(3·17 and 3·81 Å respectively). The hydrogen bonding $H_2O_I \cdots S_{II}$ satisfies particularly well the angular criterion of Donohue (1952) but the same cannot be said for $H_2O_{II} \cdots S_{II}$.

The calculations at the refinement stage were performed on the IBM 650 computer of the *Centro Calcoli e Servomeccanismi della Università di Bologna* using the programmes of L. H. Jensen for the structure factors calculations and those of R. Shiono for the differential synthesis. The cost of the computing work was borne by the *Consiglio Nazionale delle Ricerche*. It is a pleasure to thank all these people and Prof. L. Cavalca for his valuable interest.

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The Structures of Substituted Triazolopyrimidines. Part I. 2-Amino 5-propyl 7-methyl s-triazolo [2,3-c] Pyrimidine Hydrochloride

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(*Received* 27 *April* 1961)

The molecular structure of $C_9H_{13}N_5 . HCl$, a biologically active triazolo–pyrimidine, has been determined by X-ray methods. The crystals are monoclinic, with the unit-cell parameters

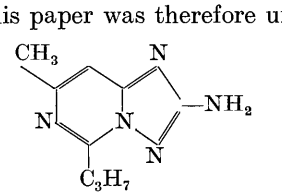
$$a = 22{\cdot}30 \pm 0{\cdot}07,\ b = 6{\cdot}41 \pm 0{\cdot}02,\ c = 16{\cdot}76 \pm 0{\cdot}05\ \text{Å},\ \beta = 107{\cdot}7 \pm 0{\cdot}5°.$$

There are eight molecules in the unit cell, and the space-group is $C2/c$. The three-dimensional Patterson synthesis confirmed this space group, and excluded the alternative, Cc. The structure was solved by the use of Buerger's minimum function, which was derived graphically from the Patterson synthesis. Refinement by Fourier and least-squares methods was continued until the final average standard deviation of the atomic positions was 0·017 Å.

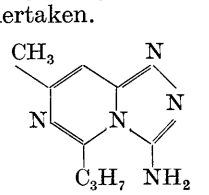
The substance was shown to be a triazolo [2,3-*c*] pyrimidine, with the structure I. The two fused rings are planar and inclined at 6° to each other. The bonds in the fused ring system are all shorter than normal single-bonds, but simple resonance theory is not adequate to explain them. The molecules are linked by a spiral chain of hydrogen bonds 3·18 and 3·30 Å long between the chloride ion and the primary amine group N10; there are also other inter-ionic contacts less than 3·5 Å long which cannot all be hydrogen bonds.

Introduction

In the course of work on a variety of substituted triazolopyrimidines which have interesting biological properties, a substance with the empirical formula $C_9H_{13}N_5$ was isolated, and was thought to be the triazolo [2,3-*c*] pyrimidine, I, or the [4,3-*c*] isomer, II, (Davies, Miller & Rose 1960; Miller & Rose 1960). The chemical and spectroscopic evidence was not conclusive however, and the X-ray analysis described in this paper was therefore undertaken.



I



II

Experimental

The base $C_9H_{13}N_5$ did not crystallise well from any of the usual solvents, but its hydrochloride, $C_9H_{13}N_5.HCl$, yielded a fibrous polycrystalline solid on slow evaporation of an ethanol solution, and suitable single crystals for X-ray analysis were obtained from this material. The following measurements were made, using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å):

$C_9H_{13}N_5.HCl$, molecular weight: 227·71
Symmetry: monoclinic
Cell dimensions: $a = 22{\cdot}30 \pm 0{\cdot}07$ Å
$b = 6{\cdot}41 \pm 0{\cdot}02$
$c = 16{\cdot}76 \pm 0{\cdot}05$
$\beta = 107{\cdot}7 \pm 0{\cdot}5°$
Cell volume: 2282·3 Å^3
Assumed no. of molecules per cell: 8
Density calculated: 1·325 g.cm.$^{-3}$
Space group: $C2/c$ (or Cc)

It was impossible to measure the density by flotation, since the crystals dissolved immediately in all the liquids normally used. The assumption that there are eight molecules in the unit cell gives a reasonable value for the density.

The systematically absent reflections show the space-group to be $C2/c$ or Cc:

$$hkl\text{: } h+k \text{ odd; } h0l\text{: } (h \text{ odd}),\ l \text{ odd}.$$

A crystal of approximate cross-section $0{\cdot}05 \times 0{\cdot}05$ mm.^{2} was used to record the intensity data. Equi-inclination multiple-film Weissenberg photographs were taken of the six layers $k = 0$–5, and the intensities were estimated visually using standard scales. 2102 independent reflections were obtained, with a range of intensities of 1200 to 1. The Lorentz and polarisation factors were applied, but no absorption correction was considered necessary, since the linear absorption coefficient using copper $K\alpha$ radiation is only 28·3 cm.$^{-1}$. For each individual layer the average temperature factor and the factor required to place the intensities on an approximately absolute scale were calculated by Wilson's (1942) method.

Structure determination

The Patterson synthesis $P(UW)$ was computed from the 225 $h0l$ reflections. It showed several maxima of approximately equal weight, each of which was taken in turn to be the chlorine-chlorine rotation vector. Two-dimensional Fourier syntheses were calculated, using the observed structure factors with signs determined by these chlorine positions, but on none of them could an acceptable trial structure be placed. Sign-determination methods were also applied to the unitary structure factors of the $h0l$ zone, with no better success.

The three-dimensional Patterson synthesis $P(UVW)$ was therefore computed, and was first used to decide between the two possible space groups. If the space-group is $C2/c$, and the chlorine atom is at (x, y, z), the largest peaks to be expected are:

$(0\,0\,0)$, $(\frac{1}{2}\,\frac{1}{2}\,0) \pm$:

$(2x,\ 2y,\ 2z)$, $(2x,\ -2y,\ 2z)$ (single-weight rotation peaks)

$(2x,\ 0,\ \frac{1}{2}+2z)$, $(0,\ 2y,\ \frac{1}{2})$ (double-weight reflection peaks)

If the space-group is Cc, there are two molecules in the asymmetric unit with two chlorine atoms in unrelated positions $(x_1y_1z_1)$ and $(x_2y_2z_2)$. The principal peaks in the Patterson synthesis will then be:

$(0\,0\,0)$, $(\frac{1}{2}\,\frac{1}{2}\,0) \pm$:

$(0,\ 2y_1,\ \frac{1}{2})$, $(0,\ 2y_2,\ \frac{1}{2})$ (single-weight reflection peaks)

$(x_1-x_2,\ y_1-y_2,\ z_1-z_2)$
$(x_1-x_2,\ -y_1+y_2,\ z_1-z_2)$
$(x_1-x_2,\ y_1+y_2,\ \frac{1}{2}+z_1-z_2)$
$(x_1-x_2,\ -y_1-y_2,\ \frac{1}{2}+z_1-z_2)$ (double-weight peaks)

The most prominent maxima in the $P(UVW)$ synthesis for this compound are at (0·464, 0, 0·288) and (0, 0·208, $\frac{1}{2}$), with a smaller peak at (0·464, 0·208, 0·788). The space-group is therefore $C2/c$, and the coordinates of the chlorine atom are (0·232, 0·104, 0·394).

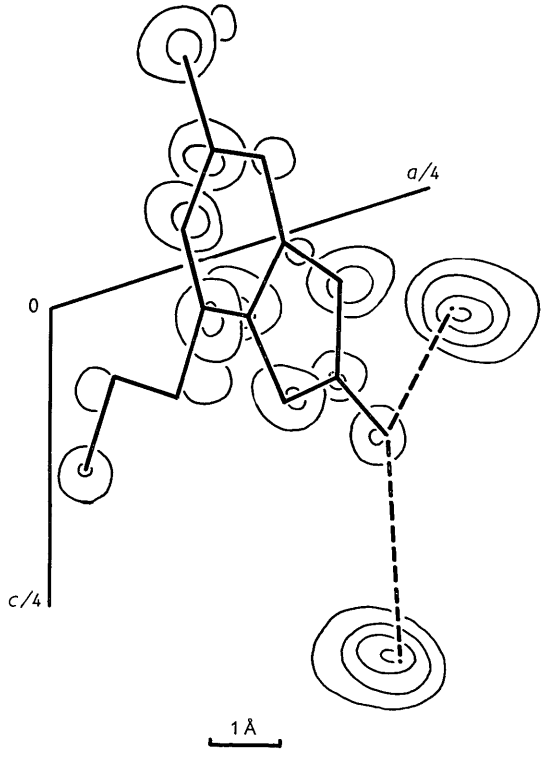


Fig. 1. The M_8 minimum function, viewed down the b-axis, showing the maxima for one complete molecule and the final atomic positions.

Buerger's (1951) minimum function was then derived graphically from the Patterson synthesis, taking the chlorine atom position to be (0·232, 0·100, 0·394). Three successive superpositions led to a three-dimensional $M_8(x\,y\,z)$ map with the symmetry $C2/c$, which is shown in projection in Fig. 1. This map gives a complete solution of the structure so far as the general stereochemistry of the molecule is concerned. Each unit cell contains eight chlorine atoms and eight groups of fourteen lower peaks of approximately equal weight, each group representing a molecule with the structure I; there are no other significant peaks.

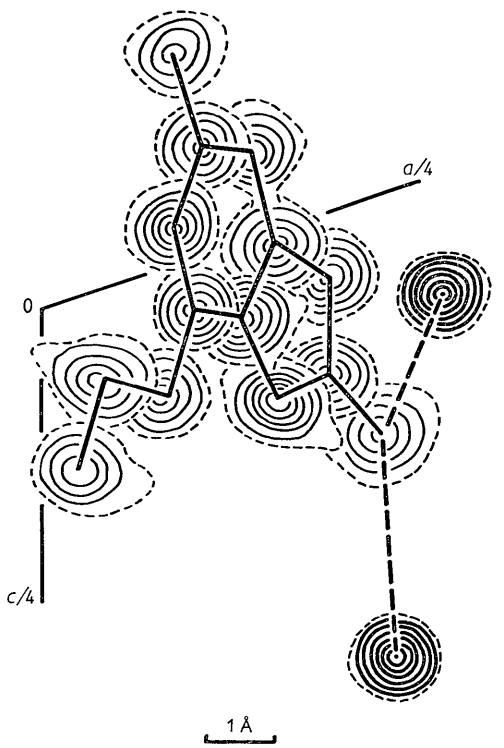


Fig. 2. Electron density distribution corresponding to Fig. 1. Contour intervals 5 e.Å^{-3} round chloride ions, 2 e.Å^{-3} elsewhere: 2 e.Å^{-3} contour dashed.

Structure refinement

The structure derived from the minimum function was confirmed by means of a three-dimensional Fourier synthesis, and then improved by several cycles of least-squares refinement using only the diagonal terms of the least-squares matrix, and using isotropic temperature factors. The weight given to each term was $\sqrt{w}=[20(20+F_o^2)]^{\frac{1}{2}}$, the constant 20 being approximately $F^2_{\min.}$. The atomic scattering factors used were those of Berghuis *et al.* (1955), the values for nitrogen being used for all the carbon and nitrogen atoms, and the hydrogen atoms being ignored. The refinement was interrupted several times between cycles and any necessary changes in the individual scale factors of the six sets of structure factors $k=0-5$ were made.

When the discrepancy factor R had fallen from 0·435 to 0·274 a second three-dimensional Fourier synthesis was computed, and is illustrated in a composite projection in Fig. 2.

Refinement by the least-squares process was continued until a total of 16 cycles had been calculated. The value of $\Sigma w(F_o-F_c)^2/\Sigma wF_o^2$, which measures the progress of the refinement, had by then become constant at 0·16, and the calculated shifts in the parameters had also become negligible. The average standard deviation in the atomic positions was 0·017 Å.

A difference synthesis was then computed, and the residual electron density was within the limits $\pm$ 1·2 e.Å^{-3}; it was negative (–0·5 e.Å^{-3}) at the carbon atom positions and zero or slightly positive at the nitrogen atom positions. No hydrogen atoms bonded to atoms in the ring system could be seen, though the hydrogen atoms in the propyl chain were visible. The final value of the discrepancy factor R (0·238) could be reduced by further refinement, using the correct scattering factors for carbon and nitrogen, and including the hydrogen atoms, but it is not certain that this would lead to a marked improvement in the estimated standard deviations.

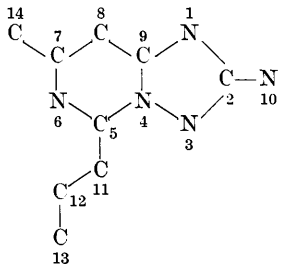
Table 1. *Final atomic coordinates (fractional), temperature factor coefficients* and standard deviations* (Å)

Atom	x	y	z	B	$a\sigma(x)$	$b\sigma(y)$	$c\sigma(z)$
Cl	0·2320	0·1087	0·3954	3·6783	0·00236	0·00280	0·00246
N1	0·1949	0·0795	0·0569	3·7489	0·00920	0·00908	0·00942
C2	0·1930	0·1004	0·1371	4·4806	0·01037	0·00980	0·01119
N3	0·1588	0·2691	0·1438	3·1608	0·00739	0·00884	0·00764
N4	0·1355	0·3407	0·0648	3·3278	0·00790	0·00942	0·00808
C5	0·1035	0·5277	0·0455	3·0418	0·00733	0·00858	0·00782
N6	0·0884	0·5861	−0·0303	3·1132	0·00765	0·00782	0·00823
C7	0·1104	0·4803	−0·0892	4·2846	0·00920	0·01163	0·00984
C8	0·1422	0·3065	−0·0720	4·3459	0·00971	0·01087	0·00967
C9	0·1579	0·2313	0·0113	3·9933	0·00861	0·01027	0·00913
N10	0·2257	−0·0228	0·2024	4·3911	0·00983	0·01106	0·01040
C11	0·0844	0·6300	0·1101	3·8525	0·00894	0·00944	0·00936
C12	0·0437	0·8236	0·0769	4·7162	0·01031	0·01178	0·01035
C13	0·0263	0·9352	0·1502	5·1284	0·01122	0·01139	0·01209
C14	0·0911	0·5788	−0·1793	5·6848	0·01190	0·01167	0·01278

* Temperature factor = $\exp[-B(\sin\theta)^2/\lambda^2]$.

Results and discussion

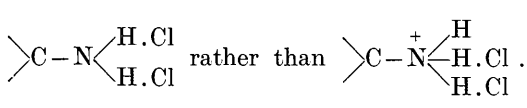
The atomic parameters obtained from the analysis are given in Table 1, and the bond-lengths and bond angles in Table 2(a), the atoms being numbered as follows:



The list of observed and calculated structure factors is appended as Table 3.

Each of the two fused rings is almost exactly planar, and since these two planes are inclined at only 6° to each other the whole molecule is approximately planar. The arrangement of the molecules in the crystal is determined mainly by their packing: they lie in the (510) and (5$\bar{1}$0) planes (spacing 3·52 Å) and it is remarkable that even the propyl side-chains lie in these planes. The molecules are linked by a spiral chain of N10–Cl bonds 3·18 and 3·30 Å long (Fig. 3), agreeing reasonably well with the rather wide range of values of 3·19 ± 0·07 for $-NH_3^+$–Cl or 3·27 ± 0·08 Å for $-NH_2$–Cl hydrogen bonds (Fuller, 1959).

The two N10–Cl bonds and the N10–C2 bond are nearly coplanar (Table 2 (c)), and the length of the N10–C2 bond (1·37 Å) indicates that it has some double-bond character presumably due to a resonance contribution from the planar form $>C=\overset{+}{N}H_2$; the coordination round N10 thus appears to be



The N1–Cl link is short enough (3·29 Å) to be a hydrogen bond, though the steric arrangement is not entirely favourable. The N4–Cl link is also short (3·31 Å) but cannot be a hydrogen bond for steric reasons. This N4–Cl link, like the other close contacts listed in Table 2(b) is thus probably ionic in character.

Table 2(*a*). *Bond lengths and angles*

	Length (Å)	Stand. dev. (Å)		Angle (°)	Stand. dev. (°)
N1 –C2	1·366	0·027	C2 –N1 –C9	106·8	1·6
C2 –N3	1·347	0·026	N1 –C2 –N3	110·4	1·8
C2 –N10	1·366	0·028	N1 –C2 –N10	124·2	1·9
N3 –N4	1·348	0·020	N3 –C2 –N10	125·1	1·9
N4 –C5	1·382	0·022	C2 –N3 –N4	104·5	1·5
N4 –C9	1·348	0·025	N3 –N4 –C5	122·9	1·4
C5 –N6	1·267	0·021	N3 –N4 –C9	111·5	1·4
C5 –C11	1·437	0·025	C5 –N4 –C9	124·3	1·5
C11–C12	1·538	0·030	N4 –C5 –N6	116·9	1·5
C12–C13	1·570	0·033	N4 –C5 –C11	118·0	1·5
N6 –C7	1·404	0·026	N6 –C5 –C11	124·8	1·6
C7 –C14	1·571	0·034	C5 –N6 –C7	121·3	1·5
C7 –C8	1·305	0·030	N6 –C7 –C8	122·6	1·9
C8 –C9	1·417	0·029	N6 –C7 –C14	115·4	1·8
C9 –N1	1·352	0·025	C8 –C7 –C14	121·8	2·0
			C7 –C8 –C9	117·6	2·0
N10–Cl	3·305	0·018	N1 –C9 –C8	136·6	1·9
N10–Cl′	3·178		N1 –C9 –N4	106·5	1·6
			N4 –C9 –C8	116·7	1·7
			C5 –C11–C12	111·9	1·6
			C11–C12–C13	110·1	1·8

Table 2(*b*). *Intermolecular and inter-ionic distances and angles**

	Length (Å)	Stand. dev. (Å)		Angle (°)	Stand. dev. (°)
Cl–N‴1	3·29	0·017	C2–N10 –Cl	119·3	1·3
–N″1	3·41	0·017	C2–N10 –Cl′	100·6	1·3
–N′3	3·47	0·015	Cl –N10 –Cl′	139·8	0·6
–N′4	3·31	0·015			
–C‴8	3·47	0·021	C‴2–N‴1–Cl	157·0	1·3
–C′9	3·46	0·020	C‴9–N‴1–Cl	93·6	1·1
–N10	3·30	0·019			
–N″10	3·18	0·019			
N10–N″3	3·32	0·023			

* Atoms in the molecule at x, y, z are unprimed
$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ have one prime
$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ have two primes
$x, -y, \frac{1}{2}+z$ have three primes.

Table 2(*c*). *Distances of atoms from the best planes*

(i) Best plane through N1, C2, N3, N4, C9, N10:

$$-0{\cdot}7778X - 0{\cdot}6015Y - 0{\cdot}1826Z + 3{\cdot}6148 = 0$$

Distances from plane:

N1	−0·0129 Å	N4	0·0192 Å	[Cl	−0·4142 Å[*
C2	0·0250 Å	C9	−0·0039 Å	[Cl′	0·5849 Å]
N3	−0·0265 Å	N10	−0·0004		

(ii) Best plane through N4, C5, N6, C7, C8, C9, C11, C14:

$$-0{\cdot}8125X - 0{\cdot}5267Y - 0{\cdot}2496Z + 3{\cdot}6256 = 0$$

Distances from plane:

N4	0·0301 Å	C8	0·0021 Å	[C12	0·0641 Å]*
C5	−0·0254 Å	C9	−0·0148 Å	[C13	0·0151 Å]
N6	0·0396 Å	C11	−0·0130 Å		
C7	−0·0110 Å	C14	−0·0066 Å		

(iii) Best plane through C2, N10, Cl, Cl′:

$$-0{\cdot}8633X - 0{\cdot}4870Y - 0{\cdot}1332Z + 3{\cdot}6354 = 0$$

Distances from plane:

C2	−0·0165 Å	Cl	−0·0099 Å
N10	0·0350 Å	Cl′	−0·0092 Å

(iv) Angles between planes:
Pyrimidine ring (ii) and triazole ring (i): 6·1°
Triazole ring (ii) and C2, N10, Cl, Cl′ (iii): 8·6°

Coordinate system:

$$X = ax + cz\cos\beta,\quad Y = by,\quad Z = cz\sin\beta$$

* The atoms in square brackets were not included in the calculation of the best planes.

N.B. All results quoted in Table 2 have been calculated on the Mercury computer, using more decimal places than are quoted here.

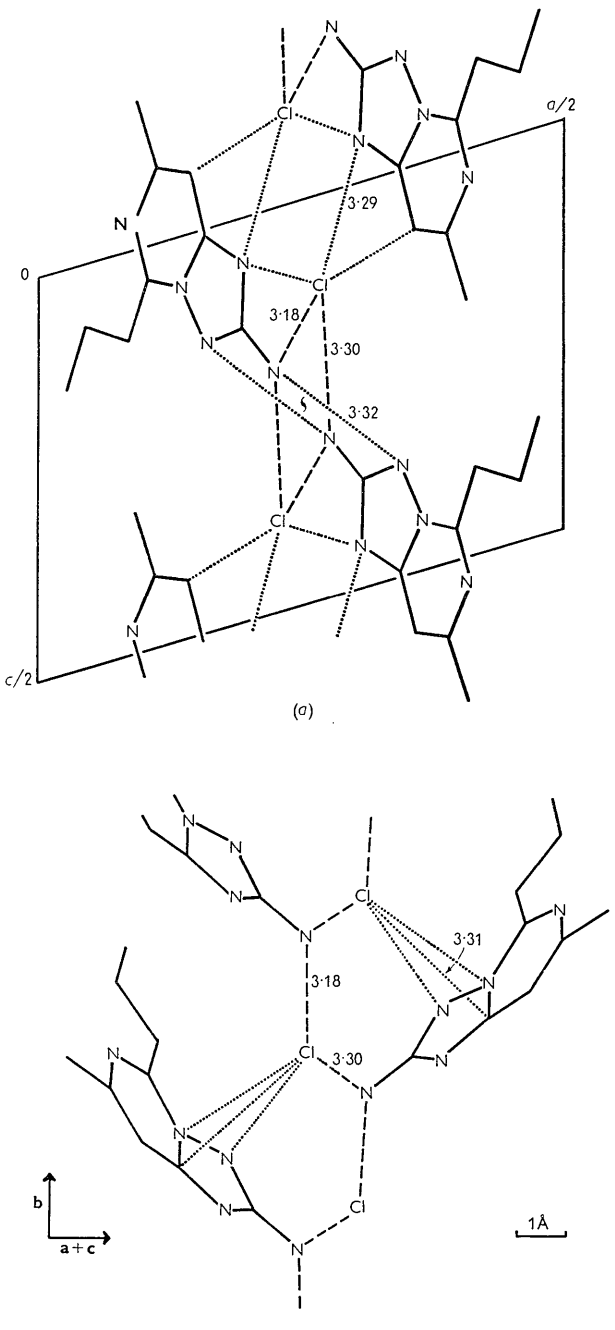
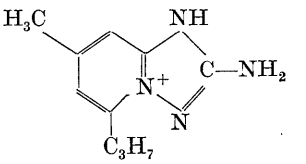


Fig. 3. Projections of the structure showing the hydrogen bonds (dashed) and other interionic contacts less than 3·5Å long (dotted): (*a*) on (010), (*b*) on (101).

The molecule has considerable aromatic character, shown by its planarity and by the lengths of the bonds in the fused ring system, which are less than normal single-bond lengths. The principal resonance form is probably



but it does not appear to be possible to give an adequate explanation of the observed bond-lengths by simple consideration of resonance between the various possible valency forms. In this it resembles caffeine and some other pyrimidine derivatives (Sutor, 1958): a further point of resemblance, besides the shape of the fused ring system, is that the bonds C5–N6 and C7–C8 are very short, with lengths corresponding to double bonds both in caffeine and in the present compound. The bond-lengths do not agree with those predicted from the 'ring atom' radii suggested for pyrimidine and purine derivatives by Spencer (1959), no doubt because in this compound the six- and five-membered rings are fused with a carbon and a nitrogen atom in the bridge, and not with two carbon atoms.

We are indebted to Dr F. L. Rose, F. R. S. & Dr G. W. Miller for suggesting the problem, providing specimens and discussing the chemistry of this series of compounds. All the longer calculations were performed on the 'Mercury' computer, under the supervision of Dr B. Richards of the I.C.I. Computing Section, Wilton Works. The programmes used are listed below, and we thank their writers for supplying copies of the programmes and giving much valuable advice on their use: General Fourier syntheses (Mr O. S. Mills, Manchester University). Least-squares refinement C2/c (isotropic temperature factors) (Mr O. S. Mills). Distance-angle routine (Dr R. A. Sparks, Oxford University). Data reduction, intensities to structure factors (J.M.R.). Best plane through a set of points (J.M.R.).

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Table 3. *Observed and calculated structure factors*

The three columns contain the values of l, $10F_o$, $10F_c$. Each group is headed by an ✱ and the common values of h and k for that group. Unobserved reflections are marked by *, and the minimum observable $10F$ is given instead of $10F_o$.

• 0	0	
0	9000	-
2	1705	2371
4	-1881	-2034
6	-675	-790
8	-539	-307
10	125	145
12	-101*	-62
14	-154	-51
16	-130*	-66
18	110*	52
20	101	144
• 2	0	
0	-1199	-1372
2	-990	-965
4	332	188
6	557	472
8	-844	-807
10	-643	-728
12	710	633
14	367	331
16	-253	-78
18	-103*	-125
20	-51*	-195
-2	894	917
-4	948	874
-6	599	364
-8	345	229
-10	-332	-181
-12	-428	-296
-14	-152	-196
-16	132*	37
-18	-163	-123
-20	-82*	-87
• 4	0	
0	-689	-1040
2	-1088	-1200
4	-1215	-1339
6	757	535
8	1291	1153
10	632	613
12	-412	-250
14	-340	-241
16	171	96
18	92*	148
-2	-1455	-1658
-4	-144	-71
-6	-1281	-915
-8	-470	-351
-10	755	388
-12	98*	75
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-5	-601	-540
-6	256	259
-7	-108	-1
-8	-126	-145
-9	268	203
-10	-82Å	-19
-11	-84Å	-40
-12	-85Å	-116
-13	104Å	28
-14	-147	-90
-15	-101Å	-11
-16	96Å	18
-17	90Å	12
-18	-81Å	-41
-19	265	191

• 16 2

0	82Å	4
1	-408	-466
2	-84Å	-95
3	170	208
4	-183	-152
5	300	328
6	168	181
7	-210	-169
8	242	207
9	-261	-310
10	81Å	43
11	-71Å	-51
12	56Å	52
-1	-245	-255
-2	278	327
-3	195	183
-4	80Å	103
-5	367	315
-6	-211	-211
-7	228	261
-8	82Å	29
-9	-270	-259
-10	-85Å	-156
-11	-272	-273
-12	121	82
-13	290	163
-14	440	291
-15	352	305
-16	150	114
-17	84Å	73
-18	74Å	12
-19	-188	-166

• 18 2

0	104Å	39
1	229	229
2	-104Å	-26
3	-104Å	-98
4	102Å	98
5	-162	-159
6	-200	-153
7	-90Å	-37
8	-83Å	-143
9	74Å	106
10	62Å	49
-1	720	293
-2	84Å	74
-3	-119	-6
-4	-184	-142
-5	-84Å	-82
-6	-331	-308
-7	85Å	61
-8	-147	-105
-9	175	195
-10	148	189
-11	104Å	173
-12	-102Å	-11
-13	-100Å	-44
-14	96Å	37
-15	-254	-183
-16	200	148
-17	-76Å	-30
-18	65Å	57
-19	116	98

20	2	
0	-145	-85
1	-103Å	-42
2	99Å	114
3	97Å	65
4	93Å	14
5	88Å	100
6	-83Å	-87
7	-74Å	-34
8	-63Å	-34
-1	-104Å	-120
-2	104Å	24
-3	-104Å	-95
-4	104Å	93
-5	334	284
-6	104Å	32
-7	446	413
-8	-104Å	-88
-9	206	18
-10	-95Å	-120
-11	-399	-320
-12	97Å	18
-13	-313	-245
-14	-178	-153
-15	117	53
-16	-181	-106
-17	106	31
-18	50Å	33

• 22 2

0	94Å	70
1	-91Å	-6
2	-88Å	-67
3	-83Å	-100
4	-77Å	-45
5	70Å	23
6	60Å	39
-1	96Å	122
-2	-98Å	-13
-3	140	50
-4	141	162
-5	-339	-331
-6	368	310
-7	-387	-313
-8	255	209
-9	136	198
-10	133	56
-11	272	281
-12	-124	-158
-13	-83Å	-6
-14	-110	-100
-15	-192	-180
-16	-60Å	-48
-17	-110	-121

• 24 2

0	-157	-146
1	74Å	89
2	-69Å	-57
3	122	199
-1	-82Å	-113
-2	85Å	17
-3	-83Å	-146
-4	88Å	32
-5	-88Å	-55
-6	-88Å	-25
-7	-88Å	-13
-8	-86Å	-24
-9	-85Å	-73
-10	82Å	35
-11	-78Å	-117
-12	74Å	76
-13	68Å	20
-14	61Å	47
-15	89	164

• 26 2

0	53Å	13
-1	59Å	59
-2	-99	-97
-3	147	178
-4	-69Å	-51
-5	-70Å	-24
-6	-115	-159
-7	-70Å	-112
-8	-112	-131
-9	-67Å	-8
-10	63Å	14
-11	59Å	85

• 1 3

0	-43	-62
1	536	896
2	-587	-775
3	-458	-226
4	-42Å	-61
5	-529	-420
6	228	286
7	-57Å	-36
8	454	440
9	534	571
10	-70Å	-68
11	287	231
12	-230	-210
13	-262	-213
14	91Å	54
15	-87Å	-144
16	175	101
17	-70Å	-61
18	125	91
-1	381	800
-2	295	349
-3	-265	-255
-4	-145	-219
-5	268	218
-6	-50Å	-101
-7	456	355
-8	-456	-333
-9	822	307
-10	-198	-40
-11	311	294
-12	197	131
-13	-275	-128
-14	92Å	45
-15	-416	-284
-16	83Å	14
-17	-75Å	-12
-18	-90	-31
-19	152	119

• 3 3

0	-312	-247
1	422	633
2	125	101
3	670	572
4	123	97
5	620	545
6	462	530
7	60Å	119
8	310	262
9	-530	-529
10	102	130
11	-348	-362
12	93Å	33
13	-92Å	-23
14	-259	-197
15	-117	-14
16	-122	-116
17	-63Å	-66
18	-46Å	-37
-1	29Å	56
-2	-264	-240
-3	-270	-242
-4	-217	-118
-5	512	612
-6	-49Å	-51
-7	385	381
-8	546	462
-9	-503	-441
-10	95	74
-11	-291	-231
-12	-276	-132
-13	172	95
-14	-241	-128
-15	293	207
-16	-121	-53
-17	78Å	54
-18	111	95
-19	-156	-135

• 5 3

0	59	44
1	187	149
2	-248	-244
3	-805	-1005
4	470	412
5	-492	-504
6	200	219
7	310	322
8	-68Å	-77
9	299	297
10	-235	-249
11	75Å	54
12	-278	-242
13	-245	-163
14	85Å	22
15	-144	-55
16	67Å	25
17	110	110
-1	476	408
-2	38Å	93
-3	356	270
-4	103	83
-5	-411	-309
-6	72	26
-7	-804	-779
-8	-404	-392
-9	183	132
-10	147	101
-11	220	185
-12	251	217
-13	-418	-368
-14	93Å	24
-15	-437	-402
-16	-141	-145
-17	-102Å	-101
-18	-162	-130
-19	115	114

• 7 3

0	387	394
1	-87	-79
2	849	766
3	446	483
4	8	-44
5	116	110
6	-246	-425
7	303	239
8	-269	-501
9	194	116
10	-191	-204
11	169	99
12	360	203
13	274	329
14	199	115
15	138	127
16	79	51
-1	-796	-1072
-2	-156	-176
-3	-533	-496
-4	-558	-559
-5	473	476
-6	-195	-147
-7	330	275
-8	437	362
-9	-434	-372
-10	-68Å	-78
-11	-128	-159
-12	-74Å	-72
-13	224	217
-14	-93Å	-20
-15	234	139
-16	-89Å	-16
-17	-80Å	-20
-18	-71Å	-5
-19	-59Å	-26

• 9 3

0	-259	-220
1	56Å	59
2	-325	-276
3	-269	-528
4	231	288
5	-67Å	-108
6	99	133
7	282	266
8	-120	-169
9	-93Å	-22
10	-92Å	-32
11	-254	-181
12	85Å	50
13	-79Å	-33
14	170	141
15	93	58
-1	598	631
-2	-169	-132
-3	183	74
-4	317	245
-5	-592	-625
-6	295	240
-7	-122	-98
-8	70	29
-9	288	174
-10	70Å	97
-11	189	125
-12	-75Å	-56
-13	443	392
-14	131	123
-15	128	128
-16	122	66
-17	-159	-60
-18	-179	-106
-19	174	115
-20	-114	-66

• 11 3

0	-183	-99
1	-421	-408
2	101	61
3	308	357
4	-221	-229
5	116	138
6	-105	-116
7	-459	-512
8	317	296
9	-257	-274
10	260	240
11	84Å	73
12	77Å	35
13	68Å	77
14	-169	-159
-1	-588	-530
-2	-60Å	-35
-3	-367	-429
-4	-309	-279
-5	271	176
-6	-149	-47
-7	569	578
-8	329	281
-9	176	94
-10	237	125
-11	-256	-181
-12	117	74
-13	-230	-197
-14	-92Å	-107
-15	89Å	45
-16	84Å	3
-17	144	164
-18	106	102
-19	-113	-45

• 13 3

0	286	300
1	263	279
2	-71Å	-41
3	-152	-209
4	74Å	13
5	-75Å	-1
6	93Å	102
7	303	268
8	-90Å	-38
9	87Å	87
10	-82Å	-45
11	-164	-163
12	-66Å	-48
13	-1	-192
-1	351	401
-2	94	122
-3	207	147
-4	-67Å	-88
-5	95	159
-6	-447	-404
-7	-69Å	-85
-8	-390	-365
-9	-317	-309
-10	-105	-111
-11	175	117
-12	93Å	41
-13	355	248
-14	280	261
-15	-267	-176
-16	81Å	56
-17	-243	-225
-18	-109	-91
-19	-52Å	-18

• 15 3

0	332	367
1	353	393
2	157	167
3	-75Å	-31
4	-93Å	-38
5	-92Å	-36
6	-279	-208
7	-88Å	-134
8	-84Å	-76
9	-128	-99
10	-71Å	-13
11	122	135
12	46Å	38
-1	380	468
-2	417	510
-3	-160	-149
-4	-116	-152
-5	72Å	21
-6	-406	-397
-7	478	447
-8	-179	-149
-9	242	246
-10	159	100
-11	-416	-310
-12	130	70
-13	-394	-328
-14	-153	-151
-15	187	117
-16	-77Å	-11
-17	184	103
-18	59Å	54

• 17 3

0	-304	-280
1	-398	-378
2	-155	-115
3	-92Å	-117
4	90Å	20
5	88Å	146
6	84Å	40
7	112	180
8	-73Å	-80
9	64Å	26
10	-53Å	-18
-1	-211	-175
-2	-121	-137
-3	121	222
-4	393	465
-5	-242	-234
-6	382	386
-7	-424	-491
-8	92Å	63
-9	-93Å	-15
-10	-162	-140
-11	330	249
-12	-127	-139
-13	123	138
-14	83Å	22
-15	-98Å	-79
-16	-71Å	-17
-17	-181	-140
-18	-50Å	-0

• 19 3

0	-154	-156
1	254	205
2	-215	-243
3	121	142
4	-83Å	-101
5	-77Å	-76
6	72Å	32
7	-64Å	-54
8	55Å	144
9	38Å	68
-1	-92Å	-106
-2	92Å	17
-3	-360	-369
-4	-72Å	-14
-5	-252	-211
-6	92Å	106
-7	92Å	45
-8	91Å	54
-9	90Å	27
-10	89Å	34
-11	-183	-151
-12	84Å	15
-13	-81Å	-73
-14	-76Å	-36
-15	70Å	51
-16	62Å	10
-17	72	80

• 21 3

0	-83Å	-53
1	-270	-298
2	77Å	119
3	-73Å	-123
4	68Å	95
5	61Å	119
6	52Å	22
-1	85Å	74
-2	-86Å	-103
-3	331	318
-4	88Å	15
-5	88Å	121
-6	-87Å	-69
-7	87Å	54
-8	-86Å	-39
-9	-64Å	-83
-10	-82Å	-84
-11	-80Å	-47
-12	-76Å	-21
-13	179	178
-14	179	145
-15	134	138
-16	133	124

• 23 3

0	103	131
1	65Å	80
2	61Å	37
3	54Å	35
4	-44Å	-14
-1	73Å	46
-2	75Å	85
-3	-76Å	-71
-4	-77Å	-57
-5	-78Å	-83
-6	-78Å	-78
-7	77Å	43
-8	-76Å	-78
-9	120	172
-10	71Å	65
-11	68Å	61
-12	63Å	35
-13	-58Å	-90
-14	-49Å	-66

• 25 3

0	-46Å	-47
-1	-52Å	-21
-2	-56Å	-64
-3	59Å	87
-4	61Å	19
-5	62Å	151
-6	62Å	104
-7	61Å	16
-8	113	140
-9	-94	-130
-10	-54Å	-44
-11	-49Å	-55
-12	-101	-136

• 0 4

1	-92	-75
2	-192	-150
3	-462	-585
4	528	597
5	-217	-217
6	480	418
7	368	313
8	-130	-167
9	77Å	92
10	-210	-194
11	143	105
12	103Å	48
13	141	113
14	279	253
15	89Å	84
16	79Å	8
17	65Å	63

• 2 4

0	182	237
1	-193	-318
2	241	254
3	143	145
4	-257	-229
5	-140	-176
6	-451	-510
7	185	183
8	-175	-149
9	487	519
10	-142	-62
11	149	150
12	-145	-80
13	96Å	17
14	-162	-180
15	-176	-107
16	-72Å	-37
17	-110	-83
-1	-423	-844
-2	159	121
-3	-349	-387
-4	-567	-619
-5	266	265
-6	-283	-168
-7	314	282
-8	445	465
-9	183	203
-10	328	310
-11	142	146
-12	102Å	85
-13	-101Å	-36
-14	-138	-143
-15	-92Å	-23
-16	-83Å	-45
-17	71Å	54

• 4 4

0	-422	-531
1	-111	-57
2	-51Å	-30
3	-259	-298
4	319	334
5	-171	-243
6	-122	-76
7	164	181
8	-481	-488
9	-163	-18
10	-144	-82
11	-278	-247
12	162	108
13	-94Å	-41
14	246	166
15	179	108
16	125	77
-1	-42Å	-43
-2	-436	-597
-3	149	1
-4	428	400
-5	-101	-115
-6	451	521
-7	-94	-41
-8	87Å	52
-9	-221	-233
-10	-221	-225
-11	-100Å	-46
-12	-368	-269
-13	377	302
-14	99Å	28
-15	93Å	96
-16	171	110
-17	105	25

• 6 4

0	410	519
1	56Å	80
2	-59Å	-42
3	63Å	21
4	-366	-389
5	71Å	59
6	184	103
7	-233	-220
8	69Å	67
9	-102Å	-98
10	304	275
11	-141	-6
12	-95Å	-125
13	89Å	18
14	-132	-161
15	-116	-21
-1	188	228
-2	401	399
-3	-233	-390
-4	-257	-217
-5	-101	-2
-6	-149	-99
-7	317	256
-8	-72Å	-39
-9	108	66
-10	198	210
-11	-100Å	-24
-12	139	252
-13	-203	-128
-14	-140	-129
-15	-94Å	-45
-16	-173	-135
-17	76Å	55

• 8 4

0	88	78
1	91	26
2	188	168
3	181	116
4	291	212
5	283	327
6	259	240
7	293	271
8	-203	-201
9	-144	-107
10	-154	-119
11	-134	-194
12	89Å	80
13	-134	-138
14	68Å	9
-1	-137	-63
-2	-218	-182
-3	151	149
-4	160	84
-5	378	467
-6	-153	-136
-7	246	238
-8	174	96
-9	-209	-189
-10	-130	-113
-11	-101Å	-14
-12	-163	-231
-13	101Å	44
-14	161	148
-15	-226	-121
-16	224	168
-17	-76Å	-74
-18	152	9

• 10 4

0	-100	-66
1	257	204
2	-205	-212
3	-250	-273
4	-112	-65
5	-115	-101
6	-165	-72
7	102Å	68
8	101Å	125
9	99Å	51
10	-94Å	-15
11	88Å	43
12	-79Å	-144
13	67Å	6
-1	139	114
-2	411	362
-3	-222	-216
-4	-70Å	-44
-5	101	155
-6	-618	-629
-7	268	202
-8	-508	-526
-9	139	141
-10	375	259
-11	-166	-77
-12	447	292
-13	-295	-220
-14	-253	-192
-15	-150	-134
-16	-265	-224
-17	-74Å	-79

• 12 4

0	-77Å	-27
1	-111	-54
2	372	420
3	233	120
4	101Å	69
5	144	113
6	-166	-150
7	100Å	87
8	-21Å	-212
9	-92Å	-90
10	-85Å	-45
11	76Å	10
12	157	148
-1	-164	-207
-2	-375	-411
-3	-219	-218
-4	136	84
-5	-283	-320
-6	454	490
-7	-138	-151
-8	258	276
-9	-142	-71
-10	-360	-327
-11	102Å	40
-12	-263	-168
-13	270	202
-14	155	137
-15	89Å	102
-16	81Å	76
-17	-115Å	-81

• 14 4

0	-194	-98
1	263	231
2	-526	-541
3	102Å	68
4	-101Å	-102
5	-100Å	-39
6	98Å	124
7	-94Å	-69
8	88Å	61
9	81Å	3
10	-71Å	-42
11	58Å	32
-1	115	137
-2	339	360
-3	-161	-199
-4	222	193
-5	-359	-383
-6	141	104
-7	-142	-109
-8	101Å	29
-9	265	160
-10	102Å	128
-11	101Å	29
-12	161	116
-13	95Å	50
-14	91Å	97
-15	84Å	65
-16	76Å	24
-17	144	53

• 16 4

0	-153	-115
1	-296	-266
2	289	288
3	-99Å	-39
4	137	72
5	93Å	44
6	-89Å	-163
7	-83Å	-13
8	-105	-71
9	-64Å	-40
10	80	119
-1	-102Å	-82
-2	-424	-360
-3	102Å	51
-4	-252	-196
-5	229	149
-6	144	4
-7	252	270
-8	102Å	153
-9	-101Å	-12
-10	100Å	27
-11	-98Å	-63
-12	-95Å	-77
-13	92Å	20
-14	-85Å	-93
-15	77Å	9
-16	68Å	76

• 18 4

0	289	256
1	96Å	92
2	-94Å	-18
3	-91Å	-112
4	-87Å	-27
5	-81Å	-34
6	74Å	136
7	-65Å	-20
8	131	127
-1	217	228
-2	200	175
-3	100Å	38

Table 3 (*cont.*)

-4 100± 58	-13 -51± -6	5 -211 -147
-5 -210 -116		6 -206 -215
-6 -100± -115	• 24 4	7 69± 59
-7 -140 -72	-1 -48± -84	8 -71± -73
-8 -317 -328	-2 -54± -57	9 72± 34
-9 97± 17	-3 -58± -88	10 133 167
-10 -95± -101	-4 -60± -124	11 -86± -86
-11 92± 39	-5 -61± -18	12 200 200
-12 88± 97	-6 61± 32	13 -75± -45
-13 83± 64	-7 60± 26	14 66± 32
-14 76± 91	-8 82 109	-1 105 109
-15 -67± -16	-9 -54± -49	-2 -100 -78
-16 -54± -76	-10 48± 42	-3 159 147
		-4 -278 -298
• 20 4	• 1 5	-5 189 227
0 88± 138	0 -61 -79	-6 -209 -312
1 85± 68	1 -134 -160	-7 -115 -86
2 81± 97	2 -225 -262	-8 -63± -51
3 76± 63	3 46± 33	-9 -341 -365
4 -70± -47	4 52± 7	-10 -197 -228
5 61± 17	5 247 229	-11 -89± -79
-1 25± 164	6 283 315	-12 -309 -245
-2 92± 90	7 -112 -120	-13 -84± -43
-3 93± 113	8 397 503	-14 78± 32
-4 -94± -127	9 -158 -175	-15 -144 -104
-5 94± 46	10 103 109	-16 175 136
-6 -93± -37	11 -176 -134	
-7 -92± -18	12 -290 -280	• 5 5
-8 261 239	13 -171 -84	0 -281 -340
-9 -89± -66	14 -161 -153	1 89 55
-10 86± 63	15 86 17	2 -354 -378
-11 -85± -52	-1 -98 -105	3 -193 -185
-12 -169 -176	-2 187 231	4 223 167
-13 -71± -37	-3 43± 44	5 111 48
-14 -177 -164	-4 239 314	6 238 175
-15 99 70	-5 157 136	7 230 144
	-6 -195 -92	8 72± 50
• 22 4	-7 -206 -192	9 125 2
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1 -67± -33	-9 -123 -148	11 83± 69
2 -106 -173	-10 112 94	12 -77± -34
3 -51± -43	-11 125 18	13 97 108
-1 -76± -46	-12 368 292	14 112 110
-2 -78± -43	-13 116 29	-1 -152 -122
-3 80± 38	-14 76± 24	-2 272 298
-4 81± 205	-15 66± 51	-3 51± 38
-5 -82± -24	-16 -104 -75	-4 291 314
-6 81± 23		-5 402 521
-7 -80± -66	• 3 5	-6 -283 -289
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-9 133± 64	1 176 194	-8 -388 -415
-10 -72± -34	2 334 412	-9 71± 14
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-12 61± 67	4 -255 -287	-11 -329 -200

-12 294 174	-3 -215 -269	8 99 9
-13 -84± -51	-4 416 424	9 -175 -132
-14 79± 78	-5 -211 -180	10 -69 -91
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-16 -91 -65	-7 -98 -89	-2 -102 -57
	-8 -110 -101	-3 72± 52
• 7 5	-9 -72± -61	-4 199 231
0 -82 -29	-10 -145 -174	-5 102 12
1 -189 -158	-11 -125 -74	-6 134 74
2 343 379	-12 86± 12	-7 126 105
3 -65± 739	-13 83± 52	-8 -249 -211
4 -182 -103	-14 162 145	-9 151 86
5 -70± -55	-15 70± 27	-10 -219 -157
6 -317 -371	-16 84 30	-11 -84± -43
7 72± 82		-12 -81± -56
8 -89± -41	• 11 5	-13 -76± -21
9 87± 93	0 188 262	-14 70± 82
10 83± 124	1 -71± -14	-15 -61± -14
11 77± 11	2 248 242	
12 69± 36	3 -189 -145	• 15 5
13 -58± -22	4 -103 -73	0 124 71
-1 -134 -166	5 88± 38	1 -87± -19
-2 -298 -491	6 -123 -104	2 -86± -16
-3 -297 -389	7 119 142	3 -83± -24
-4 -155 -140	8 160 97	4 -169 -175
-5 -309 -302	9 121 45	5 -108 -3
-6 263 281	10 168 157	6 -71± -66
-7 67± 36	11 -63 -84	7 -119 -53
-8 376 446	-1 237 304	8 113 137
-9 217 220	-2 -69± -19	-1 88± 44
-10 72± 72	-3 69± 41	-2 89± 33
-11 231 197	-4 -287 -317	-3 89± 28
-12 -213 -65	-5 99 40	-4 -194 -198
-13 84± 23	-6 -155 -151	-5 88± 36
-14 -111 -111	-7 187 162	-6 -170 -150
-15 -71± -17	-8 145 111	-7 -215 -154
-16 61± 24	-9 -73± -20	-8 134 94
	-10 194 155	-9 -132 -115
• 9 5	-11 87± 15	-10 227 167
0 -290 -283	-12 84± 19	-11 80± 81
1 205 225	-13 160 21	-12 -76± -11
2 -384 -512	-14 -188 -157	-13 99 34
3 185 155	-15 -66± -42	-14 -281 -234
4 -71± -39	-16 -55± -9	-15 -52± -48
5 -72± -47		
6 103 143	• 13 5	• 17 5
7 -88± -82	0 -72± -2	0 -134 -191
8 -121 -57	1 -103 -52	1 149 142
9 -83± -50	2 126 72	2 110 16
10 -153 -151	3 -88± -17	3 105 61
11 -69± -8	4 174 197	4 138 125
12 -81 -84	5 158 114	5 -89 -30
-1 -185 -167	6 214 234	6 54± 42
-2 148 75	7 -108 -10	-1 -83± -8

-2 -231 -202		
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-4 85± 61		
-5 -85± -86		
-6 151 110		
-7 118 93		
-8 -82± -29		
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-11 -73± -52		
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• 19 5		
0 101 81		
1 -68± -77		
2 -90 -89		
3 -82 -34		
4 -49± -94		
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-2 123 159		
-3 76± 13		
-4 -77± -69		
-5 -77± -54		
-6 -76± -66		
-7 -75± -32		
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-9 70± 29		
-10 201 181		
-11 -62± -51		
-12 161 128		
-13 -44± -16		
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1 -45± -36		
-1 -57± -37		
-2 -170 -174		
-3 -62± -12		
-4 63± 48		
-5 -103 -65		
-6 141 176		
-7 61± 9		
-8 59± 65		
-9 55± 26		
-10 -70 -70		
-11 -40± -15		

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The Crystal Structure of Huntite, $Mg_3Ca(CO_3)_4$

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Huntite, $Mg_3Ca(CO_3)_4$, is an ordered rhombohedral double-carbonate, based, like the simple compositions, on a deformation of the NaCl face-centered cube. Its ordering, in $R32$, affords a true structural unit in the shape of the familiar cleavage rhomb, with $a = 6{\cdot}075$ Å and $\alpha = 102° 56'$. With Ca at the origin, three Mg are disposed about face centers, one CO_3 is unique at the body center, and three CO_3 are disposed about edge centers.

Although huntite is available only as powder (of about 1 micron particle size) and involves seven variable parameters, the precision with which pertinent bond lengths are known from the simpler carbonates permits a moderately accurate evaluation of the structure.

The model arranged to conform with these known bond lengths affords a series of calculated F values for the first 46 possible index combinations, from which observed amplitudes reduced from 41 powder lines observed in this range deviate by an average of only 11%. The greatest individual departure is 34%.

Huntite, $Mg_3Ca(CO_3)_4$, was first identified by Faust (1953) from magnesite deposits of Tertiary age in Nevada. Additional deposits, formed from surface waters in the weathering zone and in caves and mine workings, have been reported by Koblencz & Nemecz (1953), Baron *et al.* (1957), Skinner (1958), and Golvanov (1959). These huntites are all characterized by grain sizes of the magnitude of 1μ, frequently with no extraneous phases detectable in powder X-ray diffraction diagrams. Huntite analyses typically include about 1% H_2O (+110 °C.), but Stevens' analysis of a Nevada sample (in Faust, 1953) calculated on a water-free basis gives satisfactory mol ratios $MgO : CaO : CO_2 = 3{\cdot}07 : 1{\cdot}00 : 4{\cdot}03$. All observed diffraction features have been indexed on a rhombohedral cell containing only $Mg_3Ca(CO_3)_4$.