maps, and refined with

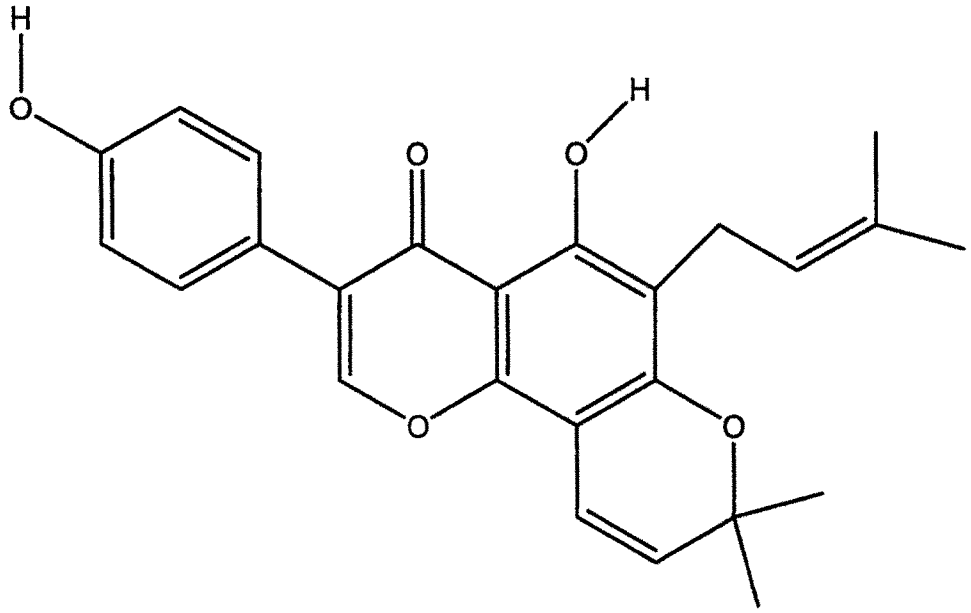

Figure 4.1: Structure of (MN-01)

isotopic displacement co-efficients. The final refinement cycle converged R= 0.1536, and wR (F^2) = 0.3951. Final cycle of refinement resulted in the residual electron density in the range and 1·297 and –1·096eÅ^{-3}

. Atomic scattering factors are taken from International Tables for X-ray crystallography[16].

The covalent structure of MN-01 is given in the figure.4.1 and an ORTEP diagram[17] of (MN-01) with the atomic numbering scheme is shown in the figure 4.2. Crystal data and other experimental details are given in the table 4.1.

4.5 RESULTS AND DISCUTION:

From the XRD data of single crystal is collected at 296k temperature with a Bruker 3-circle diffractometer. In the analysis of the crystal structure of compound MN-01, 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.

Table 4.2 displayed anisotropic displacement parameters ($Å^2 x\ 10^3$) for (MN-01). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$. Table 4.3 Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for (MN-01). The least of atomic co-ordinate and equivalent isotropic displacement parameters ($Å^2 x\ 10^3$) for MN-01. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor are given in the table 4.4. The list of structure factors are also given in Appendix-111.

Table 4.1. Crystal data and structure refinement for MN-01.

Empirical formula	C25 H24 O5	
Formula weight	404.44	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.2374(11) Å	α= 96.083(13)°.
	b = 8.4243(11) Å	β= 95.602(10)°.

	c = 21.181(4) Å γ = 107.419(7)°.
Volume	1046.1(3) $Å^3$
Z	2
Density (calculated)	1.284 Mg/m^3
Absorption coefficient	0.089 mm^{-1}
F (000)	428
Crystal size	0.46 x 0.13 x 0.07 mm^3
Theta range for data collection	2.56 to 24.74°.
Index ranges	-7<=h<=7, -9<=k<=9, -24<=l<=24
Reflections collected	12909
Independent reflections	3463 [R (int) = 0.0370]
Completeness to theta = 24.74°	97.1 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3463 / 0 / 323
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma (I)]	R1 = 0.0727, wR2 = 0.1893
R indices (all data)	R1 = 0.1237, wR2 = 0.2225
Largest diff. peak and hole	0.470 and -0.520 $e.Å^{-3}$

4.6 EVALUATION OF SYMMETRY ELEMENTS

Specimen-Single crystal of Osajin(MN-01)1.{ 5-hydroxy-3-(3-hydroxyphenyl)-8,8-dimethyl-6-(3-methylbut-2-enyl)-4H.8H-pyrano[2,3-h]chromen-4-one],}.

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 =P-1

Cell contstants: a = 6.2374(11) Å , b = 8.4243(11) Å, c = 21.181(4) Å,α= 96.083(13)°

β= 95.602(10) °,γ = 107.419(7)°

Volume =1046.1(3) $Å^3$

Z — 2

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

Number of reflections measured: 12909

Temperature of crystal during data collection: 296K

Crystal dimention =0.46 × 0.13 × 0.07 mm^3

Density calculated: 1.284 Mg/m^3

Absorption coefficient: 0.089 mm^{-1}

F (000) : 428

Theta range : 2.56 to 24.74°.

Index ranges : -7<=h<=7, -9<=k<=9, -24<=l<=24

Independent reflection: 3463 [R (int) = 0.0370]

Completeness to theta = 24.74° 97.1 %

Goodness of fit on F2 = 1.048

Refinement method: Full Matrix least- squares on F2

Largest diff.peak and hole: 0.470 and -0.520 e.Å^{-3}

4.7 DATA COLLECTION AND REDUCTION

The size of the crystal 0.46 × 0.13 × 0.07 mm^3 Symmetry P-1 is determines using a Bruker Nouius SMART CCD diffractometer. Three dimentional intensity data are collected on a bruker Nonius SMART CCD 3 circle diffractometer with MoK_α radiation(λ=·71073Å) equipped with graphite monocromator.The Bruker SMART software[12] is used for data collection and also for indexing the reflections and determining the unit cell..

4.8 STRUCTURE DETERMINATION

The structure is solved by direct method refined by full-matrix least-squares calculations using SHELXTL-97 software[14-15].In this program, E-values are calculated by a modified k-curve method (Karle, Hauptmann and Christ,1958)18.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 328 parameters are refined.

The E-statistics $<|E^2-1|> = 1.095$ imply that the crystal is chiral. The values of R(int) = 0.0370 and R(sigma) = 0.0471 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) + (0.0592 * P)^2 + 1.68 * P] where P = [Max (Fo^2, 0) + 2 * Fc^2] / 3

The final R=0·0727 for 3463 reflection and goodness of fit = 1.048

The final R indices [I>2 sigma (I)] = R1 = 0.0727, wR2 = 0.1893

R indices (all data), R1 = 0.0727, wR2 = 0.1893

A final difference Fourier synthesis revealed the maximum and minimum electron density peaks of 0.470 and -0.520 e.Å^{-3} respectively.

4.9 BOND ANGLES AND BOND LENGTHS (Å)

Selected bond lengths and bond angles of the molecule (MN-01) involving non-hydrogen atoms are given in table 4.5 and table 4.6 and those involving hydrogen atoms are in table 4.7 and table 4.8

4.10 THE PHENYL RING

In the molecule .{ 5-hydroxy-3-(3-hydroxyphenyl)-8,8-dimethyl-6-(3-methylbut-2-enyl)-4H.8H-pyrano[2,3-h]chromen-4-one]},the C—C bond lengths are normal and are in good agreement with the standard value 1.326Å[19] .However, the angle C11—C12—C13 in the molecule is slightly lower than the normal value as also found in other molecules. The C11—C12—C13 angle in the molecule is 120.The exocyclic bond lengths is C3—C11=1.495(4)Å which is shorter then the normal C3(sp^2)—C11(sp^2) single bond distance 1.527(5)Å indicates some conjugation between isoflavion group and the phenyl[20-21] ring This aspect has been clearly discussed by F.H Allen, O.Kennard and R.Taylor(1983)[22].

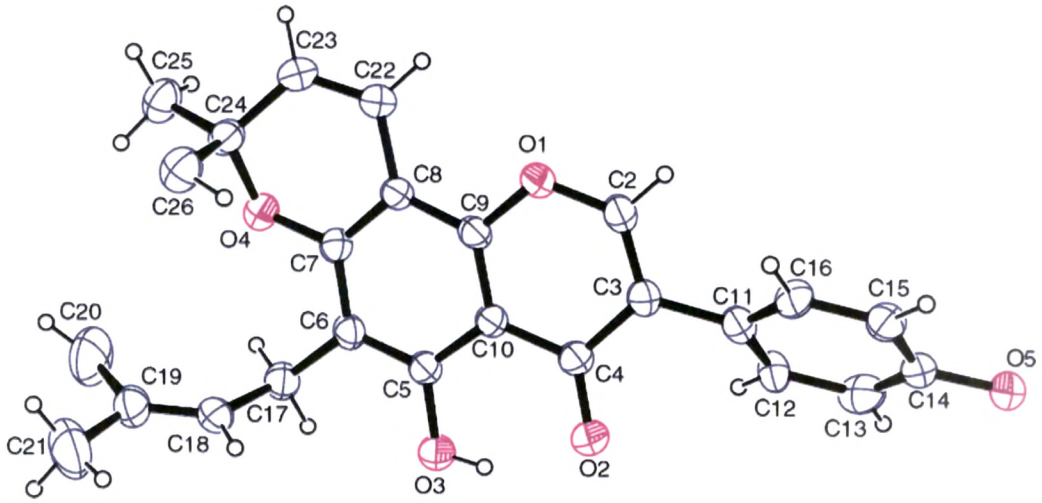

Figure 4.2: An ORTEP view of (MN-01) in 30% probability with atomic numbering scheme.

4.11 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 from the respective planes.

The torsion angles for the molecule MN-01are listed in the table 4.10.The dyhidral angle between the mean plane passing through the ring $C_3C_4C_{10}C_9O_1C_2$ and the phenyl ring $C_{11}C_{12}C_{13}C_{14}C_{15}C_{16}$ is 44(1)° which shows that the two rings are not planar. This can be confirmed by studying the torsion angles w.r.t the bond C_3-C_{11} Studying the torsion angle through the central bond $C_6 - C_5$ and $C_6 - C_7$ it is seen that C_{17} atom is coplanar with the $C_5C_6C_7C_8C_9C_{10}$ ring. After studying the torsion angle C_{22}-C_8-C_7-O_4 and C_9-C_8-C_7-C_6 the ring $C_8C_7C_6O_5C_{10}C_9C_8$ with the ring $C_8C_7O_4C_{24}C_{23}C_{22}$ are not coplanar. The benzopyranone ring system is nearly planar in both molecules and they differ significantly only in the orientation of the benzene rings, which are rotated by 56.27 (7) and 44.16 (7)° with respect to the benzopyranone systems. In the crystal structure, intermolecular O-H. . .O hydrogen bonds link the molecules into dimers.

4.12 MOLECULAR PACKING

The crystal structure is stabilized by a net work of intermolecular hydrogen bonds and normal van der Waals contacts. All the intermolecular contacts less than 4.00Å involving the non hydrogen atoms are listed in the table 4.10.The molecules of the centrosymmetric unit are held by C – H····O hydrogen bonds

The packing of the molecules of mercury[24] diagram in the crystalline space as viewed down the a-axis, b-axis and c-axis of the unit cell is depicted in figure 4.3, figure 4.4 and figure 4.5.

The details of the hydrogen bond geometry of the present structure are as follows:

D-H....A	D–H	D...A	H...A	D–H...A
O3 -H3O...O2	0.820	2.586	1.855	147.75(2)
C22 -H22...O1	0.930	2.827	2.590	94.95(2)
C12 -H12...O2	0.930	3.021	2.640	105.24(2)
C17 -H17...O4	0.970	2.768	2.476	97.00(2)
C17 -H17...O3	0.970	2.819	2.459	101.60(2)

Symmetry codes: x,y,z

The molecule contains four strong C–H····O interactions of C_{22}–H_{22}····O_1,C_{12}–H_{12}····O_2, C_{17}–H_{17}····O_4 and C_{17}–H_{17}·····O_3.Besides their one strong intermolecular D·····A interactions also observed inside the molecule with O_3·····O_2 = 2.586(0)Å.

4.13 CONCLUSION

The single crystal of osajin (MN-01){ 5-hydroxy-3-(3-hydroxyphenyl)-8,8-dimethyl-6-(3-methylbut-2-enyl)-4H.8H-pyrano[2,3-h]chromen-4-one],}has a triclinic cell with lattice parameters a = 6.2374(11) Å b = 8.4243(11) Å c = 21.181(4) Å α= 96.083(13) β= 95.602(10)° γ = 107.419(7)°.with space group P-1

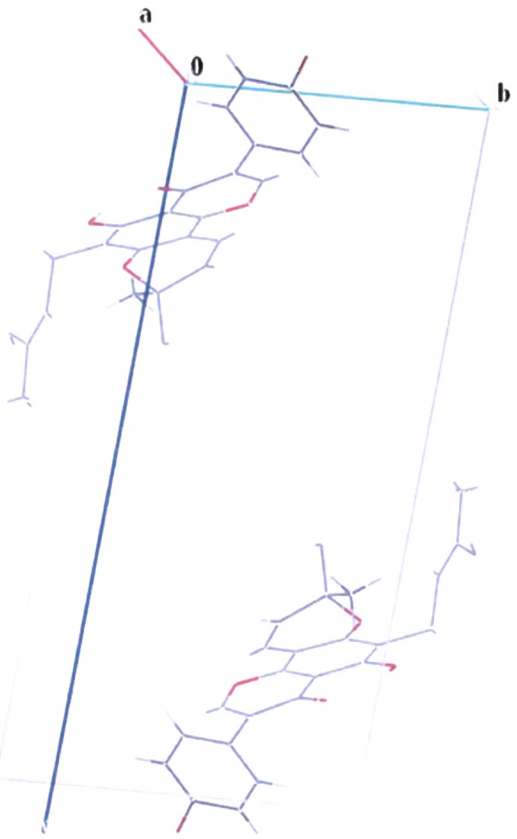

Figure 4.3: The packing of the molecules in the crystalline space as viewed down the a-axis of the unit cell.

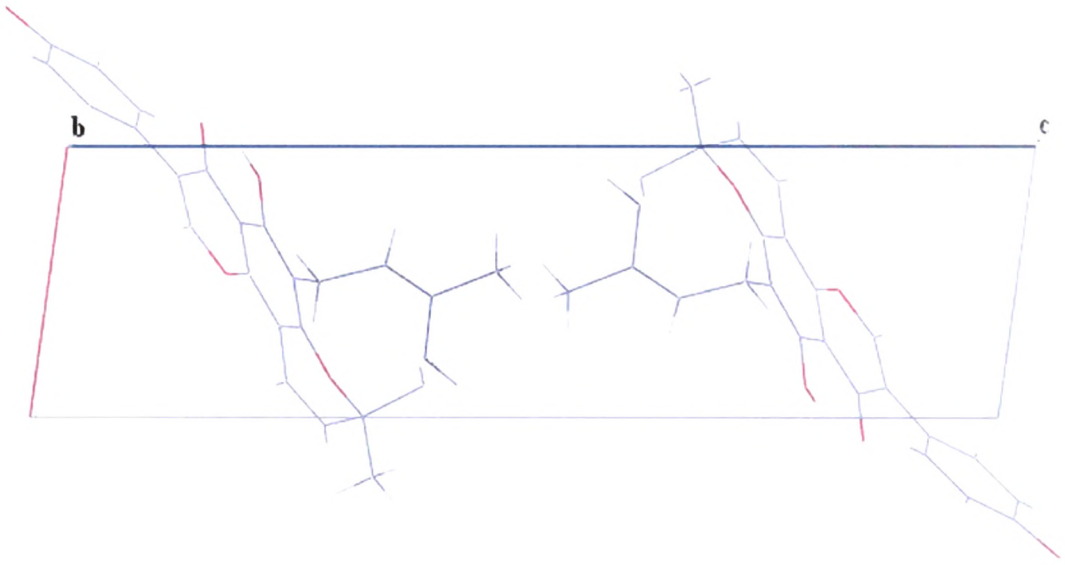

Figure 4.4: The packing of the molecules in the crystalline space as viewed down the b-axis of the unit cell.

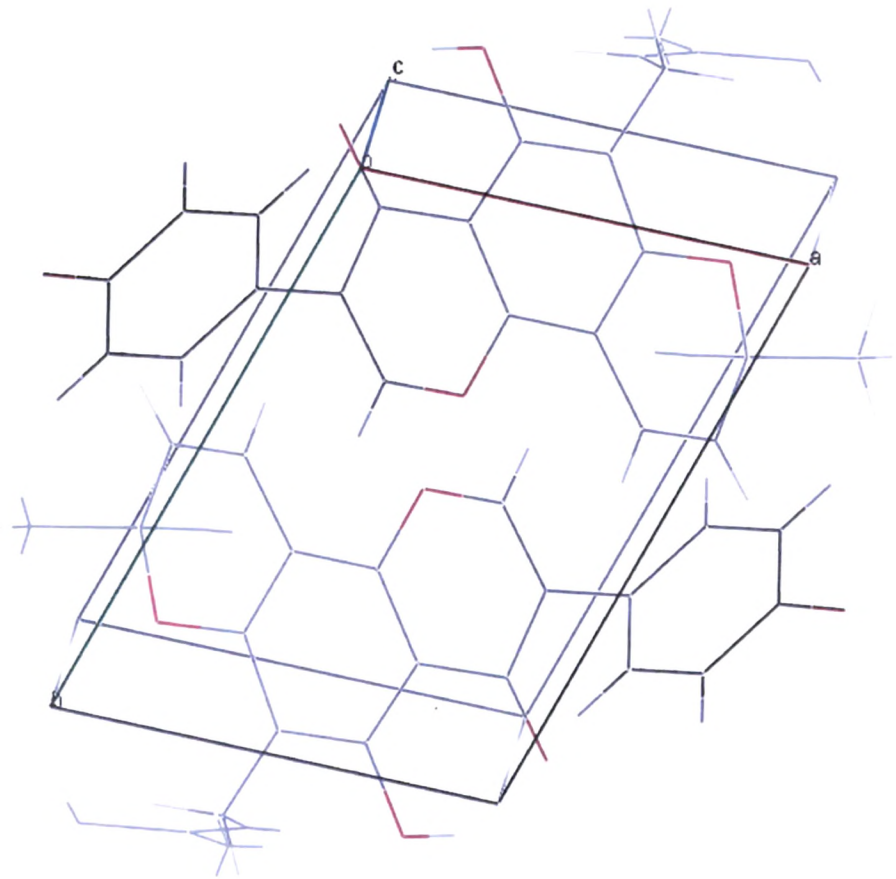

Figure 4.5: The packing of the molecules in the crystalline space as viewed down the c-axis of the unit cell.

Table 4.2: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for MN-01. The anisotropic 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(1)	81(2)	53(2)	84(2)	22(2)	-23(2)	-9(2)
O(2)	67(2)	68(2)	82(2)	24(2)	-18(2)	-6(2)
O(3)	55(2)	62(2)	58(2)	8(1)	0(1)	17(1)
O(4)	77(2)	104(3)	106(3)	63(2)	-32(2)	-14(2)
O(5)	64(2)	48(2)	57(2)	15(1)	-2(1)	6(1)
C(1)	49(2)	65(3)	52(2)	3(2)	2(2)	10(2)
C(2)	54(2)	66(3)	74(3)	13(2)	-1(2)	-2(2)
C(3)	59(2)	55(3)	61(2)	14(2)	2(2)	4(2)
C(4)	51(2)	47(2)	44(2)	9(2)	5(2)	7(2)
C(5)	50(2)	55(2)	44(2)	7(2)	5(2)	14(2)
C(6)	65(2)	48(2)	43(2)	7(2)	2(2)	13(2)
C(7)	64(2)	50(2)	46(2)	9(2)	-3(2)	2(2)
C(8)	55(2)	45(2)	42(2)	7(2)	1(2)	7(2)
C(9)	58(2)	45(2)	42(2)	11(2)	8(2)	8(2)
C(11)	68(3)	55(3)	51(2)	16(2)	2(2)	16(2)
C(12)	58(2)	58(3)	45(2)	11(2)	4(2)	14(2)
C(13)	59(2)	51(2)	48(2)	8(2)	0(2)	5(2)

C(14)	65(3)	55(3)	52(2)	17(2)	4(2)	14(2)
C(15)	74(6)	54(6)	49(6)	10(4)	1(5)	27(5)
C(16)	81(7)	87(8)	45(5)	-8(4)	5(4)	-3(5)
C(17)	63(3)	69(3)	70(3)	28(3)	-13(2)	-5(2)
C(18)	65(6)	42(6)	79(7)	6(5)	1(5)	17(4)
C(19)	64(6)	44(6)	46(5)	-9(4)	-9(4)	9(4)
C(20)	70(3)	51(3)	59(2)	7(2)	-1(2)	17(2)
C(21)	60(2)	53(2)	71(3)	20(2)	4(2)	14(2)
C(22)	84(3)	66(3)	68(3)	18(2)	-4(2)	22(2)
C(23)	168(6)	138(5)	71(3)	35(4)	13(4)	48(5)
C(24)	111(5)	164(6)	129(5)	49(5)	-8(4)	71(4)
C(25)	69(3)	87(3)	61(3)	1(2)	10(2)	27(2)
C(26)	58(3)	98(4)	72(3)	9(3)	1(2)	28(2)
C(15')	54(6)	79(7)	55(6)	20(4)	12(4)	19(4)
C(16')	51(6)	59(6)	71(7)	22(4)	9(5)	24(4)
C(18')	76(6)	64(6)	57(6)	7(4)	7(4)	28(4)
C(19')	52(6)	57(6)	49(5)	6(4)	3(4)	21(4)

Table 4.3: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for MN-01

	x	y	z	U(eq)
H(1)	9882	11937	8197	121
H(4)	16356	7989	10863	157
H(2)	-1625	5402	6850	84
H(3)	1111	5372	7616	74
H(11)	6919	5369	8782	70
H(15)	11018	9775	9834	69
H(16)	13599	9574	10663	95
H(18)	13373	5041	9791	75
H(19)	10792	5242	8962	67
H(20B)	3472	12347	7201	74
H(20A)	6024	13263	7478	74
H(21)	6991	12142	6489	74
H(23A)	6790	12258	5440	186
H(23B)	5592	13562	5247	186
H(23C)	4310	11631	5075	186
H(24B)	2334	13909	6017	192
H(24C)	1474	12315	6357	192
H(24A)	1232	12133	5607	192

H(25A)	1398	8414	5745	109
H(25C)	248	6467	5694	109
H(25B)	2626	7330	6106	109
H(26C)	-2855	8282	6742	114
H(26B)	-3216	7116	6087	114
H(26A)	-1903	9041	6144	114

Table 4.4: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters(Å^{2}x 10^3) for MN-01. U (eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

O(1)	8852(5)	12106(3)	7971(1)	81(1)
O(2)	10870(5)	10447(4)	8644(1)	79(1)
O(3)	1459(4)	9292(3)	6949(1)	59(1)
O(4)	15149(5)	7233(4)	10837(2)	105(1)
O(5)	5274(4)	6324(3)	8170(1)	59(1)
C(1)	33(6)	7732(5)	6553(2)	58(1)
C(2)	-285(7)	6298(5)	6936(2)	70(1)
C(3)	1301(6)	6288(5)	7393(2)	61(1)
C(4)	3355(6)	7724(4)	7545(2)	49(1)
C(5)	3331(6)	9216(5)	7319(2)	50(1)
C(6)	5130(6)	10726(5)	7471(2)	54(1)

C(7)	7036(7)	10680(5)	7847(2)	57(1)
C(8)	7168(6)	9219(4)	8100(2)	49(1)
C(9)	5281(6)	7779(4)	7937(2)	50(1)
C(11)	7024(7)	6350(5)	8606(2)	58(1)
C(12)	8899(6)	7664(5)	8806(2)	55(1)
C(13)	9114(7)	9197(5)	8524(2)	56(1)
C(14)	10649(5)	7528(4)	9315(1)	58(1)
C(15)	11490(7)	8826(4)	9825(2)	58(4)
C(16)	13036(7)	8706(5)	10322(2)	79(4)
C(17)	13742(5)	7288(6)	10309(2)	73(1)
C(18)	12901(7)	5990(5)	9800(2)	63(4)
C(19)	11354(7)	6110(4)	9303(2)	56(4)
C(20)	4998(7)	12282(5)	7203(2)	62(1)
C(21)	5599(7)	12295(5)	6540(2)	61(1)
C(22)	4452(8)	12492(5)	6016(2)	73(1)
C(23)	5368(12)	12485(8)	5388(2)	124(2)
C(24)	2169(10)	12734(9)	5998(3)	128(2)
C(25)	1181(7)	7461(6)	5971(2)	73(1)

Table 4.5: Bond lengths involving non hydrogen atoms [Å] for MN-01

O(3)-C(5)	1.361(4)	C(5)-C(10)	1.416(5)
O(2)-C(4)	1.254(4)	C(10)-C(9)	1.398(5)
O(4)-C(7)	1.363(4)	C(10)-C(4)	1.442(5)
O(4)-C(24)	1.464(4)	C(2)-C(3)	1.344(5)
O(5)-C(14)	1.366(4)	C(3)-C(4)	1.455(5)
O(1)-C(2)	1.352(4)	C(3)-C(11)	1.495(4)
O(1)-C(9)	1.368(4)	C(11)-C(12)	1.3900
C(24)-C(23)	1.499(6)	C(11)-C(16)	1.3900
C(24)-C(26)	1.517(5)	C(12)-C(13)	1.3900
C(24)-C(25)	1.525(5)	C(13)-C(14)	1.3900
C(23)-C(22)	1.317(5)	C(14)-C(15)	1.3900
C(22)-C(8)	1.454(5)	C(15)-C(16)	1.3900
C(8)-C(9)	1.378(5)	C(17)-C(18)	1.488(5)
C(8)-C(7)	1.394(5)	C(18)-C(19)	1.314(5)
C(7)-C(6)	1.402(5)	C(19)-C(21)	1.495(7)
C(6)-C(5)	1.377(5)	C(19)-C(20)	1.505(7)
C(6)-C(17)	1.506(5)		

Table 4.6: Bond angles involving non-hydrogen [°] for MN-01

C(7)-O(4)-C(24)	116.9(3)	O(3)-C(5)-C(10)	119.6(3)
C(2)-O(1)-C(9)	118.8(3)	C(6)-C(5)-C(10)	122.5(3)
O(4)-C(24)-C(23)	109.8(3)	C(9)-C(10)-C(5)	116.9(3)
O(4)-C(24)-C(26)	107.7(3)	C(9)-C(10)-C(4)	120.6(3)
C(23)-C(24)-C(26)	111.7(4)	C(5)-C(10)-C(4)	122.5(3)
O(4)-C(24)-C(25)	104.1(3)	O(1)-C(9)-C(8)	116.4(3)
C(23)-C(24)-C(25)	112.2(3)	O(1)-C(9)-C(10)	120.2(3)
C(26)-C(24)-C(25)	111.0(3)	C(8)-C(9)-C(10)	123.4(3)
C(22)-C(23)-C(24)	121.2(4)	C(3)-C(2)-O(1)	125.8(4)
C(23)-C(22)-C(8)	119.2(4)	C(2)-C(3)-C(4)	117.8(3)
C(9)-C(8)-C(7)	116.6(3)	C(2)-C(3)-C(11)	119.7(3)
C(9)-C(8)-C(22)	125.3(3)	C(4)-C(3)-C(11)	122.5(3)
C(7)-C(8)-C(22)	117.9(3)	O(2)-C(4)-C(10)	121.2(4)
O(4)-C(7)-C(8)	120.5(3)	O(2)-C(4)-C(3)	122.5(4)
O(4)-C(7)-C(6)	115.8(3)	C(10)-C(4)-C(3)	116.3(3)
C(8)-C(7)-C(6)	123.7(3)	C(12)-C(11)-C(16)	120.0
C(5)-C(6)-C(7)	116.9(3)	C(12)-C(11)-C(16')	65.8(4)
C(5)-C(6)-C(17)	122.3(4)	C(16)-C(11)-C(16')	88.0(4)
C(7)-C(6)-C(17)	120.7(3)	C(12)-C(11)-C(3)	118.4(3)
O(3)-C(5)-C(6)	117.9(3)	C(16)-C(11)-C(3)	121.5(3)

C(13)-C(12)-C(11)	120.0	C(15)-C(16)-C(11)	120.0
C(12)-C(13)-C(14)	120.0	C(18)-C(17)-C(6)	111.9(3)
O(5)-C(14)-C(15)	124.0(4)	C(19)-C(18)-C(17)	129.4(4)
O(5)-C(14)-C(13)	115.9(4)	C(18)-C(19)-C(21)	123.4(5)
C(15)-C(14)-C(13)	120.0	C(18)-C(19)-C(20)	121.4(5)
C(14)-C(15)-C(16)	120.0	C(21)-C(19)-C(20)	115.3(5)

Table 4.7: Bond distances (Angstrom) involving hydrogen atoms, with e.s.d's in parenthesis for MN-01.

O(3)-H(3O)	0.8200	C(20)-H(20A)	0.9600
O(5)-H(5O)	0.78(6)	C(20)-H(20B)	0.9600
C(23)-H(23)	0.9300	C(20)-H(20C)	0.9600
C(22)-H(22)	0.9300	C(21)-H(21A)	0.9600
C(2)-H(2)	0.9300	C(21)-H(21C)	0.9600
C(12)-H(12)	0.9300	C(21)-H(21B)	0.9600
C(13)-H(13)	0.9300	C(26)-H(26B)	0.9600
C(15)-H(15)	0.9300	C(26)-H(26A)	0.9600
C(16)-H(16)	0.9300	C(26)-H(26C)	0.9600
C(17)-H(17B)	0.9700	C(25)-H(25C)	0.9600
C(17)-H(17A)	0.9700	C(25)-H(25A)	0.9600
C(18)-H(18)	0.9300	C(25)-H(25B)	0.9600

Table 4.8: Bond angles (deg) involving hydrogen atoms, with e, s, d's in parenthesis for MN-01.

C(14)-O(5)-H(5O)	118(5)	H(17B)-C(17)-H(17A)	107.9
C(22)-C(23)-H(23)	119.4	C(19)-C(18)-H(18)	115.3
C(24)-C(23)-H(23)	119.4	C(17)-C(18)-H(18)	115.3
C(23)-C(22)-H(22)	120.4	C(19)-C(20)-H(20A)	109.5
C(8)-C(22)-H(22)	120.4	C(19)-C(20)-H(20B)	109.5
C(3)-C(2)-H(2)	117.1	H(20A)-C(20)-H(20B)	109.5
O(1)-C(2)-H(2)	117.1	C(19)-C(20)-H(20C)	109.5
C(13)-C(12)-H(12)	120.0	H(20A)-C(20)-H(20C)	109.5
C(11)-C(12)-H(12)	120.0	H(20B)-C(20)-H(20C)	109.5
C(12)-C(13)-H(13)	120.0	C(19)-C(21)-H(21A)	109.5
C(14)-C(13)-H(13)	120.0	C(19)-C(21)-H(21C)	109.5
C(14)-C(15)-H(15)	120.0	H(21A)-C(21)-H(21C)	109.5
C(16)-C(15)-H(15)	120.0	C(19)-C(21)-H(21B)	109.5
C(15)-C(16)-H(16)	120.0	H(21A)-C(21)-H(21B)	109.5
C(11)-C(16)-H(16)	120.0	H(21C)-C(21)-H(21B)	109.5
C(18)-C(17)-H(17B)	109.2	C(24)-C(26)-H(26B)	109.5
C(6)-C(17)-H(17B)	109.2	C(24)-C(26)-H(26A)	109.5
C(18)-C(17)-H(17A)	109.2	H(26B)-C(26)-H(26A)	109.5
C(6)-C(17)-H(17A)	109.2	C(24)-C(26)-H(26C)	109.5

H(26B)-C(26)-H(26C)109.5

H(26A)-C(26)-H(26C)109.5

C(24)-C(25)-H(25C) 109.5

C(24)-C(25)-H(25A) 109.5

H(25C)-C(25)-H(25A)109.5

C(24)-C(25)-H(25B) 109.5

H(25C)-C(25)-H(25B)109.5

H(25A)-C(25)-H(25B)109.5

Table 4.9: Torsion angles [°] for MN-01.

C(5)-O(3)-C(1)-C(2)	43.7(4)
C(5)-O(3)-C(1)-C(25)	-78.1(4)
C(5)-O(3)-C(1)-C(26)	163.7(3)
O(3)-C(1)-C(2)-C(3)	-31.0(5)
C(25)-C(1)-C(2)-C(3)	88.5(5)
C(26)-C(1)-C(2)-C(3)	-146.1(4)
C(1)-C(2)-C(3)-C(4)	2.6(6)
C(2)-C(3)-C(4)-C(9)	-169.5(4)
C(2)-C(3)-C(4)-C(5)	15.7(6)
C(1)-O(3)-C(5)-C(4)	-28.9(5)
C(1)-O(3)-C(5)-C(6)	153.6(3)
C(9)-C(4)-C(5)-O(3)	-177.4(3)
C(3)-C(4)-C(5)-O(3)	-2.2(5)
C(9)-C(4)-C(5)-C(6)	-0.2(5)
C(3)-C(4)-C(5)-C(6)	175.0(3)
O(3)-C(5)-C(6)-C(7)	179.7(3)
C(4)-C(5)-C(6)-C(7)	2.4(5)
O(3)-C(5)-C(6)-C(20)	-3.4(5)
C(4)-C(5)-C(6)-C(20)	179.3(3)
C(5)-C(6)-C(7)-O(1)	176.4(3)
C(20)-C(6)-C(7)-O(1)	-0.4(6)

C(5)-C(6)-C(7)-C(8)	-3.3(6)
C(20)-C(6)-C(7)-C(8)	180.0(3)
O(1)-C(7)-C(8)-C(9)	-177.7(3)
C(6)-C(7)-C(8)-C(9)	1.9(6)
O(1)-C(7)-C(8)-C(13)	4.1(6)
C(6)-C(7)-C(8)-C(13)	-176.3(4)
C(11)-O(5)-C(9)-C(4)	-173.7(3)
C(11)-O(5)-C(9)-C(8)	6.1(5)
C(5)-C(4)-C(9)-O(5)	178.5(3)
C(3)-C(4)-C(9)-O(5)	3.6(5)
C(5)-C(4)-C(9)-C(8)	-1.3(5)
C(3)-C(4)-C(9)-C(8)	-176.1(3)
C(7)-C(8)-C(9)-O(5)	-179.2(3)
C(13)-C(8)-C(9)-O(5)	-1.0(5)
C(7)-C(8)-C(9)-C(4)	0.5(5)
C(13)-C(8)-C(9)-C(4)	178.7(3)
C(9)-O(5)-C(11)-C(12)	-5.1(6)
O(5)-C(11)-C(12)-C(13)	-1.3(6)
O(5)-C(11)-C(12)-C(14)	177.1(3)
C(9)-C(8)-C(13)-O(2)	175.6(4)
C(7)-C(8)-C(13)-O(2)	-6.2(6)
C(9)-C(8)-C(13)-C(12)	-5.1(5)
C(7)-C(8)-C(13)-C(12)	173.0(3)

C(11)-C(12)-C(13)-O(2)	-174.6(4)
C(14)-C(12)-C(13)-O(2)	7.1(6)
C(11)-C(12)-C(13)-C(8)	6.2(5)
C(14)-C(12)-C(13)-C(8)	-172.2(3)
C(11)-C(12)-C(14)-C(15')	138.9(6)
C(13)-C(12)-C(14)-C(15')	-42.8(7)
C(11)-C(12)-C(14)-C(15)	-132.6(4)
C(13)-C(12)-C(14)-C(15)	45.8(4)
C(11)-C(12)-C(14)-C(19)	44.4(5)
C(13)-C(12)-C(14)-C(19)	-137.3(3)
C(11)-C(12)-C(14)-C(19')	-58.4(6)
C(13)-C(12)-C(14)-C(19')	120.0(5)
C(15')-C(14)-C(15)-C(16)	-60.3(4)
C(19)-C(14)-C(15)-C(16)	0.0
C(12)-C(14)-C(15)-C(16)	177.0(3)
C(14)-C(15)-C(16)-C(17)	0.0
C(15)-C(16)-C(17)-C(16')	61.3(5)
C(15)-C(16)-C(17)-O(4)	-175.9(3)
C(15)-C(16)-C(17)-C(18)	0.0
C(15)-C(16)-C(17)-C(18')	-71.1(4)
O(4)-C(17)-C(18)-C(19)	175.6(3)
C(16)-C(17)-C(18)-C(19)	0.0
C(17)-C(18)-C(19)-C(14)	0.0

C(15)-C(14)-C(19)-C(18)	0.0
C(12)-C(14)-C(19)-C(18)	-176.9(3)
C(7)-C(6)-C(20)-C(21)	94.8(4)
C(5)-C(6)-C(20)-C(21)	-81.9(5)
C(6)-C(20)-C(21)-C(22)	126.2(5)
C(20)-C(21)-C(22)-C(24)	-0.7(8)
C(20)-C(21)-C(22)-C(23)	179.3(5)

Table 4.10: Intermolecular contacts less than 4.00 Angstrom

O3	...O4	x+1, +y, +z	3.8519	0.0005
O3	...O5	-x+2,-y+2,-z+2	3.8348	0.0005
O3	...C22	x+1, +y+1, +z	3.7830	0.0005
O3	...C13	-x+2,-y+2,-z+2	3.9781	0.0006
O3	...C16	x,+y+1,+z	3.9704	0.0007
O2	...O4	x+1,+y,+z	3.7006	0.0006
O2	...C8	x+1,+y,+z	3.8444	0.0005
O2	...C7	x+1,+y,+z	3.5333	0.0005
O2	...C6	x+1,+y,+z	3.7846	0.0006
O2	...C12	-x+2,-y+2,-z+2	3.7586	0.0006
O2	...C13	-x+2,-y+2,-z+2	3.6060	0.0005
O4	...O3	x-1,+y,+z	3.8519	0.0005

O4	...O2	x-1,+y,+z	3.7006	0.0006
O4	...C5	x-1,+y,+z	3.8832	0.0005
O4	...C10	x-1,+y,+z	3.7842	0.0006
O4	...C4	x-1,+y,+z	3.7704	0.0006
O5	...O3	-x+2,-y+2,-z+2	3.8348	0.0005
O5	...O1	-x+2,-y+1,-z+2	3.8002	0.0005
O5	...C6	-x+2,-y+2,-z+2	3.8527	0.0006
O5	...C5	-x+2,-y+2,-z+2	3.7246	0.0005
O5	...C2	-x+2,-y+1,-z+2	3.3093	0.0005
O1	...O5	-x+2,-y+1,-z+2	3.8002	0.0005
O1	...C23	x+1,+y,+z	3.9926	0.0006
O1	...C15	x-1,+y,+z	3.8893	0.0006
O1	...C16	x-1,+y,+z	3.5674	0.0005
O1	...C17	x,+y-1,+z	3.7302	0.0006
C23	...O1	x-1,+y,+z	3.9926	0.0006
C23	...C17	x-1,+y-1,+z	3.8988	0.0005
C23	...H17A	x-1,+y-1,+z	3.2818	0.0004
C23	...C18	x-1,+y-1,+z	3.5328	0.0005
C23	...C19	x-1,+y-1,+z	3.9990	0.0007
C22	...O3	x-1,+y-1,+z	3.7830	0.0005
C22	...C2	x-1,+y,+z	3.8890	0.0006
C22	...C3	x-1,+y,+z	3.7070	0.0005
C22	...C4	x-1,+y,+z	3.8754	0.0005

C8	...O2	x-1,+y,+z	3.8444	0.0005
C8	...C4	x-1,+y,+z	3.9155	0.0005
C8	...C25	x+1,+y,+z	3.8851	0.0006
C7	...O2	x-1,+y,+z	3.5333	0.0005
C7	...C4	x-1,+y,+z	3.8388	0.0006
C7	...C25	x+1,+y,+z	3.8876	0.0005
C6	...O2	x-1,+y,+z	3.7846	0.0006
C6	...O5	-x+2,-y+2,-z+2	3.8527	0.0006
C6	...C25	x+1,+y,+z	3.8932	0.0005
C5	...O4	x+1,+y,+z	3.8832	0.0005
C5	...O5	-x+2,-y+2,-z+2	3.7246	0.0005
C5	...C13	-x+2,-y+2,-z+2	3.8665	0.0006
C5	...C25	x+1,+y,+z	3.7921	0.0006
C10	...O4	x+1,+y,+z	3.7842	0.0006
C10	...C13	-x+2,-y+2,-z+2	3.6375	0.0006
C10	...C25	x+1,+y,+z	3.7926	0.0006
C9	...C25	x+1,+y,+z	3.8246	0.0006
C2	...O5	-x+2,-y+1,-z+2	3.3093	0.0005
C2	...C22	x+1,+y,+z	3.8890	0.0006
C2	...C14	-x+2,-y+1,-z+2	3.9663	0.0006
C2	...C15	x-1,+y,+z	3.7500	0.0005
C2	...C16	x-1,+y,+z	3.9213	0.0006
C3	...C22	x+1,+y,+z	3.7070	0.0005

C3	...C12	-x+2,-y+2,-z+2	3.9957	0.0006
C3	...C13	-x+2,-y+2,-z+2	3.9586	0.0005
C4	...O4	x+1,+y,+z	3.7704	0.0006
C4	...C22	x+1,+y,+z	3.8754	0.0005
C4	...C8	x+1,+y,+z	3.9155	0.0005
C4	...C7	x+1,+y,+z	3.8388	0.0006
C4	...C12	-x+2,-y+2,-z+2	3.8149	0.0006
C4	...C13	-x+2,-y+2,-z+2	3.4700	0.0005
C11	...C15	-x+2,-y+1,-z+2	3.9093	0.0005
C12	...O2	-x+2,-y+2,-z+2	3.7586	0.0006
C12	...C3	-x+2,-y+2,-z+2	3.9957	0.0006
C12	...C4	-x+2,-y+2,-z+2	3.8149	0.0006
C12	...C12	-x+2,-y+2,-z+2	3.1736	0.0004
C12	...C13	-x+2,-y+2,-z+2	3.9825	0.0005
C13	...O3	-x+2,-y+2,-z+2	3.9781	0.0006
C13	...O2	-x+2,-y+2,-z+2	3.6060	0.0005
C13	...C5	-x+2,-y+2,-z+2	3.8665	0.0006
C13	...C10	-x+2,-y+2,-z+2	3.6375	0.0006
C13	...C3	-x+2,-y+2,-z+2	3.9586	0.0005
C13	...C4	-x+2,-y+2,-z+2	3.4700	0.0005
C13	...C12	-x+2,-y+2,-z+2	3.9825	0.0005
C14	...C16	-x+2,-y+1,-z+2	3.8143	0.0005
C15	...O1	x+1,+y,+z	3.8893	0.0006

C15	...C2	x+1,+y,+z	3.7500	0.0005
C15	...C11	-x+2,-y+1,-z+2	3.9093	0.0005
C15	...C15	-x+2,-y+1,-z+2	3.7286	0.0006
C15	...C16	-x+2,-y+1,-z+2	3.5641	0.0005
C16	...O3	x,+y-1,+z	3.9704	0.0007
C16	...O1	x+1,+y,+z	3.5674	0.0005
C16	...C2	x+1,+y,+z	3.9213	0.0006
C16	...C14	-x+2,-y+1,-z+2	3.8143	0.0005
C16	...C15	-x+2,-y+1,-z+2	3.5641	0.0005
C16	...C16	-x+2,-y+1,-z+2	3.9201	0.0006
C17	...O1	x,+y+1,+z	3.7302	0.0006
C17	...C23	x+1,+y+1,+z	3.8988	0.0005
C20	...C26	-x+1,-y+2,-z+1	3.7493	0.0005
C20	...C25	-x,-y+2,-z+1	3.9404	0.0007
C26	...C20	-x+1,-y+2,-z+1	3.7493	0.0005
C25	...C8	x-1, +y, +z	3.8851	0.0006
C25	...C7	x-1,+y,+z	3.8876	0.0005
C25	...C6	x-1,+y,+z	3.8932	0.0005
C25	...C5	x-1,+y,+z	3.7921	0.0006
C25	...C10	x-1,+y,+z	3.7926	0.0006
C25	...C9	x-1,+y,+z	3.8246	0.0006
C25	...C20	-x,-y+2,-z+1	3.9404	0.0007

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