The Crystal and Molecular Structure of 2,5-Dichloro-3-methoxypyrazine

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A three-dimensional X-ray structure determination of 2,5-dichloro-3-methoxypyrazine has been completed with diffractometer data. The crystals are monoclinic, space group $P2_1/c$, with lattice constants $a = 4.059$, $b = 15.773$, $c = 11.123$Å and $\beta = 90.96°$ (Z = 4). The structure was solved by Sayre's equation and all hydrogen atoms were located by difference synthesis. Full-matrix least-squares refinement of all position parameters, hydrogen isotropic temperature factors, and anisotropic temperature factors for all other atoms converged at R = 5.7% for the 1397 reflections above background. Bond distances and angles are consistent with literature values.

Introduction.

X-ray diffraction has an important role in identifying positional isomers of chlorinated heterocycles when chemical and spectroscopic methods are inconclusive. In addition to positive proof of structure, the results may yield useful information on the directing effect of ring substituents toward further substitution, which will aid in identifying analogous compounds by faster spectroscopic techniques. The geometrical data may also reveal stereochemical or electronic factors that influence the properties of the system.

Results and Discussion.

A. The Molecule.

Dichloromethoxypyrazine is obtained in good yield by the slow addition of sodium methoxide to trichloropyrazine at 20° in methanol solution (1). Our single crystal X-ray diffraction study establishes that this material is the *para*-dichloro isomer, 2,5-dichloro-3-methoxypyrazine. The molecular structure is shown in Figure 1 (2) where the thermal motion of the atoms is represented by ellipsoids of 50% probability.

Dichloromethoxypyrazine is planar within experimental error except for the methyl group which is bent slightly, but significantly, out of plane. The least-squares plane through the non-methyl atoms (excluding H(6) is given by $3.443x - 0.790y - 6.068z + 0.3657 = 0$. None of the non-methyl atoms deviates from this plane by more than 0.009Å except H(6) which is +0.013Å away, but still within its experimental error. However, the methyl carbon C(7) is +0.072Å away from the plane, an amount equivalent to an out-of-plane rotation of the O-C bond of 3.2°. This distortion is believed to arise from crystal packing forces.

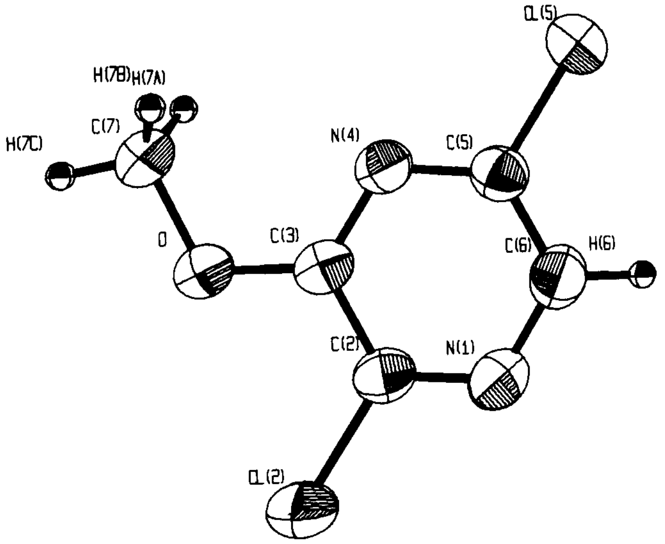

Figure 1. Arrangement of the atoms in 2,5-dichloro-3-methoxypyrazine. Atoms are shown as thermal ellipsoids of 50% probability except for isotropic hydrogens. (See Table I for bond distances and angles).

The conformation of the methoxy substituent is *syn* with respect to N(4); the *anti* conformation apparently is precluded by steric hindrance between Cl(2) and the methyl group. Although disordered methyl hydrogens are common in the solid state, they are fixed in this structure. H(7A) and H(7B) are +0.892Å and -0.788Å, respectively, from the plane of the ring and on the side of C(7) near N(4), while H(7C) is nearly in the plane (+0.035Å deviation) on the opposite side. In this conformation the O-C(3) bond bisects the H(7A)-C(7)-H(7B) angle when projected down the O-C(7) axis, and at the same time the distances

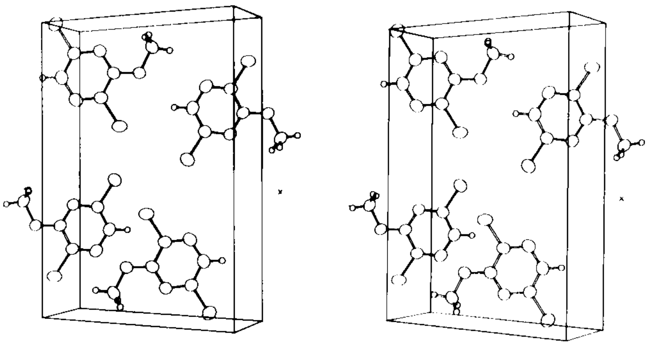

Figure 2. Stereoscopic view of the unit cell. The origin is the lower left front corner of the box, x is back, y is vertical, and z is horizontal.

of the hydrogen atoms to N(4) are maximized. The fact that the hydrogen atoms are localized in the crystal structure may be related to a potential barrier arising from interference between the N(4) lone pair electrons and the methyl hydrogens. Intermolecular contacts (3.30-3.55Å) between the methyl group and neighboring nitrogen atoms are at the normal van der Waals distance.

The methoxy oxygen forms unequal bonds of 1.450 ± 0.004Å and 1.331 ± 0.003Å with the aliphatic sp^3 and aromatic sp^2 carbons respectively. The former distance is 5 standard deviations greater than the accepted value of 1.43Å for O-C(sp^3) single bonds as in dialkyl ethers (4), while the O-C(sp^2) bond is 0.079Å shorter than that calculated by correcting the O-C(sp^3) bond length for the 0.020Å difference between the covalent radii of sp^2 and sp^3 carbons (5). These effects may indicate some resonance between oxygen electrons and π-orbitals of the unsaturated ring. (The C-O-C bond angle is 117.1 ± 0.3° and could permit sp^2 hybridization). Very similar structural parameters have been observed in other methoxy substituted aromatics (6,7) and in γ-lactones (8).

Bond distances (Table I) in the pyrazine ring show some interesting differences. The C-C bond on the disubstituted side of the ring is 10 standard deviations longer than the corresponding bond on the opposite side (C(2)-C(3), 1.412 ± 0.004Å; C(5)-C(6), 1.372 ± 0.004Å). Furthermore, the C-N bonds adjacent to the long C-C bond (N(1)-C(2), 1.303Å; N(4)-C(3), 1.315Å) are signficantly shorter than those adjacent to the short C-C bond (N(4)-C(5), 1.329Å; N(1)-C(6), 1.338Å). Unsubstituted and monosubstituted pyrazines have C-C bond distances of about 1.38Å (pyrazine (9), 1.378Å; pyrazinamide (10), 1.377, 1.389Å) in close agreement with our C(5)-C(6) distance, but in tetramethylpyrazine (11) and α-phenazine (12) the reported bond distances are considerably longer, 1.434 and 1.439Å respectively. Severe crowding, as in o-di-t-butylquinoxaline (13) produces a still longer C-C bond of 1.475Å and adjacent C-N bond distances (1.318Å) that are shorter than the C-N distance of 1.334Å in pyrazine itself (9). Thus, the N(4)-C(5), C(5)-C(6) and C(6)-N(1) bonds of 2,5-dichloro-3-methoxypyrazine are approximately equal in length to those of unsubstituted and monosubstituted pyrazines, while the N(1)-C(2), C(2)-C(3), and C(3)-N(4) bonds appear typical of polysubstituted pyrazines. Finally, we note that in X-ray diffraction studies of this kind it has been established that systematic errors due to thermal motion may be larger than the random errors (9). Thus, although the ring atoms show a relatively low degree of thermal anisotropy (Table II) and the overall temperature factor (3.98Å^2) is somewhat lower than that reported for pyrazine (9), the above interpretation must be regarded as tentative.

Bond angles (Table I) in the structure appear to be normal. The two C-N-C angles of 116.6 and 117.2° are reasonably close to the value of 115.1° found in the parent heterocycle (9). As in tetramethylpyrazine (11),

TABLE I

Bond Distances and Angles (a)

Distances (Å)		Angles (deg)	
N(1)-C(2)	1.303(3)	C(2)-N(1)-C(6)	117.2(3)
C(2)-C(3)	1.412(4)	C(3)-N(4)-C(5)	116.6(3)
C(3)-N(4)	1.315(4)	N(1)-C(2)-C(3)	122.4(3)
N(4)-C(5)	1.329(4)	N(1)-C(2)-Cl(2)	118.1(2)
C(5)-C(6)	1.372(4)	C(3)-C(2)-Cl(2)	119.5(2)
C(6)-N(1)	1.338(4)	N(4)-C(3)-O	121.5(3)
C(2)-Cl(2)	1.733(3)	N(4)-C(3)-C(2)	120.4(3)
C(3)-O	1.331(3)	O-C(3)-C(2)	118.1(3)
C(5)-Cl(5)	1.733(3)	N(4)-C(5)-C(6)	123.3(3)
C(6)-H(6)	0.98(3)	N(4)-C(5)-Cl(5)	117.0(2)
O-C(7)	1.450(4)	C(6)-C(5)-Cl(5)	119.7(3)
C(7)-H(7A)	1.01(4)	H(6)-C(6)-N(1)	121(2)
C(7)-H(7B)	1.07(4)	H(6)-C(6)-C(5)	119(2)
C(7)-H(7C)	0.94(3)	N(1)-C(6)-C(5)	120.2(3)
		C(3)-O-C(7)	117.1(3)
		O-C(7)-H(7A)	114(2)
		O-C(7)-H(7B)	108(2)
		O-C(7)-H(7C)	106(2)
		H(7A)-C(7)-H(7B)	108(3)
		H(7A)-C(7)-H(7C)	112(3)
		H(7B)-C(7)-H(7C)	108(3)

(a) Standard errors referred to the last significant digit are indicated in parentheses.

TABLE II

Root-Mean-Square Amplitudes of Thermal Vibration (a)

	Axis 1	Axis 2	Axis 3
Cl(2)	0.190(1)	0.257(1)	0.279(1)
Cl(5)	0.206(1)	0.246(1)	0.288(1)
O	0.190(3)	0.211(3)	0.274(3)
N(1)	0.203(4)	0.235(4)	0.243(4)
C(2)	0.190(5)	0.207(5)	0.228(4)
C(3)	0.193(4)	0.203(5)	0.219(4)
N(4)	0.193(4)	0.211(4)	0.216(4)
C(5)	0.203(4)	0.208(5)	0.224(4)
C(6)	0.209(5)	0.230(5)	0.249(5)
C(7)	0.186(5)	0.229(5)	0.283(5)

(a) Ordered across the table on increasing magnitude; standard errors are in parentheses.

the exocyclic angles show no distortion and have values close to 120°. All six angles about the methyl carbon are within 3 standard deviations of the tetrahedral angle, 109.5°.

B. The Crystal.

The arrangement of the molecules in the unit cell is shown in Figure 2. Crystallization occurs in sheets parallel to the $(10\bar{2})$ planes, and within each of these sheets the molecules are rather closely packed. Interatomic distances between heterocyclic rings related by the *a* translation are fairly short: C(3)-C(6), 3.502Å; C(2)-C(6), 3.547Å; C(2)-N(1), 3.551Å; C(3)-C(5), 3.553Å; and C(5)-N(4), 3.558Å. The methyl carbon, as was discussed previously, is surrounded by four nitrogen atoms at nearly equal distances: N(1) (x, ½-y, z-½), 3.502Å; N(1) (x-1, ½-y, z-½), 3.531Å; N(4) (x-1, y, z), 3.553Å; and N(4) (-x, 1-y, -z), 3.554Å, where the parenthetical transformations are to be applied to the coordinates given in Table III. Cl(2) and Cl(5) (1-x, y-½, ½-z) form the closest Cl. . .Cl approach at 3.601Å which is very nearly the sum of the van der Waals radii.

EXPERIMENTAL

A. Data Collection.

Crystals of dichloromethoxypyrazine, $C_5H_4Cl_2N_2O$, m.p. 79-81°, were supplied to us by A. Gulbenk. These were of needle-like habit, elongated on *a*, and many exhibited considerable mosaicity. A crystal of dimensions 0.14 x 0.17 x 1.05 mm which showed low mosaic spread was selected for study and mounted in a thin-walled glass capillary of 0.2 mm nominal I.D. The monoclinic space group $P2_1/c$ (C^5_{2h}) was established from the reciprocal lattice symmetry C_{2h} and the reflection conditions h0ℓ:ℓ = 2n and 0k0:k = 2n as determined from Weissenberg photographs. The crystal was then carefully centered on a Picker four-circle goniostat and aligned to set *a* collinear with the goniostat ϕ axis. Lattice constants were calculated by least-squares refinement of the setting angles of 19 reflections. The unit cell dimensions $a = 4.059 \pm 0.0006$, $b = 15.773 \pm 0.004$, $c = 11.123 \pm 0.003$Å, and $\beta = 90.96 \pm 0.01°$ give a calculated density of 1.688 gcm^{-3} for MW 179.02 and Z = 4.

The intensities of 1716 reflections were measured using the θ-2θ scan mode of the diffractometer and MoKα radiation (λ = 0.71069Å) from the (002) reflection of a highly oriented graphite crystal monochromator. The X-ray tube was set at a 4° take-off angle, and a detector aperture 6.0 mm square was placed 30 cm from the crystal. Attenuators prevented counting rates greater than 12,000/sec. Data were collected in the region of $0.001 \leqslant \sin\theta \leqslant 0.450$ ($0 < 2\theta \leqslant 54°$). Each reflection was scanned at 2°/min over a range of 2.2° to 2.5°, and background counts were taken for 10 seconds at each end of the scan by the stationary-crystal-stationary-counter technique. The (062) reflection was monitored after every 50 measurements and was acceptably stable with a maximum deviation of 4% from the mean. An error $\sigma(I) = [(0.02I)^2 + N_o + k^2N_b]^{1/2}$ was assigned to the net intensity $I = N_o - kN_b$, in order to establish weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement. Here N_o is the gross count, N_b is the background count, k is the ratio of scan time to background time, and the F^2 are the intensities, I, corrected for Lorentz and polarization effects by the expression $Lp^{-1} = (2 \sin 2\theta)/(\cos^2 2\theta_m + \cos^2 2\theta)$ where $2\theta_m$ is the monochromator setting angle, 12.52°. The 319 reflections for which either of the conditions $I > 0$ or $\sigma(I)/I < 0.5$ was not met were defined to be below background and were not used in the refinement. The linear absorption coefficient, μ, for MoKα radiation is 8.43 cm^{-1}, and no absorption corrections are necessary.

B. Solution and Refinement of the Structure.

The absolute scale factor and overall temperature factor, as computed by Wilson's method, were used to calculate a set of normalized structure factors $E_{hk\ell}$ (14). The signs of 182 reflections for which $|E| \geqslant 1.5$ were determined using the multiple solution computer program of Long (15), which solves the phase problem by reiterative application of Sayre's equation (16). The correct solution, which assumed positive signs for (1.0.2), (1.6.11), (2.13.3), and (0.19.4) and negative signs for (1.4.0), (0.6.9), and (1.5.4) gave a consistency index

$$C = \langle |E_a \Sigma_{a=b+c} E_b E_c| \rangle / \langle |E_a| \Sigma_{a=b+c} |E_b||E_c| \rangle$$

of 0.98 after 5 cycles. The Cl, O, N and C atoms were located in an E-map (17) calculated from the 182 signs. Least-squares refinement (18,19) of these ten atoms with isotropic temperature factors gave

$$R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o| = 0.128 \quad \text{and}$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2} = 0.115$$

after three cycles. An additional cycle (20) with anisotropic thermal parameters reduced R_1 to 0.069 and R_2 to 0.078. At this stage an electron density difference map (17) revealed all the hydrogens, and they were included with isotropic temperature factors in four additional least-squares cycles which produced final discrepancy indices of R_1 = 0.057 and R_2 = 0.049. The average parameter shift in the final cycle was 0.003 σ and the maximum shift was 0.02 σ. A difference map with all atoms subtracted showed no peaks greater than 0.3 eÅ^{-3}. The standard errors given in Tables I and II were computed (22) from the variance-covariance matrix obtained in the final least-squares cycle.

TABLE III

Final Structure Parameters (a) and Standard Errors (b)

Atom	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cl(2)	0.0364(2)	0.1414(1)	0.0626(1)	903(8)	29(1)	108(1)	-6(1)	-15(2)	0(1)
Cl(5)	0.5304(2)	0.4663(1)	0.2999(1)	865(8)	40(1)	100(1)	-21(1)	-58(2)	-7(1)
O	-0.0744(6)	0.3140(1)	-0.0214(2)	786(19)	30(1)	83(2)	0(3)	-59(5)	4(1)
N(1)	0.3538(7)	0.2255(2)	0.2306(2)	682(22)	38(1)	80(2)	12(4)	0(6)	8(1)
C(2)	0.1805(8)	0.2330(2)	0.1315(3)	540(23)	30(1)	77(3)	11(4)	25(6)	0(2)
C(3)	0.1066(8)	0.3126(2)	0.0795(3)	522(23)	31(1)	71(3)	4(4)	16(6)	4(1)
N(4)	0.2145(6)	0.3828(1)	0.1302(2)	530(19)	31(1)	73(2)	5(4)	2(5)	3(1)
C(5)	0.3885(8)	0.3742(2)	0.2318(3)	517(23)	34(1)	77(3)	0(4)	9(7)	-4(1)
C(6)	0.4601(9)	0.2971(2)	0.2830(3)	680(27)	43(2)	77(3)	16(5)	-22(7)	2(2)
C(7)	-0.1307(11)	0.3960(2)	-0.0771(4)	798(33)	35(2)	89(4)	8(5)	-73(9)	10(2)
					B				
H(6)	0.5950(87)	0.2954(22)	0.3563(31)		5.5(0.9)				
H(7A)	0.0788(104)	0.4272(25)	-0.0978(35)		6.8(1.1)				
H(7B)	-0.2649(92)	0.4345(24)	-0.0163(32)		6.0(1.0)				
H(7C)	-0.2637(85)	0.3860(21)	-0.1450(31)		4.4(0.8)				

(a) The anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})]$. (b) Standard errors in parentheses.

TABLE IV

Final Observed and Calculated Structure Factors.

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  K   L  FOBS FCALC    K   L  FOBS FCALC    K   L  FOBS FCALC    K   L  FOBS FCALC    K   L  FOBS FCALC    K   L  FOBS FCALC    K   L  FOBS FCALC    K   L  FOBS FCALC    K   L  FOBS FCALC    K   L  FOBS FCALC

                       6   7   192   195   15  -1    44    43    8  -5   157   151    2  10    55    48    4   2    41    36   11   6    65    58    6-12    33    21    7   5   104   103   10  -1    54    55
 *** H =  0 ***        7   7   137   138   16   1    63    57    9   5    53    49    2-10   104   107    6  -2    76    73   11  -6   110   109    7-12    69    57    7  -5    32    19   12   1    31    28
                       9   7    41    46   16  -1    35    37    9  -5   101    95    3  10    38    30    7   2   185   191   12   6    37    37                      8   5    48    43   12  -1    29    15
  2   0   445   461   10   7    73    74   17   1    45    51   10  -5   130   129    4  10    47    47    7  -2    93    87   12  -6    42    42    *** H =  3 ***      8  -5    67    66    0  -2    35    24
  4   0   323   322   11   7   168   175   17  -1    99    99   11   5   213   217    5  10    76    77    8   2    28    19   13   6    66    72                      9   5    41    43    1  -2    27    20
  6   0   270   275   13   7    25    29   18   1    67    63   11  -5    35    44    5-10    89    86    8  -2   128   118   13  -6    58    54    0   0    98    97   10   5    59    57    2  -2    59    66
  8   0   218   222   14   7    76    81   18  -1    44    47   12   5    27    11    6  10    30    23    9   2    74    77   14   6   105   110    1   0    66    65   10  -5   114   106    3   2    51    41
 10   0   103   104   15   7    25    26    0   2   630   673   12  -5    86    55    6-10    89    84    9  -2    62    61   14  -6    39    31    2   0   117   115   11   5    75    90    3  -2    31    32
 12   0   356   363   16   7    55    61    0  -2  1943  2142   13   5    40    41    7  10    38    32   10   2    80    81   15   6    29    13    3   0    60    49   11  -5    51    44    4  -2    78    90
 14   0    63    65   17   7   103   101    1   2   139   141   13  -5    62    64    7-10    60    54   11   2   143   140   15  -6    37     2    4   0   163   156   12   5    57    55    5   2   125   127
 16   0    31    25    0   8   159   160    1  -2   690   696   14   5    82    86    8  10    63    63   11  -2   113   108   16   6    40    33    5   0   137   135   12  -5    84    88    5  -2    27    15
 18   0   141   146    1   8    69    72    2   2    60    64   14  -5    28    26    8-10    30    29   12   2    61    61    1   7   141   135    6   0    48    43   13  -5   139   139    6   2    67    69
  1   1    30    30    2   8   172   174    2  -2   289   276   15   5    44    37    9  10    81    76   12  -2    71    70    1  -7   151   153    7   0    49    48   14  -5    36    26    6  -2    36    32
  2   1   312   328    3   8   107   106    3   2   230   228   15  -5    62    60   10  10    76    74   13   2   187   186    2   7    65    66    8   0    64    58    0   6   263   269    7   2   114   114
  3   1   146   149    4   8    66    63    3  -2    24    16   16   5   107   113   10-10    57    52   13  -2    27    24    2  -7    92    88    9   0    29    24    0  -6    78    83    8   2    63    80
  4   1   371   373    5   8   111   116    4   2   101   102   16  -5    91    94   11-10    29    26   14   2   113   112    3   7    35    34   10   0    74    69    1   6    38    29    8  -2    25    32
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5	1	28	25
6	1	287	296
7	1	331	346
8	1	309	314
9	1	50	47
10	1	127	131
11	1	436	451
12	1	285	301
13	1	219	233
14	1	173	178
15	1	48	43
17	1	148	154
19	1	40	29
0	2	195	191
1	2	514	543
2	2	318	323
3	2	169	179
4	2	674	721
5	2	504	521
6	2	254	259
7	2	326	331
8	2	81	76
9	2	171	177
11	2	129	129
12	2	170	177
13	2	155	160
14	2	109	114
15	2	35	36
16	2	113	113
17	2	83	89
18	2	56	51
19	2	30	9
1	3	281	291
2	3	700	758
3	3	229	237
4	3	109	112
5	3	621	657
6	3	175	174
7	3	363	370
8	3	314	326
9	3	95	98
10	3	227	234
11	3	22	19
12	3	72	75
13	3	112	117
14	3	24	15
15	3	138	144
16	3	113	115
17	3	30	24
18	3	67	62
19	3	43	44
0	4	227	233
1	4	294	299
2	4	61	60
3	4	243	247
4	4	189	194
5	4	62	63
6	4	187	182
7	4	400	406
8	4	154	158
9	4	366	378
11	4	38	33
12	4	55	60
13	4	110	113
15	4	91	91
17	4	60	57
18	4	51	49
19	4	131	132
1	5	344	353
2	5	400	400
3	5	284	289
4	5	70	75
5	5	133	138
6	5	207	216
7	5	138	137
8	5	98	89
9	5	53	50
10	5	77	78
11	5	34	37
12	5	94	95
13	5	169	177
15	5	121	121
16	5	55	53
17	5	48	46
18	5	43	38
0	6	303	295
1	6	107	102
2	6	168	166
3	6	39	37
4	6	242	242
5	6	327	332
7	6	201	205
8	6	157	162
9	6	33	32
10	6	26	23
11	6	167	177
12	6	33	34
13	6	137	143
14	6	108	107
15	6	90	88
16	6	26	10
17	6	41	44
18	6	41	33
1	7	292	305
2	7	155	153
3	7	74	71
4	7	183	185
5	7	106	110
6	8	151	154
7	8	25	12
8	8	24	19
9	8	81	85
10	8	113	113
11	8	55	53
12	8	64	62
13	8	28	24
14	8	26	23
15	8	38	30
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7	-3	64	70
8	3	32	21
8	-3	54	58
9	3	47	37
9	-3	30	5
10	3	27	21
11	3	54	45
11	-3	34	29
0	4	119	124
0	-4	58	64
1	4	62	65
1	-4	27	27
2	4	24	9
2	-4	37	29
3	4	67	65
3	-4	44	45
4	4	55	56
5	4	45	48
5	-4	33	34
6	4	36	25
6	-4	47	54
7	4	35	31
7	-4	32	39
8	4	49	44
9	4	111	111
9	-4	31	19
10	4	49	51
10	-4	32	34
11	4	31	29
1	5	32	26
1	-5	36	43
2	5	66	62
2	-5	42	46
3	5	74	75
4	-5	29	21
5	5	41	22
6	5	32	24
6	-5	86	99
7	5	28	2
7	-5	33	20
8	5	59	58
9	-5	33	20
10	5	33	24
10	-5	29	12
0	-6	89	108
1	6	67	67
1	-6	24	18
2	6	95	92
2	-6	63	75
3	-6	33	23
4	6	43	36
5	-6	43	47
6	6	26	18
6	-6	34	17
8	6	30	18
1	7	55	53
1	-7	71	78
2	7	31	20
3	7	34	32
4	7	50	43
6	7	38	27
7	7	39	41
0	8	55	50
0	-8	37	34
1	-8	76	92
2	8	40	43
2	-8	34	23
3	8	39	37
4	-8	29	15
*** H = 5 ***			
4	0	50	35
1	-1	33	28
3	1	48	52
4	1	42	34
0	2	43	28
1	2	46	45
1	-2	27	8
2	2	27	2
3	2	57	46
1	-3	39	29

Table III lists the final atomic parameters and Table IV gives the observed and calculated structure factors.

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