

*Acta Cryst.* (1974). B30, 421

## The Crystal and Molecular Structure of 10 $\alpha$ -Cyano-1 $\alpha$ ,4 $\alpha$ $\beta$ -dimethyl-7-ethoxy-2 $\beta$ -methoxy-1,2,3,4,4a,9,10,10a-octahydro-1 $\beta$ -phenanthrenol\*

BY RICHARD H. STANFORD JR AND THOMAS C. MCKENZIE

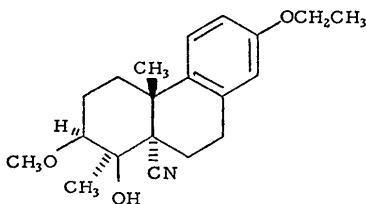
*Norman W. Church Laboratory of Chemical Biology, California Institute of Technology, Pasadena, California 91109, U.S.A.*

(Received 27 April 1973; accepted 19 September 1973)

The crystal structure of the title compound has been determined. Three-dimensional data were collected on a Datex-automated General Electric diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) to a minimum spacing of  $0.85 \text{ \AA}$  and the structure was solved by direct methods. The coordinates of all of the atoms in the molecule, the isotropic temperature factors of the hydrogen atoms, and the anisotropic temperature factors of the heavier atoms were refined by least-squares calculations. The final  $R$  index is  $0.051$ . The crystals are monoclinic, space group  $P2_1/c$  with  $a = 10.188$ ,  $b = 7.144$ ,  $c = 25.804 \text{ \AA}$ , and  $\beta = 107.15$ . The torsion angle between the hydroxyl group, O(21), and the adjacent *trans* hydrogen, H(31), along the connecting carbon-carbon bond is  $174^\circ$  rather than the expected  $180^\circ$ .

### Introduction

An alcohol,  $C_{20}H_{27}NO_3$ , was prepared as a possible intermediate for the total synthesis of the pentacyclic triterpene alnusenone. However, this alcohol was very resistant to base-catalyzed dehydration and the correctness of the assignment was questioned. Ultimately another route to alnusenone had to be taken (Ireland & Welch, 1970). The X-ray study was undertaken to confirm the structure assignment and to see if detailed examination of the molecular structure would explain why this tertiary, axial alcohol does not dehydrate.



### Experimental

Colorless prisms were obtained by slow crystallization from ethyl acetate and hexane. All of the data were obtained from one crystal with dimensions  $0.25 \times 0.40 \times 0.40 \text{ mm}$ . Unit-cell parameters were obtained from least-squares refinement of the  $2\theta$  angles of 26 reflections measured on the General Electric diffractometer. The resulting values were:

$$\begin{aligned} a &= 10.188 \pm 0.003 \text{ \AA} \\ b &= 7.144 \pm 0.002 \\ c &= 25.804 \pm 0.007 \\ \beta &= 107.15 \pm 0.03^\circ \end{aligned}$$

\* Contribution No. 4681 from the Norman W. Church Laboratory of Chemical Biology.

The absence of  $0k0$  reflections for  $k$  odd and  $h0l$  reflections for  $l$  odd indicated that the space group is  $P2_1/c$ . The crystal density, measured by flotation in heptane-carbon tetrachloride, was found to be  $1.21 \pm 0.02 \text{ g cm}^{-3}$ . With 4 molecules of molecular weight  $329.44$  per unit cell, the calculated density is  $1.22 \text{ g cm}^{-3}$ .

Intensity data were collected by the  $\theta$ - $2\theta$  scan method on a Datex-automated General Electric diffractometer with nickel-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Reflections were collected to a maximum value of  $2\theta = 130^\circ$  with a scan rate in  $2\theta$  of  $2^\circ \text{ min}^{-1}$ . Background counts were taken for 30 s at the beginning and end of each scan. The reflections whose peak counting rate exceeded about 20000 counts  $\text{s}^{-1}$  were remeasured with a lower beam intensity to minimize counting losses. Three reflections, monitored at regular intervals during the data collection, showed no significant variation in intensity.

The intensities of 2938 reflections were measured. The intensities of 98 of these reflections were observed to be less than one standard deviation above background and were assigned a value of zero with zero weight throughout the refinement process. In addition 11 other reflections, thought to suffer from serious counting losses, were assigned zero weight. The data were corrected for Lorentz-polarization effects but not for absorption ( $\mu = 6.6 \text{ cm}^{-1}$ ). The data were placed on an approximately absolute scale by Wilson's (1942) method. A Howells, Phillips & Rogers (1950) plot confirmed that the crystal was centrosymmetric. The normalized structure factors  $E$  (Karle & Karle, 1966) were calculated with a temperature parameter of  $3.6 \text{ \AA}^2$ .

### Solution and refinement of the structure

All calculations were carried out on an IBM 370/155 computer with subprograms operating under the CRYM system (Duchamp, 1964). The atomic scattering factors for carbon, oxygen, and nitrogen were taken

Table 1. Observed and calculated structure factors

Within each group the columns contain  $k$ ,  $10F_o$ , and  $10F_c$ . Reflections marked with an asterisk were assigned zero weight in the least-squares refinement.

Table with multiple columns containing reflection indices (h, k, l), observed structure factors (10Fo), and calculated structure factors (10Fc). The table is organized into groups based on reflection indices.



from *International Tables for X-ray Crystallography*. The atomic scattering factor for hydrogen is that given by Stewart, Davidson & Simpson (1965). The least-squares routine minimized the quantity  $\sum w(F_o^2 - F_c^2)^2$ . The weights,  $w$ , used throughout the refinement of the structure, were set equal to  $1/\sigma^2(F_o)^2$  which were derived from counting statistics. The variances of the intensities were calculated by the formula:

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2$$

where  $S$  is the total number of counts collected during the scan;  $B_1$  and  $B_2$  are the numbers of counts collected for each background;  $\alpha$  is the scan time to total background time ratio;  $d$  is an empirical constant of 0.02.

The phases of the 250 reflections with an  $E$  value greater than 1.69 were assigned by Long's (1965) program, which uses a reiterative application of Sayre's (1952) equation. Long's procedure yielded 16 possible phase assignment combinations for the 250 chosen reflections. Of these sixteen combinations, two had nearly the same high consistency index and also had converged in the same number of iterations. One of the two phase assignments led to an  $E$  map which could not be interpreted in terms of a chemically reasonable structure. The second of these phase assignments gave an  $E$  map in which 19 of the non-hydrogen atoms were located. The alternate calculation of structure factors and electron density maps led to the complete elucidation of the structure.

Least-squares refinement of the coordinates and the isotropic temperature factors of the heavy atoms reduced the  $R$  index,  $\sum ||F_o| - |F_c|| / \sum |F_o|$ , to 0.193. The ring hydrogen atoms were introduced at their expected

positions and refinement of the heavier atoms with anisotropic temperature factors continued. A difference electron density map revealed the positions of the remaining hydrogen atoms. Final full-matrix least-

Table 3. *Hydrogen-atom parameters and their standard deviations*

The values for the coordinates have been multiplied by  $10^3$ . The values for the isotropic temperature factors have been multiplied by 10.

	$x$	$y$	$z$	$B$
H(25)	262 (2)	822 (2)	229 (1)	44 (4)
H(26)	545 (2)	1236 (3)	436 (1)	44 (4)
H(27)	501 (2)	1032 (2)	451 (1)	38 (4)
H(28)	695 (2)	1138 (3)	518 (1)	52 (4)
H(29)	782 (2)	1163 (2)	477 (1)	45 (4)
H(30)	374 (2)	1276 (3)	365 (1)	49 (4)
H(31)	696 (2)	817 (2)	506 (1)	33 (3)
H(32)	674 (2)	606 (3)	346 (1)	46 (4)
H(33)	702 (2)	810 (3)	328 (1)	51 (4)
H(34)	513 (2)	723 (3)	263 (1)	49 (4)
H(35)	451 (2)	616 (3)	303 (1)	57 (5)
H(36)	169 (2)	1298 (3)	293 (1)	54 (4)
H(37)	48 (2)	1339 (3)	201 (1)	73 (6)
H(38)	-43 (2)	1233 (3)	233 (1)	67 (5)
H(39)	-76 (2)	1188 (4)	120 (1)	80 (6)
H(40)	-166 (3)	1085 (4)	150 (1)	87 (7)
H(41)	-174 (3)	1310 (4)	144 (1)	84 (7)
H(42)	767 (2)	1164 (3)	389 (1)	55 (4)
H(43)	684 (2)	1100 (3)	329 (1)	57 (5)
H(44)	629 (2)	1273 (3)	356 (1)	56 (4)
H(45)	741 (3)	521 (4)	464 (1)	82 (7)
H(46)	832 (3)	529 (4)	423 (1)	76 (6)
H(47)	895 (2)	582 (3)	484 (1)	70 (6)
H(48)	943 (3)	902 (4)	449 (1)	79 (6)
H(49)	861 (3)	683 (5)	579 (1)	101 (8)
H(50)	830 (3)	875 (4)	595 (1)	95 (8)
H(51)	983 (3)	828 (4)	605 (1)	90 (6)

Table 4. *Bond distances and angles and their standard deviations involving the heavier atoms*

The values for the standard deviations in bond lengths have been multiplied by  $10^3$ . The values for the standard deviations in bond angles have been multiplied by 10.

C(15)-C(1)	1.529 (2) Å	C(15)-C(1)-C(2)	109.6 (1)°	C(15)-C(1)-C(20)	112.3 (1)°
C(2)-C(1)	1.536 (2)	C(2)-C(1)-C(20)	109.8 (1)	C(2)-C(1)-O(21)	110.7 (1)
C(20)-C(1)	1.561 (2)	C(10)-C(20)-C(1)	112.3 (1)	C(16)-C(20)-C(1)	114.1 (1)
O(21)-C(1)	1.420 (2)	O(21)-C(1)-C(15)	108.4 (2)	O(21)-C(1)-C(20)	105.9 (1)
C(3)-C(2)	1.508 (2)	C(3)-C(2)-C(1)	113.4 (1)	C(3)-C(2)-O(22)	109.4 (1)
O(22)-C(2)	1.430 (2)	O(22)-C(2)-C(1)	107.8 (1)		
C(4)-C(3)	1.529 (2)	C(4)-C(3)-C(2)	112.1 (1)		
C(16)-C(4)	1.538 (2)	C(16)-C(4)-C(3)	112.2 (2)		
C(17)-C(16)	1.538 (3)	C(17)-C(16)-C(4)	109.1 (1)	C(17)-C(16)-C(18)	105.4 (1)
C(18)-C(16)	1.523 (2)	C(18)-C(16)-C(4)	112.9 (1)	C(18)-C(16)-C(20)	108.9 (1)
C(20)-C(16)	1.577 (2)	C(20)-C(16)-C(4)	108.0 (1)	C(20)-C(16)-C(17)	112.6 (1)
C(5)-C(18)	1.393 (2)	C(5)-C(18)-C(16)	120.7 (1)	C(5)-C(18)-C(19)	117.2 (1)
C(19)-C(18)	1.404 (2)	C(19)-C(18)-C(16)	121.7 (1)		
C(6)-C(5)	1.383 (2)	C(6)-C(5)-C(18)	122.9 (1)		
C(7)-C(6)	1.379 (2)	C(7)-C(6)-C(5)	119.2 (2)		
C(8)-C(7)	1.383 (2)	C(8)-C(7)-C(6)	118.9 (1)	C(8)-C(7)-O(23)	115.6 (1)
O(23)-C(7)	1.365 (2)	O(23)-C(7)-C(6)	125.4 (1)		
C(19)-C(8)	1.381 (2)	C(19)-C(8)-C(7)	122.2 (1)	C(8)-C(19)-C(18)	119.6 (1)
C(9)-C(19)	1.511 (2)	C(9)-C(19)-C(18)	122.1 (1)	C(9)-C(19)-C(8)	118.2 (1)
C(10)-C(9)	1.519 (2)	C(10)-C(9)-C(19)	115.3 (1)	C(20)-C(10)-C(9)	111.7 (1)
C(10)-C(20)	1.537 (2)	C(10)-C(20)-C(16)	109.6 (1)	C(10)-C(20)-C(14)	106.9 (1)
C(11)-O(22)	1.404 (2)	C(11)-O(22)-C(2)	115.2 (2)		
C(12)-O(23)	1.426 (2)	C(12)-O(23)-C(7)	118.0 (1)		
C(13)-C(12)	1.487 (3)	C(13)-C(12)-O(23)	108.1 (2)		
C(14)-C(20)	1.486 (2)	C(14)-C(20)-C(1)	106.3 (1)	C(14)-C(20)-C(16)	107.2 (1)
C(14)-N(24)	1.135 (2)	C(10)-C(14)-N(24)	177.7 (2)		

squares refinement of all the atoms including isotropic temperature factors for the hydrogen atoms and a secondary extinction factor (Larson, 1967) converged at an  $R$  index of 0.051 and a weighted  $R$  index,  $\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4$ , of 0.015. The secondary extinction factor,  $g$ , was  $2 \pm 1 \times 10^{-6}$ . In the last cycle of refinement the average shift of a refined parameter was 0.12 of the estimated standard deviation of that parameter.

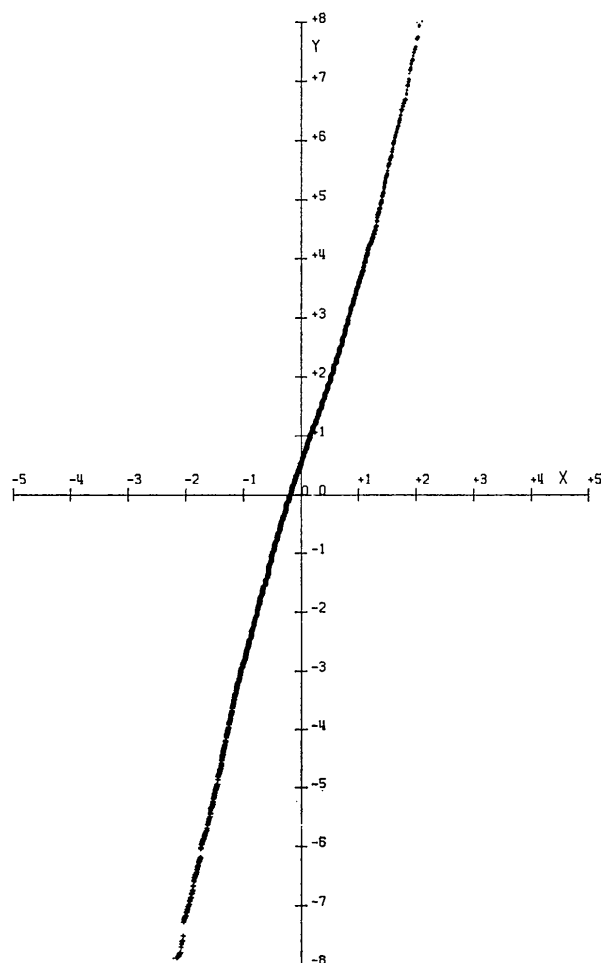


Fig. 1. Normal probability plot. The vertical ( $Y$ ) axis is the  $\Delta F/\sigma$  of the data and the horizontal ( $X$ ) axis is the expected values of the ranked moduli.

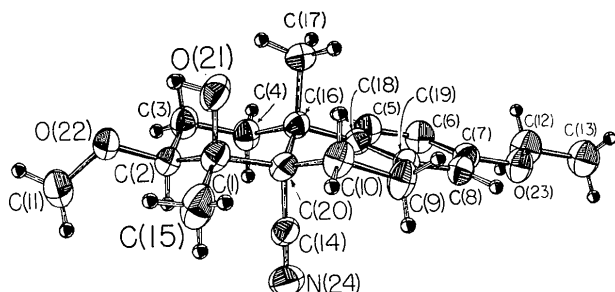


Fig. 2. ORTEP drawing of the alcohol. The hydrogen atoms are shown as spheres 0.1 Å in diameter.

The observed and calculated structure factors are listed in Table 1.

The goodness-of-fit  $[\sum w(F_o^2 - F_c^2)^2 / (m - s)]^{1/2}$ , where  $m$  is the number of observations and  $s$  is the number of parameters refined, was 3.7. This is a large value and a normal probability plot of  $(|F_o| - |F_c|)/\sigma$  against the expected values of the ranked moduli (Abrahams & Keve, 1971) of our single set of data, shown in Fig. 1, has a slope of about 3.3. This suggests that the assigned variances of the intensities are too small. The data were collected from a large, strongly scattering crystal and it is likely that our data suffer from counting losses. A plot of  $|\Delta F/\sigma|$  against  $|F_c|$  has a positive slope indicating that the more intense reflections, as expected, suffered the most from counting losses. In fact, all of the 50 very intense reflections that were remeasured with a reduced tube current were found to be suffering from counting losses of about 9%. In the calculation of the variance of the intensities a larger value for  $d$ , the empirical constant, probably should have been chosen.

The coordinates and anisotropic temperature factors of the nonhydrogen atoms and their standard deviations are given in Table 2. The positional parameters and isotropic temperature factors for the hydrogen atoms and their standard deviations are given in Table 3. The standard deviations in atomic coordinates correspond to positional uncertainties of approximately 0.002 Å for the carbon atoms and nitrogen atom, 0.001 Å for the oxygen atoms, and 0.02 Å for the hydrogen atoms. The bond distances and angles involving the non-hydrogen atoms with their respective standard deviations are listed in Table 4. Distances and angles involving hydrogen atoms and their standard deviations are listed in Table 5.

### Description of the structure

A view of the molecule drawn by a Calcomp plotter controlled by the IBM 370/155 computer using the ORTEP program (Johnson, 1965) is shown in Fig. 2. The molecule has the chair conformation and the hydroxyl group, O(21), is axial and *trans* to an adjacent hydrogen atom, H(31). However, the torsion angle between these two atoms along the connecting carbon-carbon bond is  $-174 \pm 1^\circ$  rather than the  $180^\circ$  required for concerted elimination. The ring containing the hydroxyl group is twisted from the normal conformation. The distance between the angular methyl group hydrogen, H(42), and the hydroxyl group, O(21), is 2.16 Å and this steric interaction forces atom C(1) to twist away from the angular methyl. An intramolecular hydrogen bond between O(22) and H(48), 2.33 Å long, further distorts the ring. The torsion angles between adjacent axial atoms on ring A are listed in Table 6 and reveal that the whole ring is considerably distorted. The twisting of this ring also has lengthened the bonds between atoms C(16)-C(20) and C(1)-C(20) and has compressed the bonds between C(2)-C(3) and C(3)-C(4). Whether this deviation from the ideal geom-

Table 5. Bond distances and angles (and their standard deviations) involving the hydrogen atoms

The values for the standard deviations in bond lengths have been multiplied by  $10^2$ .

H(25)–C(8)	0.96 (2)*Å	H(25)–C(8)–C(7)	117 (1)°	H(25)–C(8)–C(19)	120 (1)°
H(26)–C(4)	0.96 (2)	H(26)–C(4)–C(3)	108 (1)	H(26)–C(4)–C(16)	111 (1)
H(27)–C(4)	1.00 (2)	H(27)–C(4)–C(3)	108 (1)	H(27)–C(4)–C(16)	108 (1)
		H(27)–C(4)–H(26)	110 (2)		
H(28)–C(3)	0.99 (2)	H(28)–C(3)–C(2)	109 (1)	H(28)–C(3)–C(4)	108 (1)
H(29)–C(3)	0.97 (2)	H(29)–C(3)–C(2)	106 (1)	H(29)–C(3)–C(4)	114 (1)
		H(29)–C(3)–C(28)	108 (2)		
H(30)–C(5)	0.99 (2)	H(30)–C(5)–C(18)	118 (1)	H(30)–C(5)–C(6)	119 (1)
H(31)–C(2)	0.97 (2)	H(31)–C(2)–C(1)	106 (1)	H(31)–C(2)–C(3)	110 (1)
		H(31)–C(2)–O(22)	110 (1)		
H(32)–C(10)	0.97 (2)	H(32)–C(10)–C(9)	108 (1)	H(32)–C(10)–C(20)	111 (1)
H(33)–C(10)	0.96 (2)	H(33)–C(10)–C(9)	110 (1)	H(33)–C(10)–C(20)	106 (1)
		H(33)–C(10)–H(32)	109 (2)		
H(34)–C(9)	0.97 (2)	H(34)–C(9)–C(19)	108 (1)	H(34)–C(9)–C(10)	108 (1)
H(35)–C(9)	0.97 (2)	H(35)–C(9)–C(19)	108 (1)	H(35)–C(9)–C(10)	110 (1)
		H(35)–C(9)–H(34)	107 (2)		
H(36)–C(6)	0.96 (2)	H(36)–C(6)–C(5)	121 (1)	H(36)–C(6)–C(7)	120 (1)
H(37)–C(12)	0.97 (2)	H(37)–C(12)–C(13)	111 (1)	H(37)–C(12)–O(23)	111 (1)
H(38)–C(12)	1.01 (2)	H(38)–C(12)–C(13)	110 (1)	H(38)–C(12)–O(23)	110 (1)
		H(38)–C(12)–H(37)	107 (2)		
H(39)–C(13)	0.97 (3)	H(39)–C(13)–C(12)	111 (1)	H(39)–C(13)–H(40)	107 (2)
		H(39)–C(13)–H(41)	108 (2)		
H(40)–C(13)	0.97 (3)	H(40)–C(13)–C(12)	112 (1)	H(40)–C(13)–H(41)	111 (2)
H(41)–C(13)	1.00 (3)	H(41)–C(13)–C(12)	108 (1)		
H(42)–C(17)	0.99 (2)	H(42)–C(17)–C(16)	112 (1)	H(42)–C(17)–H(43)	108 (2)
		H(42)–C(17)–H(44)	112 (2)		
H(43)–C(17)	1.00 (2)	H(43)–C(17)–C(16)	110 (1)	H(43)–C(17)–H(44)	109 (2)
H(44)–C(17)	0.96 (2)	H(44)–C(17)–C(16)	106 (1)		
H(45)–C(15)	0.98 (3)	H(45)–C(15)–C(1)	112 (2)	H(45)–C(15)–H(46)	110 (2)
		H(45)–C(15)–H(47)	105 (2)		
H(46)–C(15)	0.97 (3)	H(46)–C(15)–C(1)	113 (2)	H(46)–C(15)–H(47)	106 (2)
H(47)–C(15)	0.99 (2)	H(47)–C(15)–C(1)	110 (1)		
H(48)–O(21)	0.86 (2)	H(48)–O(21)–C(1)	107 (2)		
H(49)–C(11)	0.95 (3)	H(49)–C(11)–O(22)	114 (2)	H(49)–C(11)–H(50)	100 (3)
		H(49)–C(11)–H(51)	118 (2)		
H(50)–C(11)	0.99 (4)	H(50)–C(11)–O(22)	106 (2)	H(50)–C(11)–H(51)	108 (2)
H(51)–C(11)	0.91 (1)	H(51)–C(11)–O(22)	108 (2)		

etry is sufficient to completely explain the resistance to dehydration is not clear since the molecule may be flexible enough to twist the required  $6^\circ$ .

Table 6. Torsion angles between adjacent axial substituents on ring A

Axial atoms	Connecting atoms	Torsion angle
14 21	20 1	174°
21 31	1 2	–174
31 29	2 3	171
29 27	3 4	–178
27 17	4 16	174
17 14	16 20	–176

The hydroxyl group, O(21), is very hindered. The adjacent methyl group, C(15), is 2.22 Å from the hydrogen atom, H(48), on the hydroxyl group, and the *cis* 1,3 diaxial hydrogens, H(29) and H(33), are 2.50 and 2.40 Å respectively from the hydroxyl oxygen, O(21). The *trans* hydrogen atom, H(31), is also hindered by carbon, C(14), of the nitrile group which is 3.08 Å away. The resonance effect of the methoxyl group, O(22), on C(2) also must decrease the ease of dehydration by decreasing the acidity of H(31). This combination of geometric, steric, and electronic effects must explain this alcohol's resistance to dehydration.

The six carbon atoms of the aromatic ring are planar. The three substituent atoms, however, are bent out of the plane. In particular, atom C(16) has been bent out by 0.164 Å. The least-squares plane of the aromatic ring is given in Table 7.

Table 7. Least-squares plane of the aromatic ring and atomic deviations from the plane

Coefficients are direction cosines relative to the crystallographic axes.

Plane through atoms C(5), C(6), C(7), C(8), C(18), and C(19)  
 $0.6753X + 0.5325Y - 0.6868Z = 0.908 \text{ Å}$

	Deviation
C(18)	0.000 Å
C(5)	–0.002
C(6)	0.001
C(7)	0.003
C(8)	–0.005
C(19)	0.004
C(16)	0.164
C(9)	0.012
C(23)	0.018

The shortest intermolecular contact is a second, 2.20 Å, hydrogen bond between O(22) and H(48) of the molecule in the equivalent position  $2-x, 2-y, 1-z$ .

Additional short intermolecular distances are 2.73 Å between O(21) and H(51) of the molecule at  $2-x, 2-y, 1-z$  and 2.35 Å between H(25) and H(43) of the molecule at  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ .

We wish to express our thanks to Professor Robert E. Ireland for providing the compound and for his encouragement throughout this project. One of us (TCM) is the recipient of a National Institutes of Health Postdoctoral Fellowship.

#### References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.

DUCHAMP, D. J. (1964). Program and Abstracts, ACA Meeting, Bozeman, Montana; paper B-14, p. 29.  
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210–214.  
 IRELAND, R. E. & WELCH, S. C. (1970). *J. Amer. Chem. Soc.* **92**, 7232–7234.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.  
 LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.  
 LONG, R. E. (1965). Ph.D. Thesis, Univ. of California at Los Angeles.  
 SAYRE, D. (1952). *Acta Cryst.* **5**, 60–65.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

*Acta Cryst.* (1974). **B30**, 427

## Preparation and Structure Determination of $Ti_8S_3$

BY J. P. OWENS AND H. F. FRANZEN

*Ames Laboratory-USAEC and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.*

(Received 1 June 1973; accepted 8 October 1973)

$Ti_8S_3$  is monoclinic  $C2/m$ ,  $a=32.69$  (1),  $b=3.327$  (2),  $c=19.36$  (2) Å,  $\beta=139.9$  (5)°,  $V=1356$  (7) Å<sup>3</sup>. The structure was determined by single-crystal methods and refined to  $R=0.08$  by least-square calculations. The composition was deduced from the structure. There are a great many structural similarities between  $Ti_8S_3$  and  $Ti_2S$ .

### Introduction

$Ti_8S_3$  was first prepared by heating 150 mg of a pelletized mixture of TiS and titanium metal with an overall Ti/S ratio of 3.0 to 1125°C. The small single crystal used in structure determination was obtained from the partially melted pellet which was a mixture of  $Ti_8S_3$  and  $Ti_2S$ . Rotation and zero and first-layer Weissenberg patterns indicated that the crystal was  $C$ -centered monoclinic with the crystal-rotation axis coincident with the unique crystallographic  $b$  axis of the unit cell. The conditions for reflection were observed to be

$$\begin{aligned} hkl: & h+k=2n \\ h0l: & h=2n \\ 0k0: & k=2n \end{aligned}$$

The possible space groups consistent with this observation are  $C2$ ,  $Cm$ , and  $C2/m$ .  $C2$  was ruled out because the unitary structure factors for the  $h0l$  and  $h2l$  reflections were essentially equal, indicating that the atoms are located in mirror planes perpendicular to the  $b$  axis.

Single-crystal X-ray diffraction data were collected with a Hilger-Watts four-circle automated diffractometer, coupled with an SDS 910 computer as described by Dahm, Bensen, Nimrod, Fitzwater & Jacobson

(1967). Peak-height intensities were measured. Zirconium-filtered Mo  $K\alpha$  radiation was used to obtain data for non-extinguished reflections in the first two octants with  $\theta \leq 30^\circ$ . Lorentz and polarization corrections were applied, but owing to the very small size of the crystal, no absorption correction was made. The crystal dimensions were approximately  $10\mu \times 10\mu \times 50\mu$ .

The fluctuation level of the counter was assumed to be proportional to the square root of the total counts and the statistical uncertainties of the intensity data were taken to be  $(A+B)^{1/2}/(A-B)$ , where  $A$  and  $B$  are peak and background counts respectively. Of the 2351 intensity data collected 713 had uncertainties less than 33%.

A Howells, Phillips & Rogers plot proved to be an inconclusive test for a center of symmetry. The structure was determined by *MULTAN* techniques (Germain, Main & Woolfson, 1971) for the non-centrosymmetric space group  $Cm$ . The criteria of this technique for judgement of the probable correctness of the various calculated solutions permitted the selection of a most probable solution. This trial structure placed atoms in 44 independent point sets. The titanium and sulfur positions were distinguished by examining the atomic coordination polyhedra. It was noted that a center of symmetry was present in the trial structure which implied that  $C2/m$  rather than  $Cm$  was the cor-