Acta Cryst. (1969). B**25**, 2140

A Neutron Diffraction Study of the Crystal Structure of the *C*-form of Yttrium Sesquioxide

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(*Received* 1 *October* 1968 *and in revised form* 24 *December* 1968)

Single-crystal neutron data have been used to refine the *C*-type structure of Y_2O_3. The value found for the six equivalent Y–O distances in the 8(*b*)-octahedron is 2·284 (3) Å; the three independent distances for the 24(*d*)-octahedron are 2·243 (4), 2·274 (4) and 2·331 (4) Å and these are significantly different. The positional parameters are more accurate than those from a single-crystal X-ray study of Y_2O_3 by Paton & Maslen (*Acta Cryst.* (1965), **19**, 307).

Introduction

Sesquioxides assume one or more of three crystal habits – the hexagonal *A*-type, the monoclinic *B*-type, and the body-centred cubic *C*-type. A *C*-sesquioxide structure was first described by Pauling & Shappell (1930) who examined the mineral bixbyite, $(Fe,Mn)_2O_3$. Subsequently many of the rare-earth *C*-type structures have been studied, principally by powder diffraction techniques. A bibliography of these analyses has been compiled by Geller, Romo & Remeika (1967).

Single-crystal X-ray refinements have been described for Y_2O_3 (Paton & Maslen, 1965), In_2O_3 (Marezio, 1966), and Sc_2O_3 (Geller *et al.*, 1967). The purpose of this single-crystal neutron study of Y_2O_3 was to improve the precision of the oxygen parameters, and consequently the interatomic distances, by taking advantage of the relatively enhanced scattering by oxygen in neutron diffraction. A further consequence of the neutron study was that absorption errors could be reduced to a negligible level on account of the low μ for thermal neutrons (0·01 cm^{-1}). Although Paton & Maslen reduced the X-ray absorption errors ($\mu = 524$ cm^{-1}) by the use of a small crystal, these errors were significant and corrections could not be applied in view of the irregular crystal shape.

Neutron diffraction powder patterns of Y_2O_3 have been interpreted by Villain (1957) and Fert (1962). These analyses were based on relatively few data owing to the limited resolution of neighbouring intensity profiles in the powder spectra.

Experimental

Single crystals of Y_2O_3 were supplied by Dr E.A.D. White of Imperial College, London, The crystals had been grown by the use of a standard type of Verneuil apparatus fitted with a tricone burner (White, 1964), the starting material being 99·995% Y_2O_3 in powdered form. This procedure was followed in order to obtain samples of substantial mosaicity and, therefore, to reduce secondary extinction effects in the data. The crystals were all highly irregular in shape, and the specimen selected for data collection was of mass 9·2 mg.

The data were measured at the A.E.R.E. PLUTO reactor with a Ferranti automated three-circle diffractometer in the cone-setting (Furnas & Harker, 1955). The neutron beam directed at the specimen by reflexion from the (422) planes of a copper single crystal had a measured wavelength of 1·038 Å and a flux of approximately 10^6 neutrons sec^{-1} cm^{-2}. Integrated intensities

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Table 1. *Parameter e.s.d.'s for different lists of data*

Reflexion types rejected	—	$I=0$	$I<3\sigma(I)$
Total data for refinement	179	155	95
R index	0·123	0·112	0·080
Mean coordinate e.s.d.	0·0025 Å	0·0026	0·0030
Mean isotropic-*B* e.s.d.	0·049 $Å^2$	0·050	0·054

Table 2. *Atomic coordinates** ($\times 10^4$) *from single-crystal studies of C-sesquioxides*

		u	*x*	*y*	*z*
Y_2O_3	Present work	−327 (3)	3907 (3)	1520 (3)	3804 (3)
	Paton & Maslen (1965)	−333 (3)	3889 (9)	1551 (10)	3789 (8)
In_2O_3	Marezio (1966)	−335 (1)	3912 (12)	1558 (11)	3796 (13)
Sc_2O_3	Geller *et al.* (1967)	−351 (2)	3928 (7)	1528 (7)	3802 (7)

* e.s.d.'s ($\times 10^4$) in parentheses.

were recorded against a monitored incident beam while stepping the counter over a range of 5° in increments of two minutes of arc. The total counting time per reflexion was approximately ten minutes, divided equally between the peak and background portions of the profile.

A total of 179 reflexions was measured out to the limit $\sin\theta/\lambda < 0{\cdot}74$ Å^{-1}, and for 134 of these the intensity value exceeded the estimate of standard deviation based on counting statistics. A conventional counter-data reduction formula gave small negative values for the intensities of 24 reflexions which were subsequently adjusted to zero. These 'zero' intensities were included in the final least-squares refinement. Absorption corrections were not applied. However, the error resulting from absorption was less than 0·5% of I_{obs} for all reflexions.

Crystal data

Y_2O_3, yttrium sesquioxide (yttria)
Space group, *Ia*3 (body-centred cubic)
$Z=16$
$a_0=10{\cdot}604$ Å (Paton & Maslen, 1965)
$\mu=0{\cdot}011$ cm^{-1} for neutrons ($\lambda=1{\cdot}038$ Å)
$=524$ cm^{-1} for X-rays ($\lambda=1{\cdot}5418$ Å).

Refinement

The *C*-type structure of Y_2O_3 conforms to the cubic space group *Ia*3 with yttrium ions at the 8(*b*) $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and 24(*d*) $(u,0,\frac{1}{4})$ Wyckoff positions, and oxygen ions at the 48(*e*) (x,y,z) general positions. On the assumption that the ions execute harmonic vibrations the following restrictions are imposed upon the yttrium anisotropic temperature factor coefficients: $b_{11}=b_{22}=b_{33}$ and $b_{12}=b_{13}=b_{23}$ for the 8(*b*)-sites, and $b_{12}=b_{13}=0$ for the 24(*d*)-sites (Peterse & Palm, 1966). Therefore, assuming that the neutron scattering lengths are known accurately, there are seventeen parameters to be determined, including the scale factor.

During the course of this study, Dr E. N. Maslen pointed out that the symmetry conditions for the yttrium b_{ij}-parameters as used by Paton & Maslen in the X-ray refinement were incorrect. At his request the X-ray refinement has been repeated, and the results of these calculations are reported below.

(*a*) *Neutron refinement*

The parameters were refined by full-matrix least-squares minimization of the quantity $\Sigma w(F_o^2-kF_c^2)^2$; absolute weighting factors w were assigned from the inverse variance of F_o^2. The scattering lengths of yttrium and oxygen atoms were fixed at 7·86f* (Atoji, 1963) and 5·77f (Hughes & Schwartz, 1958) respectively.

The widely followed practice of setting a 'limit of observation' at, say, the three-sigma level of the data, and then eliminating reflexions for which the intensity estimate, I, is less than $3\sigma(I)$, was not adopted since the concept 'limit of observation' is meaningless for counter data. All reflexions were included in the refinement at the absolute weight derived from counting statistics. In order to assess the effect of rejecting data subject to the ratio $I/\sigma(I)$, the structure was refined with individual isotropic temperature factors for three lists of data–(i) all reflexions, (ii) reflexions for $I>0$, and (iii) reflexions for $I>3\sigma(I)$. The results of these calculations are shown in Table 1. Rejection of data at the three-sigma level increased the mean estimated standard deviation for the positional parameters by 20%, and that for the isotropic thermal parameters by 10%. The increase in e.s.d. values caused by rejection of reflexions with zero intensity was only marginal (*ca.* 2%). As expected the R index for the 'three-sigma' data is much lower than that for the complete set of data, since the weakest reflexions were omitted in the former case.

The final sets of positional and thermal parameters, determined from the anisotropic refinement using the complete set of data, are given in Tables 2 and 3, respectively. The estimates of standard deviations are those derived from the formula,

$$\sigma_t=\{a_{tt}\}^{1/2},$$

where a_{tt} is the appropriate diagonal element of the inverse to the least-squares matrix. After the last cycle of refinement all parameter shifts were less than 0·01 of the corresponding e.s.d. The final value of $[\Sigma w(F_o^2-kF_c^2)^2/(m-n)]^{1/2}$, where m is the number of observations and n the number of parameters, was 0·88 compared with the ideal value of unity for absolute weights. The R index, defined as $\Sigma\,|F_o^2-kF_c^2|/\Sigma\,F_o^2$, was 0·115 for the complete set of data and 0·105 for the non-zero reflexions; the corresponding indices based on F_o were 0·118 and 0·100, respectively.

A list of F_o^2, kF_c^2 and $\sigma(F_o^2)$ is given in Table 4.

Table 3. *Anisotropic temperature factor coefficients* with e.s.d.'s* ($\times 10^4$)

		Neutron	X-ray	
Y(1)	b_{11}	5·4 (1·5)	22 (2)	$(=b_{22}=b_{33})$
	b_{12}	2·6 (2·2)	0 (1)	$(=b_{13}=b_{23})$
Y(2)	b_{11}	7·7 (2·0)	19 (3)	
	b_{22}	5·1 (1·8)	28 (2)	
	b_{33}	10·4 (2·0)	22 (2)	
	b_{23}	2·9 (2·1)	1 (1)	$(b_{12}=b_{13}=0)$
O	b_{11}	5·6 (2·0)	22 (9)	
	b_{22}	9·7 (2·0)	28 (9)	
	b_{33}	6·1 (2·2)	16 (7)	
	b_{12}	−2·6 (1·8)	−2 (6)	
	b_{13}	1·8 (1·7)	1 (6)	
	b_{23}	0·8 (1·9)	14 (7)	

* Defined such that the temperature factors are of the form $\exp\{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)\}$.

*f designates the fermi unit, 10^{-13} cm.

(b) X-ray refinement

Two modifications were made to the model given by Paton & Maslen. First, the symmetry relations for the coefficients of the anisotropic temperature factor were amended as described above. Second, the relativistic SCF form factor of Y^{3+} (Cromer & Waber, 1965) was preferred to the curve derived by Paton & Maslen by interpolation from the SCF form factors for Ce and Sc. The real component of the anomalous dispersion correction for Cu Kα radiation, $-0{\cdot}67$ electrons (Cromer, 1965), was applied to the Y^{3+} form factor.

The structure was refined by full-matrix least-squares minimization of $\Sigma\, w(F_o - kF_c)^2$, the weights w being set at the inverse of F_o^2 as recommended by Paton & Maslen. The final lists of parameters for the X-ray data are given in Tables 2 and 3 for comparison with the neutron diffraction values. The e.s.d. values were calculated in the manner for photographic data,

$$\sigma_i = \{a_{ii} \times \Sigma w(F_o - kF_c)^2/(m-n)\}^{1/2}.$$

The final R index, based on F_o, was 0·084 compared with the value of 0·082 quoted by Paton & Maslen.

Discussion

Positional parameters

A comparison of the atomic coordinates from the present study with the values determined from the X-ray data of Paton & Maslen is given in Table 2. The parameter differences expressed as multiples of the e.s.d. of the difference are 1·8, 1·9, 2·9 and 1·8 for u,x,y and z, respectively, and these differences are therefore insignificant. Although the two determinations of u are of comparable precision, the oxygen e.s.d.'s from the neutron study are substantially lower.

Further comparison of the neutron diffraction Y_2O_3 coordinates with those for In_2O_3 and Sc_2O_3 in Table 2 shows no significant differences between corresponding oxygen atom coordinates. However, while the Y_2O_3 and In_2O_3 u parameters are in reasonable agreement, their

Table 4. *Observed* (FO) *and calculated* (FC) *structure factor squares with the corresponding estimated standard deviation of* F_o^2 (E.S.D.)

H	K	L	(FO)	(FC)	E.S.D.
4	0	0	0.	2.5	4.9
6	0	0	13.6	10.4	5.7
10	0	0	42.9	40.3	8.5
12	0	0	24.4	27.0	8.6
14	0	0	274.7	271.2	14.3
2	2	0	0.	0.4	5.0
4	2	0	0.	3.8	4.9
6	2	0	0.	3.0	5.5
3	2	0	59.1	53.7	7.9
10	2	0	108.9	98.8	10.0
12	2	0	100.3	118.8	10.6
14	2	0	65.2	56.1	9.8
6	4	0	15.6	15.1	6.4
8	4	0	10.4	1.4	6.6
10	4	0	44.3	41.6	8.4
12	4	0	265.4	266.6	13.7
14	4	0	18.7	16.9	8.7
6	5	0	12.6	17.7	7.1
8	5	0	102.9	98.5	10.0
10	6	0	3.1	1.9	7.8
12	6	0	150.1	165.2	16.6
14	6	0	123.2	142.2	16.4
8	8	0	357.9	355.8	15.2
10	8	0	50.1	42.1	9.2
12	8	0	22.7	16.9	8.6
10	10	0	50.2	41.8	9.7
4	1	1	3.3	5.9	5.0
6	1	1	32.4	36.9	6.2
8	1	1	75.8	75.4	8.2
10	1	1	9.9	1.8	7.4
12	1	1	0.	1.3	7.2
14	1	1	57.2	60.1	9.4
3	2	1	18.7	25.6	5.2
5	2	1	26.3	20.4	5.7
7	2	1	238.5	225.6	10.6
9	2	1	0.	0.7	6.6
11	2	1	166.0	172.9	11.7
13	2	1	18.4	17.7	8.6
15	2	1	229.8	246.7	18.6
4	3	1	20.4	23.3	5.6
5	3	1	90.5	80.2	7.6
8	3	1	31.9	30.9	7.2
10	3	1	31.5	31.0	8.2
12	3	1	19.2	5.2	8.3
14	3	1	3.8	5.3	7.7
5	4	1	36.0	27.8	6.1
7	4	1	0.	5.8	5.9
9	4	1	20.5	19.6	7.6
11	4	1	38.3	27.9	8.6
13	4	1	0.	2.4	7.4
15	4	1	3.0	11.1	10.6
6	5	1	13.6	0.6	6.4
8	5	1	0.	0.1	6.5
10	5	1	146.6	138.7	11.1
12	5	1	96.8	97.5	10.7
14	5	1	62.6	53.0	9.5
7	6	1	25.6	15.8	7.6
9	6	1	69.2	71.3	9.7
11	6	1	262.7	270.7	14.3
13	6	1	13.5	14.3	8.8
8	7	1	33.6	20.6	8.6
10	7	1	58.8	47.0	9.5
12	7	1	24.8	30.2	9.0
9	8	1	29.8	19.1	9.0
11	8	1	19.0	20.4	8.7
13	8	1	57.6	60.8	13.5
10	9	1	18.2	19.5	8.6
12	9	1	40.9	34.7	12.5
11	10	1	0.8	4.8	8.0
4	2	2	8.0	6.5	5.3
5	2	2	339.0	342.3	11.7
3	2	2	29.5	30.7	7.4
10	2	2	211.0	196.0	12.1
12	2	2	99.1	102.0	10.7
14	2	2	92.7	91.1	10.8
3	3	2	142.2	154.1	7.7
5	3	2	25.8	31.8	6.3
7	3	2	56.0	51.3	7.7
9	3	2	21.2	6.4	7.7
11	3	2	69.5	75.0	9.7
13	3	2	4.0	0.9	8.4
15	3	2	0.	0.0	11.0
4	4	2	0.6	2.2	5.4
6	4	2	27.3	14.6	9.2
8	4	2	24.9	31.3	7.6
10	4	2	145.1	141.0	11.0
12	4	2	30.0	20.0	8.9
14	4	2	131.9	108.8	16.0
5	5	2	20.8	19.2	9.0
7	5	2	21.0	6.0	10.0
9	5	2	148.1	136.0	15.2
11	5	2	72.0	61.0	13.2
13	3	2	52.4	51.7	12.5
6	6	2	252.9	255.4	16.9
3	6	2	27.7	20.3	11.6
10	6	2	74.6	76.4	14.2
12	6	2	8.4	23.7	12.3
7	7	2	183.1	176.3	16.3
9	7	2	85.5	61.4	13.9
11	7	2	26.1	10.5	11.5
13	7	2	0.	2.3	10.9
8	8	2	13.5	4.4	11.1
10	8	2	120.2	134.7	16.1
12	8	2	28.0	30.2	12.3
9	9	2	61.7	49.6	13.6
11	9	2	16.0	1.4	11.6
10	10	2	55.0	52.2	13.0
4	3	3	0.	13.5	7.4
6	3	3	0.	1.7	8.2
8	3	3	27.4	35.7	10.8
10	3	3	41.9	46.4	12.0
12	3	3	24.4	22.3	11.8
14	3	3	11.5	16.3	12.1
5	4	3	9.7	20.0	8.6
7	4	3	13.4	21.7	9.8
9	4	3	31.8	7.7	11.2
13	4	3	34.9	32.6	12.9
6	5	3	24.3	22.9	9.9
9	5	3	160.7	158.7	15.7
10	5	3	0.	3.2	10.9
12	5	3	0.	6.0	12.2
7	6	3	226.9	234.4	16.7
9	6	3	10.1	30.3	12.1
11	6	3	63.1	47.3	13.3
13	6	3	0.	19.8	11.0
8	7	3	37.8	35.8	12.1
10	7	3	0.	6.2	11.4
12	7	3	10.5	0.6	11.6
9	8	3	60.8	53.2	14.2
11	8	3	14.5	16.3	11.9
10	9	3	89.6	96.4	14.5
4	4	4	7.7	0.2	8.3
8	4	4	608.3	630.3	25.1
10	4	4	57.2	64.7	13.3
12	4	4	17.3	19.2	12.3
5	5	4	0.	3.0	8.5
7	5	4	21.4	11.8	10.6
9	5	4	48.2	60.4	12.9
11	5	4	10.2	22.0	12.4
13	5	4	2.0	0.0	10.9
5	6	4	45.7	39.9	11.7
8	6	4	75.3	87.1	12.9
10	6	4	63.0	67.3	13.3
12	6	4	132.8	133.6	15.9
7	7	4	3.6	14.6	9.9
9	7	4	1.9	2.5	10.8
11	7	4	25.4	19.9	11.6
8	8	4	6.2	3.5	10.4
10	8	4	0.	0.0	11.0
9	9	4	29.7	7.3	11.7
11	9	4	6.0	8.7	10.6
10	10	4	77.5	73.0	13.1
6	5	5	163.0	158.6	14.7
8	5	5	115.9	95.1	14.6
10	5	5	0.	11.2	10.4
12	5	5	5.5	2.4	10.9
7	6	5	131.3	129.9	14.5
9	6	5	0.	1.9	10.6
11	6	5	12.4	19.1	11.5
8	7	5	70.6	52.0	12.7
10	7	5	6.4	15.0	11.4
12	7	5	0.	0.3	10.5
9	8	5	0.	16.9	11.1
11	8	5	97.0	97.0	14.5
10	9	5	183.5	191.6	17.0
6	6	6	75.9	78.7	13.0
8	6	6	11.2	3.2	10.4
10	5	6	86.6	103.9	14.5
12	5	6	184.4	180.2	17.4
7	7	6	0.	7.6	10.3
9	7	6	22.0	4.6	11.6
11	7	6	83.5	72.7	13.6
8	8	6	1.0	0.1	11.1
10	8	6	233.3	233.7	18.9
9	9	6	163.8	167.0	16.9
8	7	7	18.5	20.0	11.0
10	7	7	66.9	60.9	13.7
9	8	7	3.5	7.4	11.1
8	8	8	66.8	52.6	13.2

Table 5(*a*). *Cation–oxygen distances** (Å) *for C-sesquioxides*

		M(1)–O		M(2)–O			
		a_0	d_1	d_2	d_3	d_4	Mean
Y_2O_3	Present work	10·604	2·284 (3)	2·331 (4)	2·274 (4)	2·243 (4)	2·282
In_2O_3	Marezio (1966)	10·117	2·175 (8)	2·228 (8)	2·190 (8)	2·127 (8)	2·185
Sc_2O_3	Geller *et al.* (1967)	9·810	2·122 (7)	2·163 (7)	2·093 (7)	2·079 (7)	2·112

* e.s.d.'s. (Å) in parentheses.

values differ by 5σ and 8σ, respectively, from the value for Sc_2O_3. Hence it appears unlikely on this evidence that the *C*-sesquioxides are completely isostructural.

Interatomic distances

The *C*-sesquioxides can be considered as distorted fluorite structures with doubling of the fluorite lattice parameter and with a quarter of the anions removed. The mean catio–noxygen distance should be proportional to the lattice parameter. In each of the slightly distorted 8(*b*)-octahedra there are two oxygen vacancies along one of the body-diagonals of the fluorite anion sublattice, and the six cation-oxygen distances are equivalent. These distances are designated d_1 in the list of interatomic distances for Y_2O_3, In_2O_3 and Sc_2O_3 in Table 5(*a*). The grossly distorted 24(*d*)-octahedra, with two oxygen atoms missing from one of the anion face-diagonals, have three pairs of non-equivalent distances (d_2, d_3 and d_4).

Table 5(*b*). *Values of Δd_2, Δd_3 and Δd_4* in the 24(d)-octahedra*

	Δd_2	Δd_3	Δd_4
Y_2O_3	0·047 Å	−0·010 Å	−0·041 Å
In_2O_3	0·053	0·015	−0·048
Sc_2O_3	0·041	−0·029	−0·043
Mean	0·041	−0·008	−0·044

* $\Delta d_2 = d_2 - d_1$, *etc.*

On energetic grounds the mean 24(*d*) distance should be equal to the 8(*b*) distance. The values in Table 5(*a*) show this to be the case for all three sesquioxides within experimental accuracy. A plot of the arithmetic mean of the four distances (2·283, 2·180 and 2·114 Å for Y_2O_3, In_2O_3 and Sc_2O_3, respectively) *versus* a_0 is shown

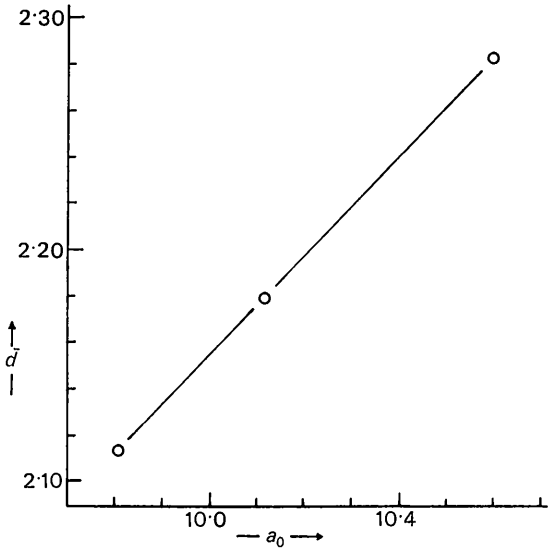

Fig. 1. Plot of the mean cation–oxygen distance ($\bar{d}$) *versus* lattice parameter (a_0) for Y_2O_3, In_2O_3 and Sc_2O_3.

in Fig. 1. The linear relation is of the form,

$$\bar{d} = 0{\cdot}21542(5)a_0 + 0{\cdot}00004(5)\,,$$

as determined by least squares. Hence it is proposed that the mean cation–oxygen distances in the *C*-sesquioxides are given by $0{\cdot}2154a_0$ (see also Geller *et al.*).

Marezio observed significant differences between d_2, d_3 and d_4 in In_2O_3 and attributed these differences to the different repulsive forces on the three sets of oxygen atoms, each of which has a different environment on account of the two unoccupied sites of the fluorite anion sublattice. According to this argument the condition $d_2 > d_3 > d_4$ should exist for all *C*-sesquioxides. Reference to Table 5(*b*) shows that within experimental accuracy the same differences are observed for Y_2O_3 and Sc_2O_3. The mean values of the differences Δd_2, Δd_3 and Δd_4 are 0·04, −0·01 and −0·04 Å. These values can be used together with the linear relation described above to predict the four distances for any of the *C*-sesquioxides with reasonable precision by the use of only the lattice parameter. For example, bixbyite has the lattice parameter 9·40 Å and therefore should have values of 2·02, 2·06, 2·01 and 1·98 Å for d_1, d_2, d_3 and d_4, respectively. The corresponding values determined by Dachs (1956) from X-ray powder diffraction data (2·01, 2·24, 1·92 and 1·90 Å) do not confirm these values. These discrepancies can probably be attributed to the limitation of the powder technique for intensity measurement imposed by profile resolution.

Clearly any further work on the *C*-sesquioxides should be based on single-crystal data, preferably measured by neutron diffraction.

Thermal parameters

The anisotropic temperature factor coefficients are given in Table 3 and compared there with the X-ray values given by Paton & Maslen. There is no correspondence between the two sets and, as might be expected, the X-ray values for the diagonal terms of the b_{ij}-matrix are considerably higher on account of absorption errors in the X-ray data.

Application of the *R* factor significance test of Hamilton (1965) clearly shows the validity of assuming an anisotropic model for the neutron data refinement. Considering the hypothesis that all atoms vibrate isotropically the *R* factors for the restrained model, R_t, and the unrestrained model, R_a, are 0·123 and 0·115, respectively. The *R* factor ratio is

$$R = R_t/R_a = 1{\cdot}061\,.$$

The number of degrees of freedom for the refinements is 162 and the dimension of the hypothesis is 8. At the 0·025 level of significance *R* is found to be 1·055 and hence the hypothesis can be rejected at this level. The root-mean-square amplitudes, $(\overline{r_i^2})^{1/2}$, for Y(1), Y(2) and O listed in Table 6 with the corresponding direction cosines show that there is a similar degree of anisotropy for the three atoms. Therefore it is reasonable to state that each of the atoms displays a significant de-

gree of anisotropic vibration, assuming that systematic errors in the experimental data are insignificant.

Table 6. *Ellipsoids of vibration to the unit-cell axes (neutron refinement)*

	i	$(\overline{r_i^2})^{1/2}$	a_{ia}	a_{ib}	a_{ic}
Y(1)	1	0·078 Å	0·577	0·577	0·577
	2	0·040	0·816	−0·408	−0·408
	3	0·040	0·000	0·707	−0·707
Y(2)	1	0·082	0·000	0·403	0·915
	2	0·066	1·000	0·000	0·000
	3	0·047	0·000	0·915	−0·403
O	1	0·080	−0·468	0·837	−0·282
	2	0·060	0·355	0·471	0·808
	3	0·045	0·809	0·278	−0·518

One of the authors (B. H. O'C.) is indebted to the United Kingdom Atomic Energy Authority for a Research Group Fellowship. It is a pleasure to thank Dr B. T. M. Willis for his interest in the study.

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The Crystal Structure of 5-Methyluridine*

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(*Received* 2 *December* 1968)

5-Methyluridine was crystallized from aqueous ethanol as the hemihydrate in the form of orthorhombic needles, space group $P2_12_12$ with $a=14{\cdot}026$, $b=17{\cdot}302$, $c=4{\cdot}861$ Å and four molecules per cell. The crystal structure has been determined by a three-dimensional, X-ray diffraction analysis. Intensity data were collected on photographic film and estimated visually. The structure was solved from the Patterson function with the help of Fourier techniques and packing considerations. Refinement by a full-matrix, least-squares method has led to a final R value of 0·075 for 1294 reflections and to estimated standard deviations in bond lengths for the non-hydrogen atoms between 0·006 and 0·007 Å. The torsion angle describing the relative orientations of the sugar residue and the pyrimidine base is −29·4°. Atom C(3′) of the sugar residue is displaced by about 0·60 Å from the least-squares plane through the other four ring atoms and lies on the same side of the plane as C(5′). This plane also makes an angle of 71·9° with the least-squares plane through the six ring atoms of the pyrimidine base. Of the twelve atoms within, or bonded to, the pyrimidine ring, only C(1′) deviates significantly, by 0·083 Å, from the least-squares plane through the six ring atoms.

1. Introduction

The structure of 5-methyluridine (Fig. 1) has been determined as one in a series of compounds being studied in these laboratories to provide accurate bond lengths and angles and conformational information useful in structural studies of the nucleic acids.

As far as the authors are aware, ten X-ray analyses have been reported, to date, for uridine and thymidine derivatives (Huber, 1957; Trueblood, Horn & Luzzati, 1961; Harris & McIntyre, 1964; Shefter, Barlow, Sparks & Trueblood, 1964; Shefter & Trueblood, 1965; Camerman & Trotter, 1965; Haschemeyer & Sobell, 1965; Iball, Morgan & Wilson, 1966, 1968). The most accurate determinations seem to be for β-adenosine-2′-uridine-5′-phosphoric acid (Shefter *et al.*, 1964) and 5-fluorodeoxyuridine (Harris & MacIntyre, 1964) for which the estimated standard deviations (e.s.d.'s) are slightly larger than those reported here for 5-methyluridine.

* Contribution No. 3753 from the Gates and Crellin Laboratories of Chemistry.

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