interaction angle S–O(13)–I′ is 140°. No attempt has been made to locate the hydrogen atoms in the structure.

The authors wish to thank the U.S. Atomic Energy Commission for financial support under contract AT(11-1)-120, the staff of the Indiana University Research Computing Center for assistance in performing the computations, and Kirsten Folting Streib for modification of some of the programs used in these determinations.

References

ARCHER, E. M. (1948). *Acta Cryst.* **1**, 64.
BALLARD, R. E. & EDWARDS, J. W. (1964). *J. Chem. Soc*, p.4868.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
CRUICKSHANK, D. W. J. & JONES, D. W. (1963). *Acta Cryst.* **16**, 877.
CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.
DATTA, S. K. (1959). Ph.D. Dissertation, Indiana University.
DAWSON, B. (1960). *Acta Cryst.* **13**, 403.
GROTH, P. & HASSEL, O. (1965). *Acta Chem. Scand.* **19**, 1733.
HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
International Tables for X-ray Crystallography (1959). Vol. II, p.295. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962). Vol. III, p.202. Birmingham: Kynoch Press.
LINGAFELTER, F. C. & DONOHUE, J. (1966). *Acta Cryst.* **20**, 321.
MATSUMURA, K. (1927). *J. Amer. Chem. Soc.* **49**, 810.
MERRITT, L. L., JR & WALKER, J. K. (1944). *Anal. Chem.* **16**, 387.
NASANEN, R. & EKMAN, A. (1952). *Acta Chem. Scand.* **6**, 1384.
PALENIK, G. J. (1964*a*). *Acta Cryst.* **17**, 687.
PALENIK, G. J. (1964*b*). *Acta Cryst.* **17**, 696.
RAE, A. I. M. & MASLEN, E. N. (1962). *Acta Cryst.* **15**, 1285.
SASS, R. L. (1960). *Acta Cryst.* **13**, 320.
SUTTON, L. E. (1958). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Special Publication No.11. London: The Chemical Society.
THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 239.
WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.

Acta Cryst. (1970). B**26**, 744

The Crystal Structure of Bis-(2-methylpentane-2,4-dioxydimethyltitanium), $[(CH_3)_2TiO_2C_6H_{12}]_2$

BY AKIE YOSHINO, YASUSUKE SHUTO* AND YOICHI IITAKA

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo, Japan

(*Received* 3 *July* 1969)

The crystal structure of bis-(2-methylpentane-2,4-dioxydimethyltitanium), $[(CH_3)_2TiO_2C_6H_{12}]_2$, has been determined by the X-ray diffraction method. The crystals are monoclinic with space group $P2_1/n$ and the unit-cell dimensions are, $a=14{\cdot}16$, $b=12{\cdot}95$, $c=12{\cdot}09$ Å, $\beta=103{\cdot}0°$. There are four formula units, $[(CH_3)_2TiO_2C_6H_{12}]_2$, per unit cell. The atomic parameters were refined by the block-matrix least-squares method allowing for anisotropic thermal vibration. The final R value for 1107 observed structure factors was 0·158.

The structure of the complex molecule was found to consist of two units with essentially the same structure, 2-methylpentane-2,4-dioxydimethyltitanium, joined together by a shared oxygen atom at the 4-position to form a binuclear dimer molecule. Each of the two titanium atoms coordinates three oxygen and two methyl carbon atoms forming a trigonal bipyramidal pentacoordinated group. The lengths of the titanium–methyl-carbon bonds range from 2·11 to 2·19 Å.

Introduction

During the last decade a number of organometallic complexes containing titanium have been synthesized and their structures and catalytic activities in polymerization reactions of ethylene and other olefins have been investigated (Natta & Mazzanti, 1960). Most of these compounds, however, involve the cyclopentadienyl groups which are bound to titanium by means of σ–π bonds and only a few compounds have been reported in which the alkyl groups are bound to the titanium atom through σ bonds. Among the latter type of compound, dicyclopentadienyl dimethyltitanium (Piper & Wilkinson, 1956) is the only substance which is stable at room temperature.

* Permanent address: Research department, Idemitsu Kosan Co. Ltd., Tokuyama, Yamaguchi-Prefecture, Japan.

One of the present authors (Shuto, 1969) has synthesized a new complex having the formula $[(CH_3)_2TiO_2C_6H_{12}]_2$ by means of the Grignard reaction. This compound is stable at room temperature and its chemical properties have been studied in detail. However, it has not been possible to determine the structure of the complex conclusively by any other method than X-ray diffraction.

Experimental

$[(CH_3)_2TiO_2C_6H_{12}]_2$ was synthesized by treatment of $Cl_2TiO_2C_6H_{12}$ with a Grignard reagent (methylmagnesium iodide) in tetrahydrofuran solution. The latter compound was prepared by the reaction of bis(2-methylpentane-2,4-diol)titanium (Yamamoto & Kambara, 1959) with titanium tetrachloride in benzene solution. The crystals of $[(CH_3)_2TiO_2C_6H_{12}]_2$ grown from pentane solution were monoclinic prisms elongated along the b axis with well developed $\{101\}$ and $\{10\bar{1}\}$ faces. They were pale yellow in colour becoming opaque upon exposure to air owing to reaction with oxygen and water. When a small amount of water is present they undergo a rapid change and decompose to methane and a titanate. Several crystals were then covered with wax and sealed in Lindemann glass capillaries which were filled with nitrogen gas.

The cell dimensions and space group were determined from Weissenberg and precession photographs taken with Cu $K\alpha$ radiation.

Crystal data

$[(CH_3)_2TiO_2C_6H_{12}]_2$, M.W. 388·24.
Monoclinic,
$a = 14{\cdot}16 \pm 0{\cdot}01$, $b = 12{\cdot}95 \pm 0{\cdot}01$, $c = 12{\cdot}09 \pm 0{\cdot}01$ Å,
$\beta = 103{\cdot}0° \pm 0{\cdot}2°$.
$U = 2160{\cdot}6$ Å^3.
$D_x = 1{\cdot}191$ g.cm^{-3}.
Linear absorption coefficient for Cu $K\alpha$ radiation, 20·9 cm^{-1}.
$F(000) = 832$.
Absent reflexions, $h0l$ when $h+l=2n+1$,
$0k0$ when $k=2n+1$.
Space group, $P2_1/n$.

The three-dimensional reflexions of $h0l$–$h8l$ and $hk0$–$hk2$ were recorded with nickel filtered Cu $K\alpha$ radiation on equi-inclination Weissenberg photographs taken about the b and the c axes respectively. The intensities of these reflexions were visually estimated by using a standard scale.

The X-ray specimens used for the intensity measurement were prisms of about $0{\cdot}3 \times 0{\cdot}3 \times 0{\cdot}3$ mm in size. Since the μR values of these specimens were about 0·62, no absorption correction was applied. All the intensity data were then corrected for Lorentz and polarization factors. The resulting values were put on a single scale and a total of 1107 structure factors were evaluated. A Wilson plot gave an approximate scale factor and an overall temperature factor B of 0·86 Å^2.

Determination of the structure

The positions of the titanium atoms were determined from the three-dimensional sharpened Patterson function. It was soon noticed that both of the two crystallographically independent titanium atoms were situated approximately on the glide planes at $y=\frac{1}{4}$ and $\frac{3}{4}$. Since the y coordinates of the titanium atoms are rather special, two plausible arrangements of these atoms could be considered depending on whether the predominant peaks on the Harker section were the real Harker peaks or non-Harker peaks. Although two

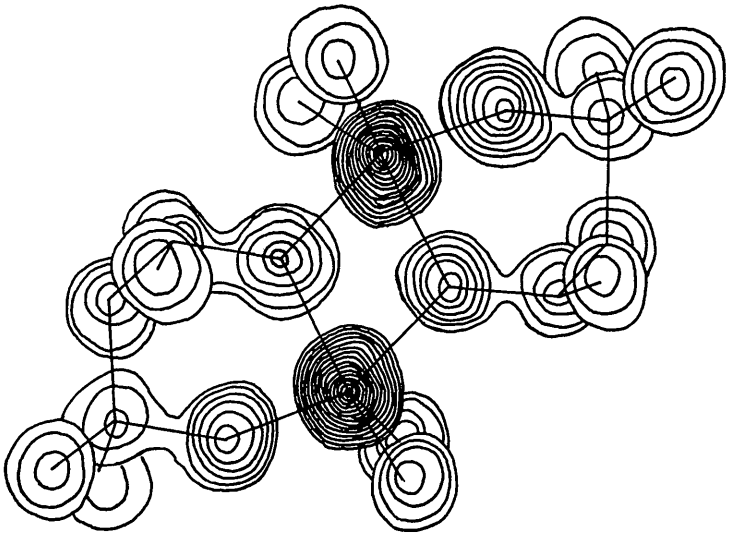


Fig. 1. Composite electron density contour sections superimposed on (010). The atomic configuration of the complex molecule illustrating the contour map is shown in Fig. 2. Contours are drawn at intervals of 1 e.Å^{-3}, starting at 1 e.Å^{-3}.

structural models could be constructed on the basis of these two arrangements and they refined equally well using the two-dimensional ($h0l$) data, the three-dimensional analysis by the method of Fourier and difference Fourier syntheses led to the correct answer. The pseudo-mirror symmetries which appeared on $y=\frac{1}{4}$ and $\frac{3}{4}$ as a result of the special arrangement of the titanium atoms, were eliminated by putting the methyl carbon atom C(4) off the mirror plane.

The structure was then refined by Fourier and difference Fourier methods coupled with least-squares calculations. The final refinement of the atomic parameters was carried out by the block-matrix least-squares method using the program by Okaya & Ashida (1967). In this calculation, all the atoms except hydrogen were included and the individual anisotropic thermal vibrations were allowed for. The weighting system adopted for the final three cycles of calculation was:

$$\sqrt{w}=9\cdot1/F_o, \text{ when } 9\cdot1<F_o,$$
$$\sqrt{w}=1 \quad , \text{ when } 1\cdot8<F_o\leq 9\cdot1,$$
$$\sqrt{w}=0 \quad , \text{ when } F_o\leq 1\cdot8 .$$

The final R value was 0·158 for all 1107 observed reflexions.

At this stage the final Fourier synthesis was computed. The resulting superimposed contour sections, illustrating the three-dimensional electron density distribution, are shown in Fig. 1. The final fractional

Table 1. *Final atomic parameters and their standard deviations*

x, y and z are the fractional coordinates. The temperature factors are expressed in the form

$$T=\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right].$$

The e.s.d.'s given in parentheses are in units of the least significant digits given for the corresponding parameters.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti(1)	0·0008 (3)	0·2362 (4)	1·0212 (4)	0·0035 (2)	0·0069 (5)	0·0043 (3)	−0·0006 (3)	0·0015 (2)	−0·0001 (3)
Ti(1′)	0·2144 (4)	0·2319 (5)	0·9689 (4)	0·0048 (3)	0·0067 (5)	0·0069 (4)	−0·0011 (3)	0·0015 (3)	−0·0001 (4)
O(1)	−0·0178 (11)	0·2657 (14)	1·1573 (14)	0·0033 (9)	0·0061 (17)	0·0071 (15)	−0·0027 (10)	0·0005 (10)	0·0011 (13)
O(2)	0·1442 (12)	0·2273 (15)	1·0921 (13)	0·0047 (10)	0·0081 (19)	0·0048 (13)	−0·0017 (11)	0·0035 (10)	−0·0004 (13)
O(1′)	0·2321 (14)	0·2417 (18)	0·8284 (15)	0·0059 (12)	0·0133 (24)	0·0065 (15)	−0·0021 (14)	0·0041 (12)	0·0001 (16)
O(2′)	0·0753 (11)	0·2107 (16)	0·8957 (14)	0·0026 (9)	0·0084 (18)	0·0081 (16)	−0·0009 (11)	0·0027 (10)	−0·0015 (14)
C(1)	0·0251 (20)	0·3126 (33)	1·2736 (23)	0·0047 (18)	0·0173 (41)	0·0059 (23)	−0·0023 (23)	0·0023 (17)	0·0013 (27)
C(2)	0·1348 (21)	0·3195 (22)	1·2646 (17)	0·0090 (22)	0·0043 (24)	0·0016 (14)	−0·0009 (18)	0·0036 (15)	0·0024 (16)
C(3)	0·1780 (23)	0·2291 (22)	1·2167 (22)	0·0087 (22)	0·0042 (27)	0·0057 (21)	0·0023 (19)	0·0003 (19)	0·0000 (20)
C(4)	−0·0054 (20)	0·2343 (30)	1·3494 (25)	0·0042 (15)	0·0169 (43)	0·0090 (27)	0·0029 (23)	0·0040 (18)	0·0051 (29)
C(5)	−0·0202 (22)	0·4194 (27)	1·2716 (35)	0·0054 (21)	0·0068 (33)	0·0209 (49)	0·0043 (22)	−0·0017 (27)	−0·0020 (32)
C(6)	0·1695 (27)	0·1152 (24)	1·2584 (21)	0·0140 (31)	0·0038 (27)	0·0039 (20)	0·0035 (23)	0·0030 (22)	0·0009 (18)
C(7)	−0·1004 (25)	0·1160 (29)	0·9715 (21)	0·0118 (29)	0·0124 (36)	0·0030 (20)	−0·0035 (25)	0·0054 (20)	−0·0035 (22)
C(8)	−0·0675 (22)	0·3729 (29)	0·9319 (29)	0·0044 (17)	0·0120 (37)	0·0122 (34)	0·0004 (22)	0·0018 (20)	−0·0002 (29)
C(1′)	0·1865 (27)	0·2680 (24)	0·7147 (28)	0·0109 (29)	0·0036 (28)	0·0113 (32)	−0·0014 (21)	0·0003 (26)	0·0017 (24)
C(2′)	0·0751 (18)	0·2716 (21)	0·7058 (21)	0·0043 (14)	0·0055 (26)	0·0057 (20)	0·0026 (17)	−0·0008 (14)	−0·0002 (19)
C(3′)	0·0298 (17)	0·1880 (23)	0·7806 (18)	0·0041 (15)	0·0058 (24)	0·0030 (16)	−0·0012 (16)	0·0004 (14)	0·0009 (17)
C(4′)	0·2164 (24)	0·1870 (33)	0·6312 (21)	0·0081 (23)	0·0175 (42)	0·0028 (18)	0·0044 (27)	0·0016 (18)	−0·0028 (24)
C(5′)	0·2258 (35)	0·3776 (29)	0·6835 (29)	0·0176 (43)	0·0085 (36)	0·0095 (33)	0·0012 (31)	0·0069 (32)	0·0024 (27)
C(6′)	0·0511 (23)	0·0720 (27)	0·7556 (21)	0·0082 (23)	0·0108 (34)	0·0037 (21)	−0·0031 (23)	0·0018 (18)	−0·0014 (21)
C(7′)	0·3133 (15)	0·1142 (26)	1·0367 (26)	0·0001 (10)	0·0112 (32)	0·0117 (29)	0·0013 (16)	−0·0000 (15)	−0·0033 (26)
C(8′)	0·2739 (22)	0·3836 (30)	1·0258 (30)	0·0054 (19)	0·0106 (36)	0·0148 (38)	−0·0063 (22)	−0·0009 (24)	−0·0074 (30)

atomic coordinates and temperature factors are given in Table 1, together with their standard deviations.

The average values of the standard deviations in the positional parameters were estimated as: for titanium atoms, $\sigma(r)=0{\cdot}015$ Å, for oxygen atoms, $\sigma(r)=0{\cdot}018$ Å and for carbon atoms $\sigma(r)=0{\cdot}031$ Å. The observed and calculated structure factors are listed in Table 2. The atomic scattering factors used for the present structure determination were: for titanium, those of Freeman & Watson (1961) and for oxygen and carbon, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

Discussion of the structure

The molecular structure

Figs. 1 and 2 show the structure of the complex molecule viewed along the *b* axis. The intramolecular bond lengths and angles calculated from the atomic coordinates given in Table 1 are shown in Figs. 2 and 3. Contrary to the expectation based on the various chemical and spectral data, it is now shown that the complex molecule has a binuclear dimer structure. It consists of two essentially identical structural units of 2-methylpentane-2,4-dioxy-dimethyltitanium, joined

Table 2. *Observed and calculated structure factors*

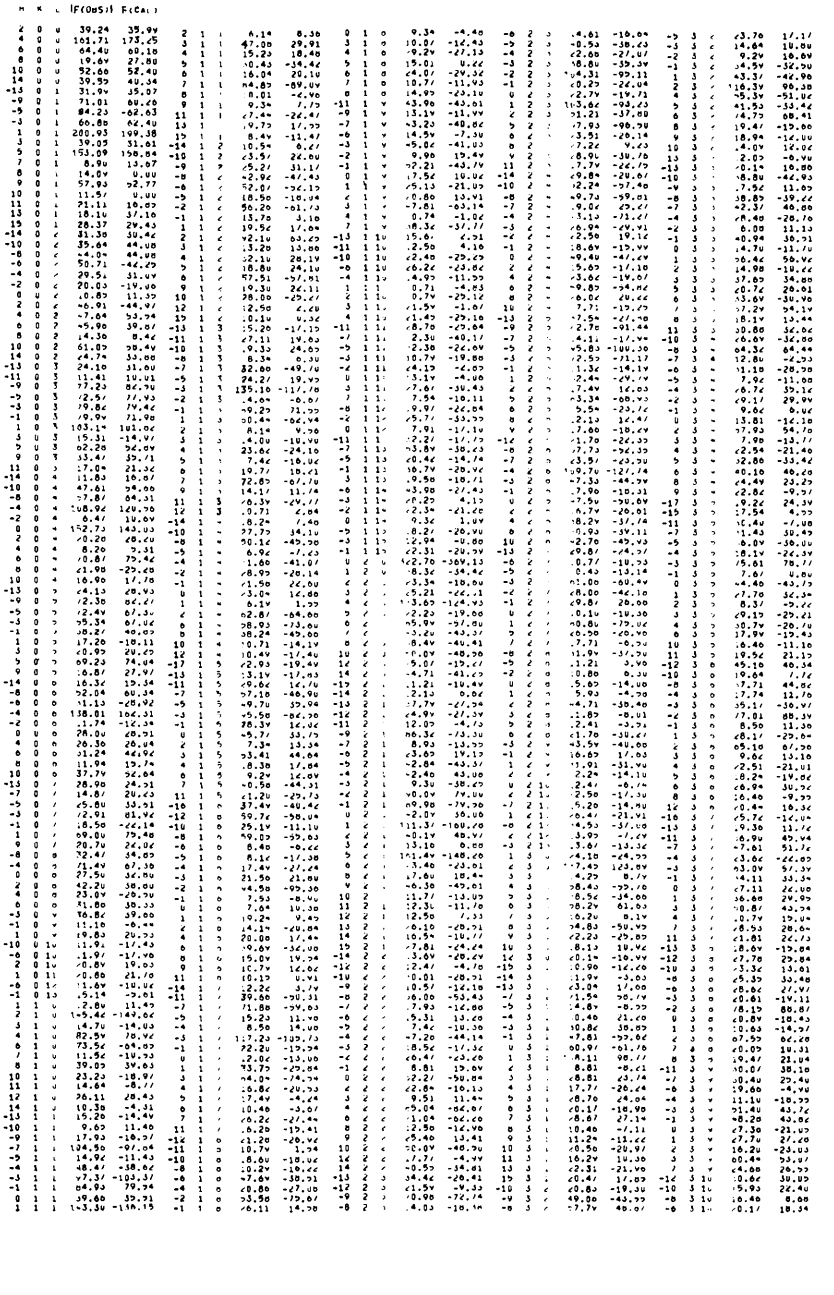
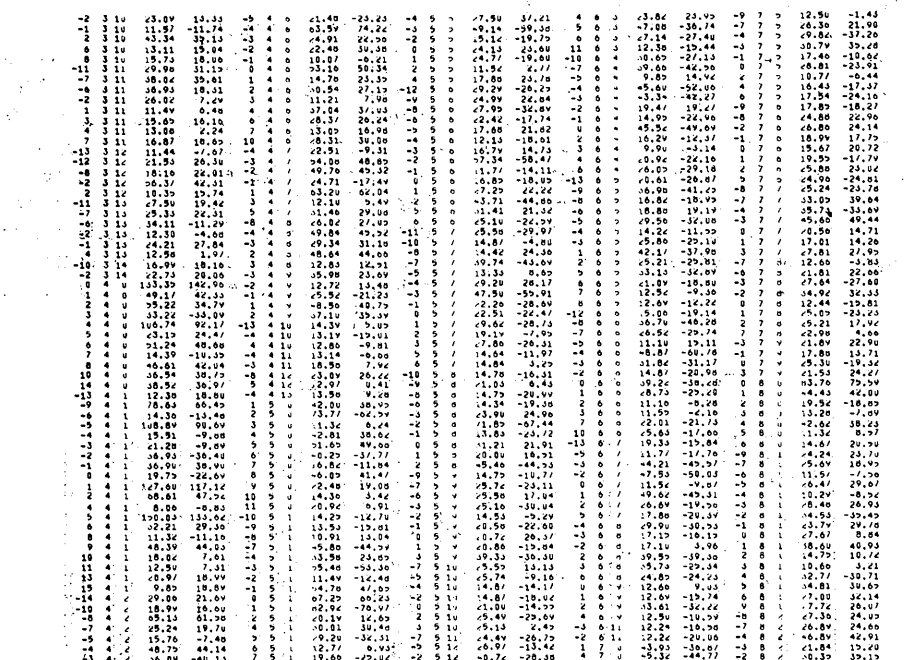


Table 2 (*cont.*)



together by sharing their oxygen atoms at the 4-position to form a binuclear complex molecule. Although these two structural units are not related by any strict symmetry element and they are crystallographically independent, the complex molecule has a pseudo-twofold rotation axis passing through the midpoint between the two titanium atoms. The ligand molecule, 2-methylpentane-2,4-diol, has an asymmetric carbon atom at the 4-position and each complex molecule consists of the same kind of optically active ligand molecules. The present crystal is composed of two kinds of such complex molecules which are mutually antipodic and related by a centre of symmetry.

It is to be noted that each titanium atom coordinates three oxygen and two carbon atoms at distances ranging from 1·77 to 2·19 Å, forming a pentacoordinated group. The configuration of the coordinated atoms around each titanium atom is trigonal bipyramidal. In Table 3 the bond distances and angles are listed in groups of similar type. It will be seen that the Ti–O distances vary considerably: the shortest is as short as 1·77 Å while the longest is 2·06 Å. These Ti–O distances can be divided into two categories: the longer bonds which range from 1·97 to 2·06 Å are all found in the oxygen μ-bridges while the shortest two, 1·77 and 1·78 Å, do not participate in the bridge.

In inorganic compounds, titanium atoms usually adopt the octahedral coordination, but in some cases they adopt the fivefold coordination. Table 3 shows the Ti–O distances found in various inorganic compounds. In the case of fivefold coordination, the arrangement of the ligand atoms about the titanium atom is either

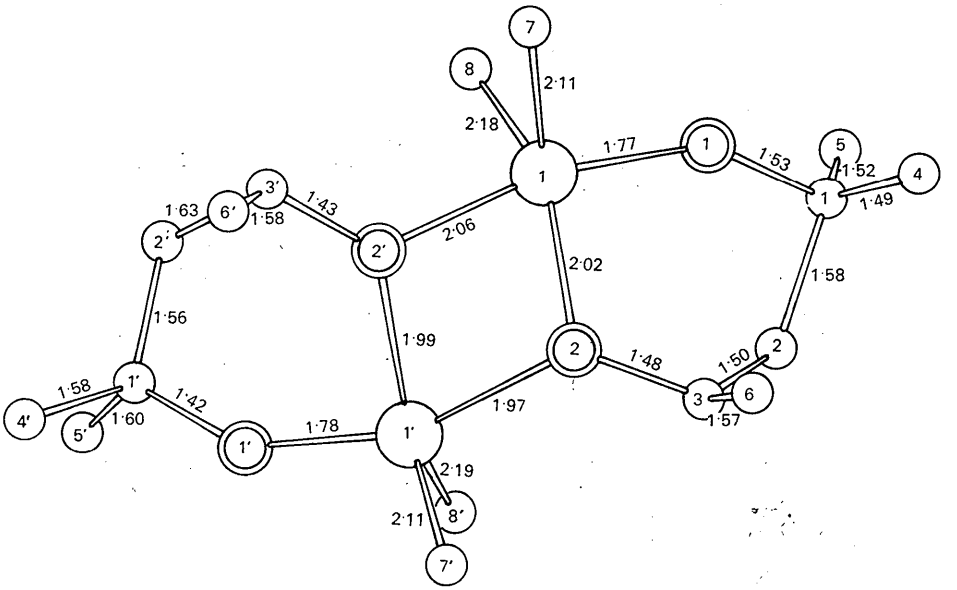


Fig. 2. The structure of the complex molecule showing the configuration and the bond lengths (Å). Large circles indicate titanium, small circles carbon and double circles oxygen atoms.

Table 3. Ti–O *distances found in various inorganic compounds*

Compound	Ti–O distances	No. of equivalent bonds	Reference
	Sixfold Ti coordination		
Rutile	1·944 Å	4	Baur (1955; 1956)
	1·988	2	
Anatase	1·937	4	Cromer & Herrington (1955)
	1·964	2	
Brookite	1·87	1	Baur (1961)
	1·92	1	
	1·94	1	
	1·99	1	
	2·00	1	
	2·04	1	
$BaTiO_3$	1·86	1	Shirane, Jona & Pepinsky (1955)
(Tetragonal)	2·00	4	
	2·17	1	
$PbTiO_3$	1·78	1	Shirane, Jona & Pepinsky (1955
(Tetragonal)	1·98	4	
	2·38	1	
	Fivefold Ti coordination		
Y_2TiO_5	1·78	1	Mumme & Wadsley (1968)
	1·87	1	
	1·91	1	
	1·94	2	
$K_2Ti_2O_5$	1·57	1	Andersson & Wadsley (1961)
	1·67	1	
	2·00	1	
	2·00	2	
$Ba_2TiSi_2O_8$	1·66	1	Moore & Louisnathan (1967)
(Fresnoite)	2·00	4	

Table 4. *Bond lengths arranged in groups of similar type*

The e.s.d.'s are given in parentheses.

Present complex		Dichlorodiphenoxytitanium (Watenpaugh & Caughlan, 1966)	
Ti–O bonds		Ti–O bonds	
Ti(1) –O(1)	1·77 (0·02) Å	Ti(1)–O(5)	1·744 (0·010) Å
Ti(1′)–O(1′)	1·78 (0·02)		
In oxygen μ-bridges		In oxygen μ-bridges	
Ti(1) –O(2)*	2·02 (0·02)	Ti(1)–O(4)*	1·910 (0·009)
Ti(1) –O(2′)*	2·06 (0·02)	Ti(1)–O(4′)*	2·122 (0·009)
Ti(1′)–O(2)*	1·97 (0·02)		
Ti(1′)–O(2′)*	1·99 (0·02)		
Distance between titanium atoms		Distance between titanium atoms	
Ti(1) –Ti(1′)	3·225 (0·007)	Ti(1)–Ti(1′)	3·274 (0·003)
Ti–C bonds		Ti–Cl bonds	
Ti(1) –C(7)	2·11 (0·04)	Ti(1)–Cl(2)	2·209 (0·006)
Ti(1′)–C(7′)	2·11 (0·04)	Ti(1)–Cl(3)	2·219 (0·006)
Ti(1) –C(8)	2·18 (0·04)		
Ti(1′)–C(8′)	2·19 (0·04)		
C–O bonds		C–O bonds	
C(1) –O(1)	1·53 (0·03)	C(12)†–O(5)	1·359 (0·019)
C(1′)–O(1′)	1·42 (0·04)	C(6)†—O(4)*	1·422 (0·014)
C(3) –O(2)*	1·48 (0·03)		
C(3′)–O(2′)*	1·43 (0·03)		
C–C bonds			
C(1) –C(2)	1·58 (0·04)		
C(1) –C(4)	1·49 (0·05)		
C(1) –C(5)	1·52 (0·05)		
C(2) –C(3)	1·50 (0·04)		
C(3) –C(6)	1·57 (0·04)		
C(1′)–C(2′)	1·56 (0·05)		
C(1′)–C(4′)	1·58 (0·05)		
C(1′)–C(5′)	1·60 (0·05)		
C(2′)–C(3′)	1·63 (0·04)		
C(3′)–C(6′)	1·58 (0·05)		
Mean value	1·561		

* Bridging oxygen atoms.
† Phenyl carbon atoms.

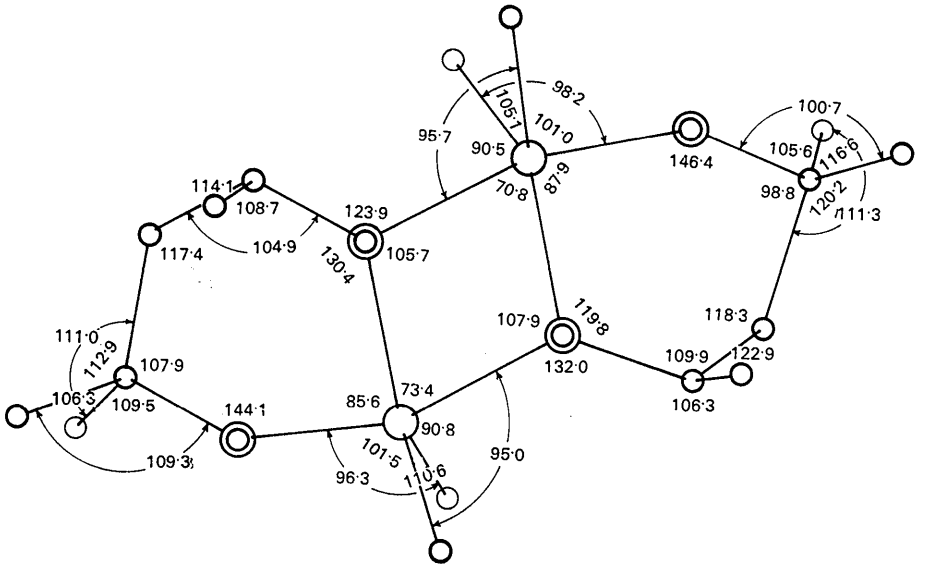


Fig. 3. Bond angles (°). Some of the angles subtended at the titanium atoms not shown in this Figure are presented in Fig. 4.

Table 5. *Deviations of atoms from the least-squares planes*

The planes are of the form $AX+BY+CZ=D$, where X, Y, Z and D are in Å units relative to the axes a^*, b and c.

Planes involving titanium atoms

Present complex				Dichlorodiphenoxytitanium*	
Ti(1)	0·143 Å	Ti(1′)	−0·113 Å	Ti(1)	−0·184 Å
C(7)	−0·046	C(7′)	0·036	Cl(2)	0·055
C(8)	−0·041	C(8′)	0·034	Cl(3)	0·057
O(2)	−0·056	O(2′)	0·043	O(4)	0·072
A	−0·2789	*A*	−0·2943	*A*	0·0176
B	0·2041	*B*	−0·0448	*B*	0·8528
C	0·9384	*C*	0·9546	*C*	0·5219
D	0·7160	*D*	−1·9038	*D*	7·4232
Ti(1)	0·011	Ti(1)	0·005	Ti(1)	−0·003
Ti(1′)	0·013	Ti(1′)	0·006	Ti(1′)	−0·003
O(2)	−0·043	O(2′)	−0·020	O(4)	0·010
C(3)	0·019	C(3′)	0·009	C(6)	−0·005
A	0·0279	*A*	−0·0766	*A*	0·9971
B	0·9994	*B*	0·9738	*B*	−0·0672
C	0·0180	*C*	−0·2142	*C*	0·0360
D	3·0519	*D*	2·9192	*D*	4·5736
Ti(1)	−0·044	Ti(1′)	−0·058	Ti(1)	0·000
O(2)	−0·009	O(2)	0·034	O(4)	0·000
O(2′)	0·025	O(2′)	−0·012	O(4′)	0·000
O(1)	0·028	O(1′)	0·036	O(5)	0·000
A	0·1078	*A*	−0·1636	*A*	0·9978
B	0·9810	*B*	0·9865	*B*	−0·0565
C	−0·1612	*C*	−0·0046	*C*	0·0333
D	3·0059	*D*	2·5413	*D*	4·6369

Ti(1)	0·000 Å	Ti(1)	−0·015
Ti(1′)	−0·000	Ti(1′)	−0·027
O(4)	0·000	O(2)	−0·209
O(4′)	−0·000	O(2′)	−0·219
O(5)	−0·000	O(1)	0·228
O(5′)	0·000	O(1′)	0·242
A	0·9978	*A*	−0·0226
B	−0·0565	*B*	0·9962
C	0·0333	*C*	−0·0841
D	4·6369	*D*	3·0411
Ti(1)	−0·000	Ti(1)	0·181
Ti(1′)	0·000	Ti(1′)	0·169
O(4)	0·011	O(2)	−0·029
O(4′)	−0·011	O(2′)	−0·007
C(6)	−0·005	C(3)	−0·153
C(6′)	0·005	C(3′)	−0·162
A	0·9972	*A*	−0·0279
B	−0·0659	*B*	0·9949
C	0·0358	*C*	−0·0964
D	4·5790	*D*	2·8383

Planar groups in ligand molecules

Ti(1)	−0·052	Ti(1′)	−0·060
O(1)	0·035	O(1′)	0·035
O(2)	0·065	O(2′)	0·082
C(3)	−0·048	C(3′)	−0·058
A	0·1461	*A*	−0·2107
B	0·9784	*B*	0·9775
C	−0·1464	*C*	−0·0121
D	3·0095	*D*	2·3845

Distances from the above planes

C(1)	0·530	C(1′)	0·515
C(2)	0·906	C(2′)	0·881
C(6)	−1·586	C(6′)	−1·584

* Calculated from the coordinates given by Watenpaugh & Caughlan (1966).

square pyramidal (in Y_2TiO_5 and $Ba_2TiSi_2O_8$) or trigonal bipyramidal (in $K_2Ti_2O_5$).

In organic compounds, titanium atoms exhibit both the sixfold and fivefold coordination as in the case of inorganic compounds. Some examples of the structure in which the pentacoordinated titanium atom is involved are shown below.

In dichlorodiphenoxytitanium, $[TiCl_2(OC_6H_5)_2]_2$ (Watenpaugh & Caughlan, 1966), the two titanium atoms are joined together through two oxygen μ-bridges and each titanium atom is surrounded by three oxygen and two chlorine atoms in the form of a trigonal bipyramid. The complex molecule possesses a centre of symmetry in place of the twofold rotation axis found in the present compound. The three kinds of Ti–O bonds have lengths 1·910, 2·122 and 1·744 Å and the two kinds of Ti–Cl bonds are 2·209 and 2·219 Å. The two longest Ti–O bonds are associated with the oxygen μ-bridges.

A similar binuclear dimer structure of titanium complexes has been found in diethoxytitanium dichloride, $[TiCl_2(OC_2H_5)_2]_2$ (Haase & Hoppe, 1968*a*), in which the titanium atom is surrounded by three oxygen atoms at distances of 1·77, 1·96 and 2·02 Å and by two chlorine atoms at 2·19 and 2·20 Å. In di(tetraethylammonium) tetrachlorooxotitanate, $[N(C_2H_5)_4]TiCl_4O$ (Haase & Hoppe, 1968*b*), the titanium atom is coordinated by two sets of four chlorine atoms at distances of 2·34 and 2·32 Å and by an oxygen atom at 1·79 Å, the configuration of the complex ion being tetragonal pyramidal. The structure of the complex molecule found in the present compound may be compared with those found in dichlorodiphenoxytitanium and diethoxytitanium dichloride. All of these molecules take a binuclear dimer structure involving two titanium atoms of trigonal bipyramidal fivefold coordination. The bond lengths and angles are compared in Table 4. The structure of diethoxytitanium dichloride will not be discussed further here, since the published data are still preliminary (Haase & Hoppe, 1968*a*). Fig. 4 illustrates the coordination around the titanium atoms involved in the above two compounds. As shown in Table 5, each of the equatorial planes of the trigonal bipyramids formed by Ti(1), O(2), C(7), C(8) and Ti(1′), O(2′), C(7′), C(8′) in the present compound and Ti, Cl(2), Cl(3), O(4) in dichlorodiphenoxytitanium are roughly coplanar, the sums of the mean-square deviations of the atoms from the plane being 0·027, 0·017 and 0·04 Å^2 respectively. In all these three cases, the angle between the two bonds joining the central titanium atom and the apexes of the pyramid deviates considerably from 180°, indicating a strong distortion of the coordination polyhedra. It should be noted that the Ti–O distances involved in the oxygen μ-bridges are nearly of the same order of magnitude as those found in rutile, anatase and brookite, whereas the Ti–O distances which are not involved in the bridge are extremely short. In rutile, anatase and brookite, the oxygen atoms are shared by the titanium atoms, like those in the μ-bridge, and the Ti–O distances are considered to correspond to the sum of the ionic radii of titanium and oxygen. In dichlorodiphenoxytitanium and in the present compound, each of the two bridged oxygen atoms takes a planar bonding configuration and the dihedral angles between the two planes Ti(1), O(4), C(6), Ti(1′) and Ti(1), O(4′), C(6′), Ti(1′) in the former compound and Ti(1), O(2), C(3), Ti(1′) and Ti(1), O(2′), C(3′), Ti(1′) in the latter are 0° and 14°35′ respectively.

A particularly noteworthy feature of the present structure is the presence of Ti–C bonds which are considered to have a nearly pure σ-bond character. The lengths of these bonds range from 2·11 to 2·19 Å, and the difference between the two bonds attached to each titanium atom seems to be significant, although the difference is almost within the limit of experimental error. Thus, the bond Ti(1)–C(8) is longer than Ti(1)–C(7) by 0·07 Å and Ti(1′)–C(8′) is 0·08 Å longer than Ti(1′)–C(7′). The chemical shifts observed in the nuclear magnetic resonance spectra of the two kinds

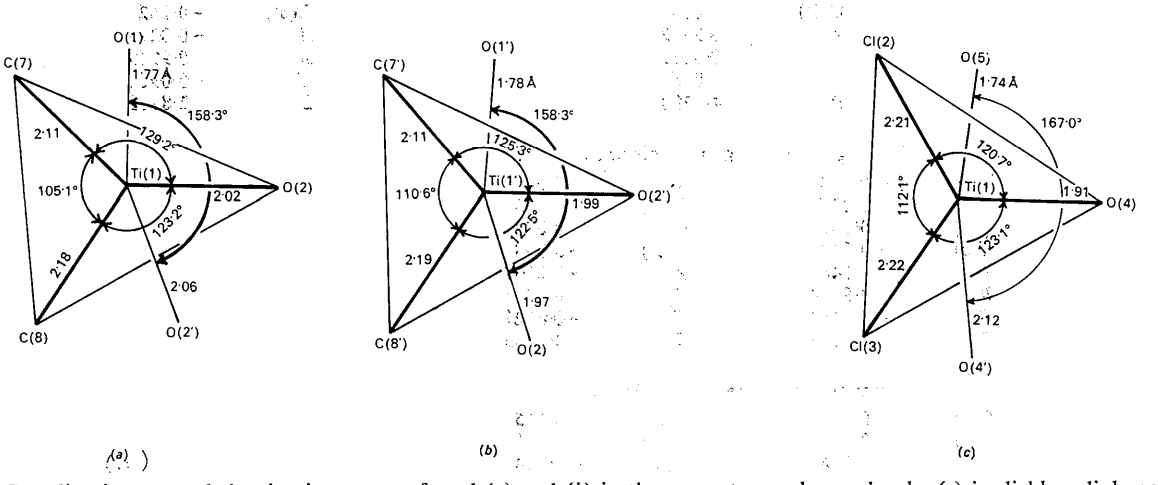


Fig. 4. Coordination around the titanium atoms found (*a*) and (*b*) in the present complex molecule, (*c*) in dichlorodiphenoxytitanium (Watenpaugh & Caughlan, 1966).

of methyl protons [protons in the $C(7)H_3$ and $C(8)H_3$ groups which are equivalent to $C(7')H_3$ and $C(8')H_3$ respectively, in solution] differ slightly, indicating that they are not equivalent. The reaction properties investigated in the present compound indicate that the Ti–C bonds are quite labile and active for many chemical reagents. In a protonic solvent, the compound undergoes a rapid change to give methane gas and a titanate. Some of these investigations suggest a difference in reactivity of the two kinds of methyl group (Shuto, 1969).

The distances between the titanium and carbon atoms may be compared with those found in TiC. This structure is known to be of the sodium chloride type, but the composition varies over wide range. For the equimolar compound, the lattice constant was reported to be $a=4{\cdot}321$ Å and the shortest distance between the titanium and carbon atoms may be estimated to be about 2·16 Å. Organometallic complexes containing titanium have been extensively investigated by Natta and the structures of several cyclopentadienyl complexes have been elucidated by the X-ray diffrac-

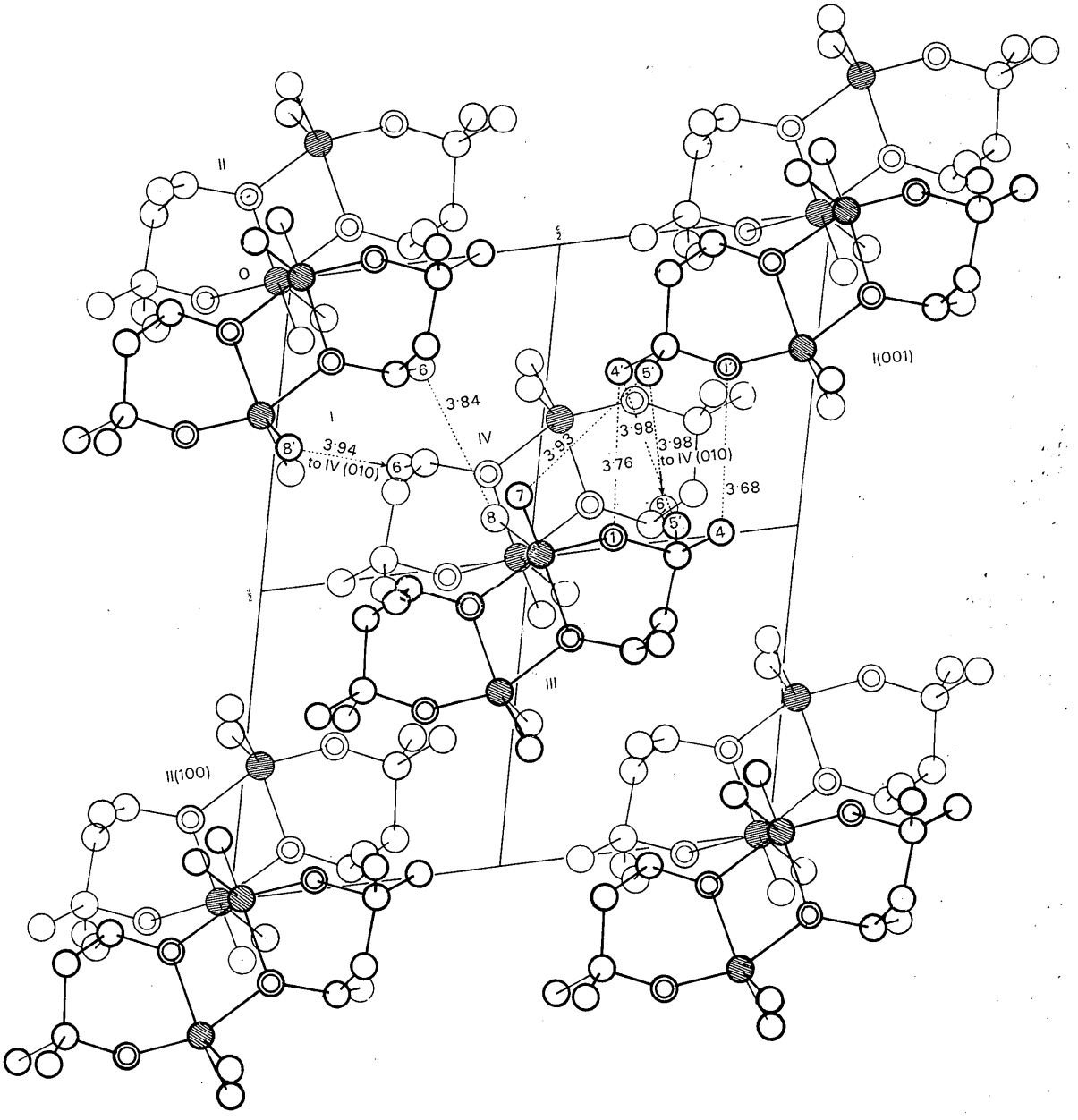


Fig. 5. Projection of the crystal structure along the *b* axis. Closest intermolecular contacts shorter than 4 Å are shown by dotted lines. Open circles indicate carbon, double circles oxygen and shaded circles titanium atoms.

tion method (Natta & Mazzanti, 1960). In $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ and in $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$, the plane of the cyclopentadienyl group is perpendicular to the line joining the titanium atom to the centre of the group, and the five Ti–C distances are all equal (about 2·4 Å). The cyclopentadienyl groups are considered to be bound to the titanium atom by means of σ–π bonds. A similar type of bond is found in tris-cyclooctatetraen-dititanium (Dietrich & Dierks, 1966).

The conformation of the ligand molecules may be described as follows. The atoms Ti(1), O(1), C(1), C(2), C(3) and O(2) form a six-membered ring and take a puckered conformation. As shown in Table 5, the four atoms, Ti(1), O(1), O(2) and C(3) are coplanar within the maximum deviation of 0·07 Å and the two atoms C(1) and C(2) are displaced from the plane by 0·53 and 0·91 Å respectively, in the same direction. The side chain methyl carbon atom C(6) is oriented in the axial direction from C(3). As is clearly seen in Table 5, the other half of the complex molecule, consisting of the atoms Ti(1′), O(1′), C(1′), C(2′), C(3′) and O(2′), adopts essentially the same conformation. The C–O and C–C bond lengths found in the ligand molecules are in the range 1·42–1·53 and 1·49–1·63 Å respectively, and their mean values, 1·465 and 1·561 Å, are not far from the normal C–O and C–C single-bond lengths.

The crystal structure

The projection of the structure viewed along the *b* axis is shown in Fig. 5. Fig. 6 is another projection of the structure viewed along the *c* axis, in which some of the short intermolecular distances, less than 4·00 Å, are shown by dotted lines. The positions of the molecules are as follows: I$(x,y,z-1)$; II$(\bar{x},\bar{y},\bar{z}+1)$; III$(x+\frac{1}{2}, \bar{y}+\frac{1}{2}, z-\frac{1}{2})$; IV$(\bar{x}+\frac{1}{2}, y-\frac{1}{2}, \bar{z}+\frac{3}{2})$, with the x, y and z coordinates as given in Table 1. The subscript attached to the molecule number indicates translations along the three edges of the unit cell. As seen in these Figures, the molecules are packed together mainly through van der Waals forces between the methyl groups and there are no abnormal features in the packing.

The authors wish to express their thanks to Miss H. Nakamura for assistance in this work.

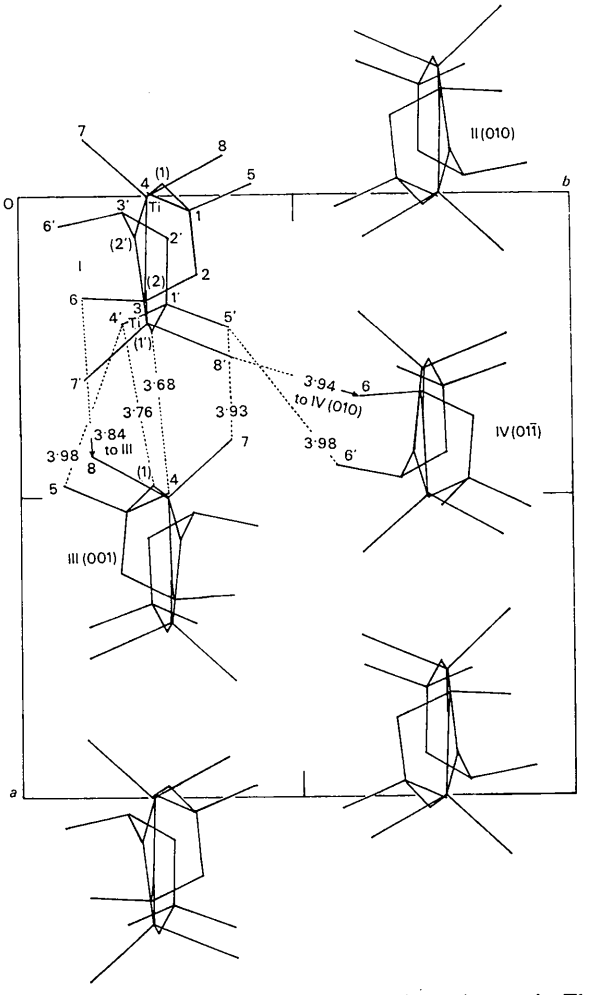


Fig. 6. Projection of the crystal structure along the *c* axis. The numbers in parentheses are the oxygen atom numbers. The closest intermolecular distances less than 4 Å are shown.

References

ANDERSSON, S. & WADSLEY, A. D. (1961). *Acta Chem. Scand.* **15**, 663.

BAUR, W. H. (1955). *Naturwissenschaften*, **42**, 295.

BAUR, W. H. (1956). *Acta Cryst.* **9**, 515.

BAUR, W. H. (1961). *Acta Cryst.* **14**, 214.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

CROMER, D. T. & HERRINGTON, K. (1955). *J. Amer. Chem. Soc.* **77**, 4708.

DIETRICH, H. & DIERKS, H. (1966). *Angew. Chem.* **78**, 943.

FREEMAN, A. J. & WATSON, R. E. (1961). *Acta Cryst.* **14**, 231.

HAASE, W. & HOPPE, H. (1968*a*). *Acta Cryst.* B**24**, 281.

HAASE, W. & HOPPE, H. (1968*b*). *Acta Cryst.* B**24**, 282.

MOORE, P. B. & LOUISNATHAN, J. (1967). *Science*, **156**, 1361.

MUMME, W. G. & WADSLEY, A. D. (1968). *Acta Cryst.* B**24**, 1327.

NATTA, G. & MAZZANTI, G. (1960). *Tetrahedron*, **8**, 88.

OKAYA, Y. & ASHIDA, T. (1957). *HBLS* IV. *The Universal Crystallographic Association Computing System* (I), p. 65. Japanese Crystallographic Association.

PIPER, T. S. & WILKINSON, G. (1956). *J. Inorg. Nucl. Chem.* **3**, 104.

SHIRANE, G., JONA, F. & PEPINSKY, R. (1955). *Some Aspects of Ferroelectricity*. Univ. Park, Pennsylvania.

SHUTO, Y. (1969). *Proc. 4th International Conference on Organometallic Chemistry*, Bristol, England.

WATENPAUGH, K. & CAUGHLAN, C. N. (1966). *Inorg. Chem.* **5**, 1782.

YAMAMOTO, A. & KAMBARA, S. (1959). *J. Amer. Chem. Soc.* **81**, 2663.