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X-ray Powder Diagrams of Certain n-Alkanes: Corrigenda and Extension

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From the known crystal structure of a 'key' n-alkane (in this case of n-octadecane, $C_{18}H_{38}$) it is possible
to predict quite accurately the cell dimensions and atomic coordinates of all the isostructural members
of the series. This principle has been applied to the (C_nH_{2n+2}) n even series, $n = 10$, 12, 14, and 16 and
used to predict the detailed appearance of the powder photographs. The agreement for $n = 12$ and 14
is excellent; it is less good for $n = 10$ because of preferred orientation within the specimen and for $n = 16$
because of a rather poor-quality photograph.

Introduction

It has been shown (Nyburg & Potworowski, 1973) that,
knowing the crystal structure of any one 'key' n-alkane
(for the present series of triclinic alkanes, n-octadecane;
Nyburg & Lüth, 1972), the unit-cell dimensions and
crystal structures of all other members of the iso-
structural series can be quite accurately predicted,
certainly down to $n = 6$ and as high in n as is desired.
Consequently, the appearance of the X-ray powder
photographs to be expected for the series can be pre-
dicted in detail.

Spacings and derived cell dimensions (but not inten-
sities) of the powder diagrams of the even n-alkanes
$n = 10$ through 16 were published from Oslo in 1972
[Norman & Mathisen (1972), hereinafter N & M]. Sub-
sequently in Toronto, predictive calculations on spa-
cings and intensities were carried out for these powder
diagrams. The agreement was fairly good but
some lines predicted to be moderately strong were not
observed on the photographs (Nyburg & Pickard,
1974). These discrepancies have now been traced to an
error in the matrix transforming atomic coordinates
from one system of axes to another. (The transformed
cell parameters were correct, so that d spacings were
not affected.)

Intensities of the powder lines have now been meas-
ured in Oslo and we report a comparison of predicted
and observed data.

Calculations

The choice of axes (system 1) used to describe the
structure of triclinic n-octadecane, C18, gives param-
eters $a = 4.28_5$, $b = 4.82_0$, $c = 24.89_8$ Å, $\alpha = 85.15$, $\beta =
67.8$, $\gamma = 72.7°$ (Nyburg & Lüth, 1972). The cell used
to index the powder photographs C10 through C16 in
Oslo (system 2) are related to those originally used to
describe the crystal structure of C6 and C8 (N & M,
1961a, b). The relation between cells is $a_2 = a_1$; $b_2 =
-b_1$; $c_2 = -a_1 + c_1$, as given previously (Nyburg &
Pickard, 1974).

In the original predictions of alkane crystal structures,
it was assumed that the C faces of the cells preserved the
same parameters a, b and γ throughout the series. It is
known, however, from single-crystal data, that there
are small continuous changes within a series. Accord-
ingly, for the present prediction of powder photo-
graphs, we have made use of known slight variations

Table 1. Cell dimensions (system 1) used to describe
powder diagrams of even n-alkanes, C10 through C16

n	10	12	14	16
a (Å)	4.25	4.28	4.29	4.29
b (Å)	4.805	4.81	4.82	4.81
c (Å)	14.81	17.32	19.84	22.37
α (°)	82.11	83.27	84.10	84.70
β (°)	65.20	66.13	66.82	67.37
γ (°)	74.40	74.00	73.00	73.10

in these parameters. Fig. 1 shows the actual values of a and b for single crystals of C6, C8 and C18 together with values originally used by N & M for the powder photographs of C10 through C16. (The values used by N & M for C10 appear to be too small.) We have taken

smoothed values of a and b from the curves given in Fig. 1. The angle γ also varies slightly, some 1·3°, between C10 and C16. The values originally ascribed by N & M have been adhered to. As to the remaining parameters α, β and c, both β and c have been taken
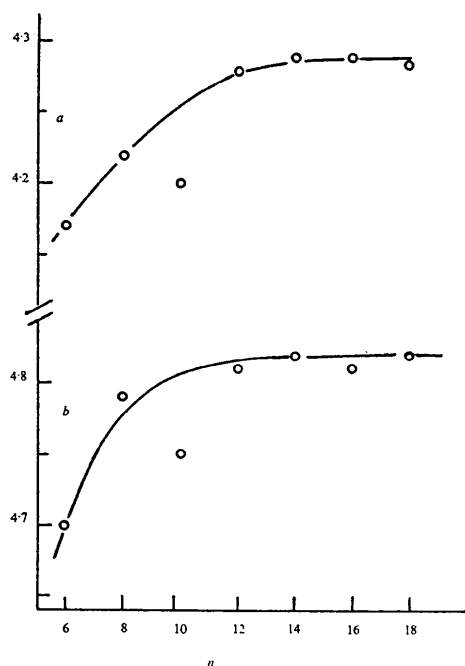

Fig. 1. Cell parameters a and b (Å) (same for both systems). Circles for C6, C8 and C18 are from single-crystal measurements, for C10–C16 from powder photographs (N & M, 1972). Smoothed values indicated by curves have been used.
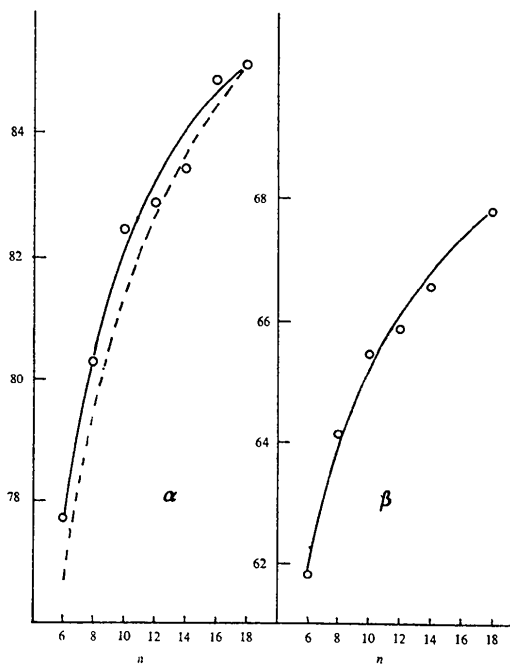

Fig. 2. Cell parameters (a) α and (b) β (°) on system 1. Circles for C6, C8 and C18 are from single crystals, the remainder from powder photographs. Smoothed values (full lines) have been used. Broken line gives values originally used by Nyburg & Pickard (1973).

Table 2. *Atomic coordinates (system* 1) *used to predict intensities of powder photographs* C10 *through* C16

| | C10 | | | C12 | | | C14 | | | C16 | | |
	x	y	z	x	y	z	x	y	z	x	y	z
C(1)	777	2559	−3985	791	2627	−4139	793	2609	−4253	795	2720	−4338
C(2)	1242	415	−3159	1305	534	−3438	1369	558	−3644	1390	686	−3801
C(3)	273	1815	−2199	372	1995	−2623	432	2081	−2936	483	2234	−3176
C(4)	737	−328	−1373	885	−99	−1923	1009	30	−2328	1078	199	−2638
C(5)	−232	1072	−413	−47	1363	−1108	72	1553	−1620	171	1747	−2013
C(6)	—	—	—	467	−731	−408	648	−498	−1012	766	−288	−1475
C(7)	—	—	—	—	—	—	−288	1026	−304	−141	1261	−850
C(8)	—	—	—	—	—	—	—	—	—	454	−774	−313
H(21)	250	4008	−4140	2481	4068	−4270	2445	4045	−4367	2446	4155	−4439
H(22)	−452	−1005	−3023	−359	−880	−3323	−259	−852	−3544	−237	−723	−3712
H(23)	1985	3257	−2348	2056	3430	−2753	2081	3513	−3048	2130	3664	−3275
H(24)	−963	−1756	−1232	−784	−1518	−1804	−623	−1384	−2226	−553	−1214	−2548
H(25)	1475	2507	−558	1632	2793	−1233	1716	2981	−1730	1815	3174	−2110
H(26)	—	—	—	−1208	−2155	−286	−988	−1916	−907	−868	−1704	−1383
H(27)	—	—	—	—	—	—	1352	2448	−411	1499	2684	−946
H(28)	—	—	—	—	—	—	—	—	—	−1184	−2194	−219
H(31)	−1905	3713	−3738	−1871	3798	−3929	−1881	3798	−4071	−1869	3917	−4178
H(32)	3962	−739	−3432	4004	−639	−3670	4078	−634	−3845	4089	−515	−3978
H(33)	−2419	2969	−1945	−2297	3166	−2410	−2247	3271	−2751	−2186	3431	−3012
H(34)	3447	−1483	−1639	3577	−1271	−2150	3712	−1162	−2526	3772	−1001	−2813
H(35)	−2933	2226	−153	−2724	2534	−890	−2613	2763	−1432	−2503	2945	−1847
H(36)	—	—	—	3150	−1903	−630	3346	−1689	−1206	3455	−1487	−1648
H(37)	—	—	—	—	—	—	−2980	2216	−113	−2821	2459	−682
H(38)	—	—	—	—	—	—	—	—	—	3138	−1973	−483
H(T)	1477	1461	−4648	1467	1487	−4702	1473	1426	−4741	1455	1520	−4770

Table 3. Powder data

The column headings in each block are: (1) hkl on system 1; (2) hkl on system 2; (3) observed 2θ (Cu $K\alpha$); (4) calculated 2θ from cells of Table 1; (5) observed relative intensity; (6) intensities calculated from atomic coordinates of Table 2.

C10

hkl (1)	hkl (2)	$2\theta_o$	$2\theta_c$	I_o	I_c
001	001	6·54	6·57	24	41·9
002	002	13·18	13·18	6	9·2
010	$0\bar{1}0$	19·40	19·18	100	91·0
003	003		19·82		3·4
011	$0\bar{1}1$	20·30	20·12	72	68·2
$01\bar{1}$	$0\bar{1}\bar{1}$		20·48		3·3
101	100	22·16	21·90	3	27·9
102	101		22·03		5·8
012	$0\bar{1}2$	23·18	23·03	10	9·3
100	$10\bar{1}$	23·98	23·73	13	100·0
103	102		24·08		1·8
112	$1\bar{1}1$		25·07		3·0
111	$1\bar{1}0$	25·38	25·10	11	75·8
004	004	26·60	26·53	2	1·7
110	$1\bar{1}\bar{1}$		26·86		12·5
$10\bar{1}$	$10\bar{2}$		27·13		1·8
013	$0\bar{1}3$	27·46	27·32	5	2·7
104	103		27·64		0·5
$11\bar{1}$	$1\bar{1}\bar{2}$		30·05		1·4
014	$0\bar{1}4$	32·70	32·49	2	0·9
005	005	33·54	33·34	2	1·5
$1\bar{1}0$	$11\bar{1}$	34·52	34·13	2	13·1
$1\bar{1}\bar{1}$	$11\bar{2}$		36·55		1·0
106	105		37·62		0·8
015	$0\bar{1}5$	38·46	38·25	2	(0·3)
116	$1\bar{1}5$		39·18		6·3
$01\bar{5}$	$0\bar{1}\bar{5}$		39·23		5·5
021	$0\bar{2}1$	39·60	39·34	13	0·7
121	$1\bar{2}0$		39·45		5·4
$1\bar{1}5$	114		41·20		4·2

C12

hkl (1)	hkl (2)	$2\theta_o$	$2\theta_c$	I_o	I_c
001	001	5·56	5·59	40	39·4
002	002	11·18	11·18	10	9·0
003	003	16·76	16·79	3	3·5
010	$0\bar{1}0$	19·24	19·19	88	88·0
011	$0\bar{1}1$	20·00	19·97	50	62·8
$01\bar{1}$	$0\bar{1}\bar{1}$		20·04		3·9
102	101		21·70		5·3
101	100	22·02	21·89	25	24·5
012	$0\bar{1}2$		22·20		8·9
004	004		22·46		1·7
103	102		22·94		2·0
100	$10\bar{1}$	23·58	23·48	100	100·0
112	$1\bar{1}1$		24·76		3·3
111	$1\bar{1}0$	24·88	24·96	63	73·0
104	103		25·42		0·7
013	$0\bar{1}3$	25·54	25·53	2	2·9
113	$1\bar{1}2$		25·84		0·5
$10\bar{1}$	$10\bar{2}$ } 26·34	26·24	10	2·1
110	$1\bar{1}\bar{1}$ }	26·40		12·9
005	005	28·08	28·17	1	1·0
$11\bar{1}$	$1\bar{1}\bar{2}$	28·92	28·92	1	1·6
014	$0\bar{1}4$	29·70	29·61	<1	1·1
006	006		33·96		1·1
$1\bar{1}0$	$11\bar{1}$	34·40	34·16	9	12·4
$1\bar{1}\bar{1}$	$11\bar{2}$	36·50	36·15	2	0·8
107	106		37·52		0·7
121	$1\bar{2}0$		39·27		5·4
117	$1\bar{1}6$ } 39·30	39·36	10	5·8
$01\bar{6}$	$0\bar{1}6$ }	39·42		5·2
$1\bar{1}6$	115	41·17	41·55	4	4·1

C14

hkl (1)	hkl (2)	$2\theta_o$	$2\theta_c$	I_o	I_c
001	001	4·86	4·84	25	39·0
002	002	9·68	9·70	9	9·2
003	003	14·56	14·58	4	3·6
010	$0\bar{1}0$	19·24	19·26	100	91·9
004	004		19·47		1·7
$01\bar{1}$	$0\bar{1}\bar{1}$		19·80		4·3
011	$0\bar{1}1$	19·86	19·93	45	56·1
$01\bar{2}$	$0\bar{1}\bar{2}$		21·48		0·6
102	101 } 21·70	21·67	8	5·0
012	$0\bar{1}2$ }	21·73		8·6
101	100	22·02	22·05	14	22·4
103	102		22·40		2·0
100	$10\bar{1}$	23·44	23·46	70	100·0
104	103		24·12		0·9
013	$0\bar{1}3$		24·40		3·0
005	005		24·40		1·0
112	$1\bar{1}1$		24·49		3·9
111	$1\bar{1}0$	24·80	24·77	30	72·2
113	$1\bar{1}2$		25·19		0·9
$10\bar{1}$	$10\bar{2}$		25·76		2·3
110	$1\bar{1}\bar{1}$	26·00	26·00	6	15·0
014	$0\bar{1}4$		27·71		1·3
$11\bar{1}$	$1\bar{1}\bar{2}$		28·05		1·9
006	006		29·38		0·7
015	$0\bar{1}5$		31·49		0·6
007	007		34·42		0·9
$1\bar{1}0$	$11\bar{1}$	34·50	34·53	10	11·7
$1\bar{1}\bar{1}$	$11\bar{2}$		36·22		0·6
108	107		37·47		0·8
121	$1\bar{2}0$		38·99		5·9
118	$1\bar{1}7$ }	39·46		5·7
021	$0\bar{2}1$ } 39·50	39·48	11	0·6
$01\bar{7}$	$0\bar{1}\bar{7}$ }	39·49		5·1
$1\bar{1}7$	116		41·97		3·9

C16

hkl (1)	hkl (2)	$2\theta_o$	$2\theta_c$	I_o	I_c
001	001	4·20	4·29	20	38·2
002	002	8·58	8·57	15	9·2
003	003	12·62	12·87	5	3·7
004	004		17·18		1·9
010	$0\bar{1}0$	19·28	19·29	100	88·0
$01\bar{1}$	$0\bar{1}\bar{1}$		19·68		4·8
011	$0\bar{1}1$	19·80	19·86	50	60·2
$01\bar{2}$	$0\bar{1}\bar{2}$		20·96		0·6
012	$0\bar{1}2$	21·42	21·32	5	7·9
005	005		21·53		1·1
102	101		21·65		4·6
103	102		22·05		2·0
101	100	22·22	22·11	25	20·5
104	103		23·26		0·9
100	$10\bar{1}$	23·44	23·39	90	100·0
013	$0\bar{1}3$		23·50		2·9
112	$1\bar{1}1$		24·51		3·6
111	$1\bar{1}0$	24·86	24·84	50	72·7
113	$1\bar{1}2$		24·94		0·7
$10\bar{1}$	$10\bar{2}$		25·35		2·5
006	006		25·90		0·7
110	$1\bar{1}\bar{1}$	25·98	25·91	10	14·5
014	$0\bar{1}4$		26·23		1·6
$11\bar{1}$	$1\bar{1}\bar{2}$		27·65		1·7
015	$0\bar{1}5$		29·38		0·5
007	007		30·31		0·5
$1\bar{1}0$	$11\bar{1}$		34·51		11·3
008	008		34·77		0·8
$1\bar{1}\bar{1}$	$1\bar{1}\bar{2}$		35·97		0·8
109	108		37·41		0·8
121	$1\bar{2}0$		39·09		5·6
021	$0\bar{2}1$		39·51		0·6
119	$1\bar{1}8$		39·57		5·4
$01\bar{8}$	$0\bar{1}\bar{8}$		39·67		5·1
$1\bar{1}8$	117		42·19		4·0

exactly as predicted earlier [see Fig. 2(*b*) for *β*]. For *α* there is a slight discrepancy between predicted and observed values, so the necessary small changes have been made (Fig. 2*a*).

Table 1 lists the revised cell parameters based on system 1.

Atomic coordinates

The method of predicting atomic coordinates has already been described (Nyburg & Potworowski, 1973). The known structure of C18 has a C(1)–C(2) bond length of 1·491 Å. Accordingly, to predict other structures this bond has been 'stretched' about its centre to make it 1·530 Å. Hydrogen positions (C–H = 1·07 Å) have been suitably adjusted. The coordinates used, based on system 1 are given in Table 2. To compare powder data given by N & M, the Miller indices have been transformed (see Appendix for matrices).

Isotropic temperature factors were set at 4·0 and 6·0 Å^2 for C and H atoms, respectively, and structure factors calculated for those planes having spacings $\geq 2 \cdot 12$ Å. Powder intensities $I_c(hkl)$ were calculated from $p|F|^2(1 + \cos^2 2\theta)/(\sin^2 \theta \cos \theta)$ where p, the multiplicity, is two for all reflexions (triclinic system) and θ values are those for Cu *Kα* radiation.

The calculated diffraction angles and computed intensities as a percentage of the strongest reflexion (for values $> 0 \cdot 5 \%$) are set out in columns 4 and 6 in each block of Table 3.

Experimental

The powder diagrams were taken in a G.E. Debye–Scherrer camera with Ni-filtered Cu *Kα* radiation. In order to achieve smooth diffraction lines the samples were melted and refrozen several times during each exposure. *d* values were found from microphotometric readings (N & M, 1972). The microphotometric curves were not considered good enough for measuring the intensities of the lines.

Observed intensities were estimated by visual comparison of the maximum intensity of the powder lines with an intensity scale. A series of powder patterns of quartz was taken on a piece of film by moving the film holder of a Weissenberg camera between each exposure, the exposure time varying between 2 and 100 min. The two inner reflexions, 100 and 101, were then used for the intensity scale. The relative uncertainty in intensity readings was estimated as 100 % for the weakest reflexions decreasing to 25 % for the strongest ones.

Results and discussion

The observed 2*θ* values and relative intensities are set out in columns 3 and 5 in each block of Table 3.

Of the four alkanes, C12 and C14 gave powder patterns showing sharp and evenly blackened diffraction lines. For both compounds the agreement between experimental and calculated values is extremely good.

The Debye–Scherrer diagrams of C16 did not have the same quality. Thus the best film as a whole was rather weak giving a larger uncertainty in observed relative intensities than for the other compounds. Nevertheless the observed intensities are well within the tolerance limits of the theoretical model.

The only diagram that does not seem to give a satisfactory fit to the calculated values is that of C10. However, the Debye–Scherrer lines of this alkane showed a high degree of preferred orientation, the blackening varying along a line. In the previous X-ray study of the lower members of the series, C6 and C8 (N & M, 1961*a*, *b*), it was found that single crystals always grew with the shorter *a* axis in the direction of the capillary tube. If higher members show the same tendency, one would expect the reflexions from the planes of the zone axis [100] to be extraordinarily strong. This would fully explain the discrepancy between observed and calculated intensity values.

The conclusion to be drawn from the examinations must be that the proposed theoretical models of the series of triclinic alkanes are basically correct. The model scheme is also in full agreement with the single-crystal determinations of C6 and C8 (M & N, 1961*a*, *b*).

The systematics in the models lead to great similarities in the calculated patterns comparing reflexions with the same indices. Thus 100 is the strongest reflexion for all the members, the next strongest one with relative intensities varying between 85 and 91 % being 010 and so on. This observation has been utilized for a check of the indexing by N & M in their original paper (N & M, 1972). As a result, several indices of the high-angle reflexions have been corrected and weak reflecting planes have been omitted from the list in cases where two sets of indices were quoted for the same observed line. The changes would hardly influence the previous calculation of cell parameters. Table 3 contains the corrected *hkl* values.

APPENDIX

The two systems, (1) used by Nyburg & Lüth (1972) and (2) used by Norman & Mathisen (1961*a*, *b*, 1972), are related as follows:

$$(t) \quad \begin{pmatrix} a_2 \\ b_2 \\ c_2 \end{pmatrix} = \begin{pmatrix} a_1 \\ b_1 \\ c_1 \end{pmatrix} \quad \text{where } (t) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 1 & 0 & 0 \end{pmatrix}.$$

The transformation of indices is

$$(t) \quad \begin{pmatrix} h_2 \\ k_2 \\ l_2 \end{pmatrix} = \begin{pmatrix} h_1 \\ k_1 \\ l_1 \end{pmatrix}$$

and of atomic coordinates

$$(s) \quad \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}$$

where (s) is

$$\begin{pmatrix} 1 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

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Molecular Packing in Crystals of Phenoselenazine

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The crystal structure of phenoselenazine was solved by molecular-packing analysis. Trial models of the rigid molecule were oriented and positioned in the Cheshire cell. The refinement was carried out by structure-factor least-squares calculations using individual anisotropic temperature factors. The final discrepancy index was $R = 0.051$ for 601 reflexions which were more than two standard deviations above background. The unit cell with $a = 7.829$ (5), $b = 20.909$ (4) and $c = 5.927$ (7) Å contains four molecules. The space group is $P2_12_12_1$. The molecule has the same folded configuration as phenothiazine but is more open. The dihedral angle is 149.6°.

Introduction

Semi-empirical potential functions, describing van der Waals interactions between pairs of non-bonded atoms, have been used in the structural analysis and the solution of the phase problem in molecular crystals (Kitaigorodsky, 1970; Giglio, 1970; Williams, 1972). The basic idea is that, neglecting the vibration energy and entropy, the non-bonded interaction energy in a crystal reaches a minimum when the molecular orientation and position are those experimentally observed.

The packing of a crystal can be obtained by minimizing the lattice energy as a function of molecular translations and rotations if the lattice constants and space group are known.

The molecular-packing analysis of phenoselenazine was undertaken as part of a series of structural analyses of organoselenium compounds. The crystal structure of 3,7-dichlorophenoselenazine (Bernier, Conde & Márquez, 1974) has already been reported.

Experimental

Samples of phenoselenazine were supplied by Professor Pino (Departamento de Química Analítica of this University) and were recrystallized by evaporation of a solution in CS_2.

Initially prepared crystals were extremely thin plates on (010), measuring only a few μm in thickness. Crystals having dimensions suitable for single-crystal work were finally obtained after a month of extremely slow evaporation at room temperature. Considerable difficulty was experienced in selecting and trimming crystals of this batch.

Weissenberg photographs were used to obtain the space group and preliminary unit-cell dimensions. Accurate lattice constants were obtained by a least-squares fit to 20 reflexions. The crystal data are summarized in Table 1.

Table 1. *Crystal data for phenoselenazine*

$a = 7.829$ (5) Å	M.W. 246
$b = 20.909$ (4)	m.p. 468 K
$c = 5.927$ (7)	$D_x = 1.70 \times 10^3$ kg m^{-3}
$V = 970.2$ (7) Å^3	Space group $P2_12_12_1$
λ(Mo $K\alpha$) = 0.7107 Å	$Z = 4$

A Nonius CAD-4 four-circle automatic diffractometer and graphite-monochromated Mo $K\alpha$ radiation were used with a scintillation detector and pulse-height discrimination. Two reflexions were monitored periodically during the data-collection process. Subsequent analysis of these reflexions indicated no crystal decomposition during the time required to collect the intensities. Reflexions were collected in the range