

## The Crystal and Molecular Structure of *sym-trans*-Di- $\mu$ -phenoxyhexaphenoxydiphenolatodititanium(IV)

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The crystal structure of *sym-trans*-di- $\mu$ -phenoxyhexaphenoxydiphenolatodititanium(IV),  $[\text{Ti}(\text{OC}_6\text{H}_5)_4\text{-HOC}_6\text{H}_5]_2$  has been determined by Patterson and heavy-atom methods. The crystal is monoclinic, space group  $P2_1/n$ , with cell constants  $a = 10.491$  (12),  $b = 18.409$  (28),  $c = 13.858$  (17) Å, and  $\beta = 101.54$  (25)°, containing two dimeric units per cell. Refinement by full-matrix least-squares methods yielded a final  $R$  value of 0.081. The dimer, which has two titanium atoms bridged by two phenoxy groups, is located on a center of symmetry. There are three phenoxy Ti–O bond lengths: 1.789 (9), 1.842 (11), and 1.884 (10) Å, a phenol Ti–O bond length of 2.200 (11) Å, and two equal phenoxy Ti–O bridging distances of 2.027 (10) and 2.045 (11) Å. The Ti–O–C bond angles of 168.9 (10) and 175.1 (11)°, found for two of the phenoxy oxygen atoms, are nearly linear. A decrease in the Ti–O bond distances results in a corresponding increase in the Ti–O–C bond angles for the three phenoxy groups. Hydrogen-bonding between the axial phenol and phenoxy oxygen atoms is suggested by the short oxygen–oxygen contact distance of 2.671 (13) Å, the Ti–Ti–O bond angles of 86.7 and 75.8°, and the dihedral angle of 1.4° between the two planes formed by these atoms.

### Introduction

The composition of tetra-alkoxytitanates has resulted in various molecular complexities reported from cryoscopic studies. Several results indicate that the molecular complexity increases with concentration for normal alkoxides to a limiting value of three. This value is in agreement with other studies, although if careful exclusion of moisture is maintained no concentration dependence is observed (Cullinane, Chard, Price, Millward & Langlois, 1951; Caughlan, Smith, Katz, Hodgson & Crowe, 1951; Martin & Winter, 1961, 1963; Bradley & Holloway, 1964). Ebullioscopic studies yield a value for molecular complexities of 2.5 or less with no concentration dependence (Bradley, Mehrotra & Wardlaw, 1953). Tertiary alkoxides appear to be monomeric, presumably due to steric effects of the bulky alkyl groups (Bradley, Mehrotra & Wardlaw, 1952).

Crystal structures of three tetra-alkoxytitanates are tetrameric rather than trimeric in the solid state (Ibers, 1963; Caughlan & Witters, 1965; Wright & Williams, 1968). The coordination about the titanium is octahedral, with three different titanium–oxygen bonds. There are singly bonded oxygen atoms, oxygen atoms involved in bridging two titanium atoms, and oxygen atoms bridging three titanium atoms.

Dichlorodialkoxytitanates in the solid state have trigonal bipyramidal coordination about the titanium atom, with bridging alkoxides in a dimeric unit (Caughlan & Watenpaugh, 1966; Haase & Hoppe, 1968).

In connection with structural studies of organic compounds of titanium, we are interested in the origin of the color in the titanates and the coordination about the titanium atom. The four-membered ring is especially

important in that all the titanates studied so far are colored when this ring is present. Tetra-alkoxytitanates are all colorless and are tetrameric in the solid state.

We report here the structure of *sym-trans*-di- $\mu$ -phenoxyhexaphenoxydiphenolatodititanium(IV), which is the first structure of an alkoxide dimer of titanium with octahedral coordination about the titanium atom. A preliminary report of this structure has appeared elsewhere (Svetich & Vogé, 1971).

### Experimental

*sym-trans*-Di- $\mu$ -phenoxyhexaphenoxydiphenolatodititanium(IV) was prepared by alcohol interchange. Reagent grade tetraisopropoxytitanium(IV) was added to reagent phenol (Matheson, Coleman and Bell) in a 1:5 molar ratio. Immediate formation of the orange-red product was observed upon combination of the two materials. The mixture was warmed and stirred in a moisture-free environment for a half hour period, followed by removal of isopropyl alcohol under reduced pressure. The solid product was recrystallized from toluene.

Several crystals were mounted in Pyrex glass capillaries, from which one crystal was selected for intensity data. The cell constants obtained from a rotation photograph around the  $a$  axis, zero and first layer Weissenberg photographs, and  $h0l$  precession photographs are:  $a = 10.491$  (12),  $b = 18.406$  (28),  $c = 13.858$  (17) Å,  $\beta = 101.54$  (25)°. The photographs were taken at room temperature with nickel-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å). Systematic extinctions are:  $0k0$ ,  $k \neq 2n$ , and  $h0l$ ,  $h + l \neq 2n$ . The absences are consistent with monoclinic space group  $P2_1/n$  (No. 14).

The density obtained by flotation in a methyl iodide/toluene solution is  $1.31 \text{ g.cm}^{-3}$ ; the calculated value is  $1.30 \text{ g.cm}^{-3}$  for  $Z=2$  centrosymmetric dimer units.

Intensity data were collected by multiple-film equi-inclination Weissenberg methods for the layers  $0kl$  through  $6kl$ , with the intensities obtained by compar-

Table 1. *Atomic coordinates for nonhydrogen atoms*

The number in parentheses is the standard deviation and refers to the least significant digits. Coordinates are  $\times 10^4$ .

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Ti(1)	4721 (3)	4424 (1)	5850 (2)	C(41)	3740 (29)	6000 (10)	5754 (12)
O(2)	6596 (9)	4926 (5)	6508 (6)	C(42)	2479 (31)	5867 (9)	5709 (12)
O(3)	4174 (11)	4649 (5)	6997 (6)	C(43)	1728 (20)	6384 (14)	6147 (15)
O(4)	5543 (10)	4539 (5)	4640 (6)	C(44)	2386 (36)	7008 (12)	6551 (14)
O(5)	3145 (9)	4202 (4)	4982 (6)	C(45)	3642 (30)	7128 (10)	6570 (14)
O(6)	5331 (10)	3522 (5)	6109 (6)	C(46)	4328 (17)	6606 (12)	6141 (12)
C(21)	7670 (26)	4665 (8)	7129 (12)	C(51)	2349 (18)	3628 (9)	5041 (13)
C(22)	7426 (20)	4256 (10)	7930 (16)	C(52)	2090 (22)	3130 (11)	4268 (15)
C(23)	8472 (38)	3999 (11)	8619 (17)	C(53)	1314 (24)	2561 (14)	4377 (22)
C(24)	9708 (33)	4136 (12)	8532 (17)	C(54)	0675 (30)	2455 (14)	5131 (28)
C(25)	9996 (25)	4573 (12)	7730 (20)	C(55)	0968 (27)	2924 (18)	5856 (18)
C(26)	8891 (34)	4794 (10)	7112 (14)	C(56)	1733 (23)	3509 (10)	5802 (15)
C(31)	3876 (16)	4682 (9)	7839 (10)	C(61)	5817 (31)	2831 (9)	6228 (10)
C(32)	3703 (19)	5363 (9)	8275 (14)	C(62)	4922 (19)	2307 (13)	6279 (13)
C(33)	3328 (21)	5369 (11)	9200 (18)	C(63)	5394 (38)	1564 (12)	6404 (15)
C(34)	3154 (23)	4738 (15)	9668 (13)	C(64)	6710 (40)	1455 (14)	6512 (16)
C(35)	3285 (19)	4088 (10)	9215 (17)	C(65)	7596 (23)	2014 (20)	6464 (13)
C(36)	3642 (17)	4057 (9)	8314 (13)	C(66)	7137 (31)	2711 (11)	6304 (13)

Table 2. *Anisotropic thermal parameters*

The form of the anisotropic temperature factors is:  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . The  $\beta$  are  $\times 10^4$ . The number in parentheses is the standard deviation and refers to the least significant digits.

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ti(1)	152.3 (49)	18.0 (9)	46.2 (17)	3.6 (19)	42.6 (21)	2.9 (12)
O(2)	112 (16)	36 (4)	46 (7)	2 (6)	-14 (8)	3 (4)
O(3)	193 (19)	32 (4)	62 (7)	0 (6)	63 (9)	2 (4)
O(4)	143 (20)	22 (4)	41 (6)	-1 (6)	38 (8)	12 (4)
O(5)	76 (2)	27 (4)	52 (6)	-15 (5)	24 (8)	1 (4)
O(6)	162 (18)	21 (4)	64 (7)	18 (6)	37 (8)	6 (4)
C(21)	109 (40)	32 (7)	57 (15)	-26 (12)	26 (18)	-18 (8)
C(22)	125 (33)	42 (8)	59 (13)	12 (12)	27 (18)	-1 (8)
C(23)	253 (57)	39 (8)	103 (19)	-18 (18)	74 (30)	7 (10)
C(24)	215 (53)	50 (10)	83 (20)	22 (16)	-10 (25)	-18 (11)
C(25)	136 (43)	52 (10)	102 (18)	-1 (15)	49 (22)	-2 (11)
C(26)	109 (43)	40 (8)	80 (16)	3 (15)	-2 (23)	-6 (9)
C(31)	165 (29)	30 (6)	50 (11)	-4 (10)	58 (14)	14 (8)
C(32)	220 (37)	29 (8)	106 (16)	8 (11)	77 (19)	1 (8)
C(33)	236 (40)	38 (9)	123 (19)	10 (13)	75 (21)	-32 (10)
C(34)	311 (44)	53 (11)	79 (15)	-16 (18)	64 (19)	26 (12)
C(35)	176 (35)	29 (8)	112 (20)	-5 (12)	22 (20)	18 (10)
C(36)	177 (33)	42 (7)	56 (13)	-11 (11)	61 (16)	-9 (8)
C(41)	92 (39)	29 (8)	70 (13)	14 (16)	46 (19)	12 (8)
C(42)	170 (41)	30 (8)	72 (13)	48 (17)	46 (19)	1 (7)
C(43)	155 (37)	48 (10)	115 (17)	3 (17)	64 (20)	35 (11)
C(44)	324 (60)	24 (9)	103 (17)	16 (19)	69 (26)	7 (9)
C(45)	215 (46)	31 (19)	97 (16)	-2 (17)	77 (22)	-3 (9)
C(46)	118 (32)	34 (8)	77 (14)	-14 (14)	23 (16)	-10 (8)
C(51)	171 (31)	41 (7)	37 (11)	-6 (11)	24 (16)	-30 (8)
C(52)	239 (40)	40 (8)	119 (18)	-52 (15)	110 (20)	-10 (10)
C(53)	81 (39)	50 (11)	193 (30)	25 (16)	37 (24)	-35 (13)
C(54)	233 (56)	52 (11)	203 (35)	-72 (19)	26 (36)	18 (15)
C(55)	324 (53)	88 (15)	104 (22)	-100 (24)	22 (25)	24 (14)
C(56)	244 (42)	43 (9)	81 (17)	-23 (15)	50 (20)	-13 (9)
C(61)	213 (44)	26 (7)	43 (11)	-17 (16)	76 (18)	-9 (6)
C(62)	120 (34)	49 (10)	98 (17)	0 (16)	36 (17)	15 (9)
C(63)	432 (66)	27 (10)	94 (16)	-22 (21)	67 (27)	2 (9)
C(64)	340 (65)	43 (11)	119 (20)	62 (23)	125 (30)	14 (10)
C(65)	198 (46)	87 (15)	69 (14)	16 (23)	85 (18)	12 (12)
C(66)	236 (47)	30 (9)	93 (15)	25 (16)	82 (21)	20 (8)

ison with a standard strip from the crystal. Nickel-filtered  $\text{Cu } K\alpha$  radiation was used for data collection.

The crystal used for intensity collection had approximate dimensions:  $0.5 \times 0.2 \times 0.2$  mm. 1485 reflections were investigated, with 1076 observed and 409 treated as unobserved. Spot size (Philips, 1956), Lorentz, and polarization corrections were applied to the intensities. Absorption corrections were not applied,  $\mu = 32 \text{ cm}^{-1}$ . The intensities were placed on a common scale by using accurately timed exposures (Buerger, 1960). The scaling is in agreement with precession data about the  $b$  axis.

### Structure determination

The structure was initially solved in space group  $P2_1/c$  by Patterson and heavy-atom methods. Transformation to  $P2_1/n$  was performed before anisotropic refinement. Atomic scattering factors for titanium are those of Hanson, Herman, Lea & Skillman (1964); factors for carbon and oxygen were taken from Cromer & Waber (1965), and those for hydrogen from *International Tables for X-ray Crystallography* (1962). Programs used for computation were the *XRAY67* program system (Stewart, 1967).

The titanium atoms were located from the Harker section and line of a three-dimensional Patterson map. A series of electron density and difference maps revealed the five oxygen atoms and four of the five phenyl rings. Several cycles of block-diagonal least-squares refinement were performed on this portion of the molecule, and the remaining phenyl ring was readily located from subsequent electron density and difference maps.

Refinement, using block-diagonal least-squares methods on all nonhydrogen atoms, lowered the residual  $R$  to 0.139, where  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . All positional parameters and isotropic temperature factors were varied. At this point, anisotropic refinement was initiated with five cycles of block-diagonal and one cycle of full-matrix least-squares methods, yielding a residual of 0.091.

The positions of the 25 phenyl hydrogen atoms were computed; the carbon-hydrogen distance was taken as  $1.0 \text{ \AA}$ . The hydrogen atoms were assigned the isotropic temperature factors of the carbon atoms to which they were bonded. The isotropic temperature factors were taken from the last cycle of isotropic least-squares refinement. Two more cycles of full-matrix least-squares refinement, with new hydrogen positions calculated after each cycle, yielded a final residual of 0.081. Refinement was terminated when the maximum shift was less than its error. The average parameter shift per error following the last cycle was less than 0.25. Unit weights were used throughout the refinement. Block-diagonal refinement was done by *BLOKLS*, and full-matrix by *ORFLS*. Reflections treated as extinct were given zero weight. Unobserved reflections having calculated structure factors less than the minimum observed structure factors were also given zero weight in the refinement. A final difference

map contained no excursions greater than  $0.4 \text{ e. \AA}^{-3}$  or less than  $-0.3 \text{ e. \AA}^{-3}$ . The quantity minimized is  $\sum w(|F_o| - |kF_c|)^2$ .

Table 1 contains the final atomic parameters along

Table 3. Atomic parameters for hydrogen atoms

	$x$	$y$	$z$	$B$
H(22)	0.652	0.414	0.801	4.9
H(23)	0.833	0.371	0.920	6.1
H(24)	0.041	0.391	0.906	5.5
H(25)	0.087	0.472	0.761	6.4
H(26)	0.899	0.510	0.654	5.3
H(32)	0.386	0.583	0.795	5.6
H(33)	0.320	0.584	0.951	6.5
H(34)	0.290	0.477	0.032	6.3
H(35)	0.312	0.363	0.955	5.3
H(36)	0.375	0.357	0.802	4.5
H(42)	0.209	0.541	0.538	4.1
H(43)	0.079	0.632	0.617	5.6
H(44)	0.191	0.740	0.685	6.1
H(45)	0.406	0.758	0.688	4.7
H(46)	0.527	0.667	0.611	4.4
H(52)	0.245	0.317	0.365	5.4
H(53)	0.119	0.219	0.384	5.7
H(54)	0.004	0.206	0.515	7.1
H(55)	0.060	0.283	0.646	7.8
H(56)	0.184	0.387	0.635	5.4
H(62)	0.400	0.246	0.624	5.6
H(63)	0.480	0.114	0.642	7.9
H(64)	0.703	0.095	0.661	5.6
H(65)	0.856	0.191	0.657	6.8
H(66)	0.774	0.312	0.623	4.2

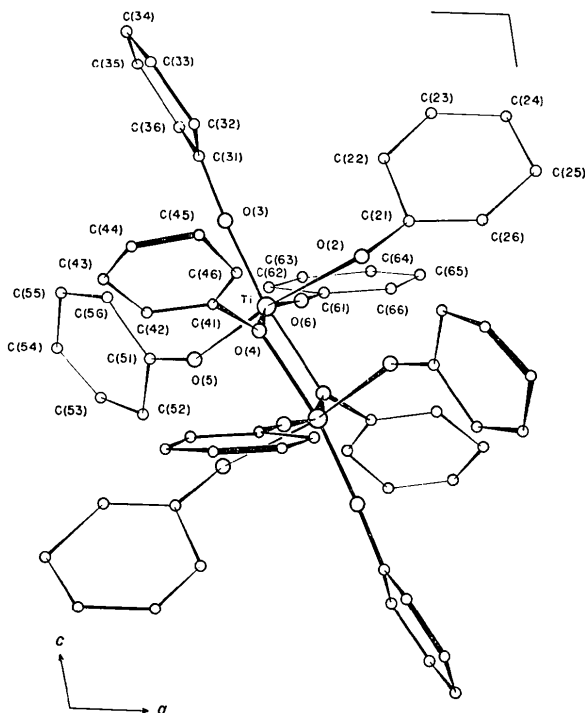


Fig. 1. A view of the  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{HOC}_6\text{H}_5$  dimer down the  $b$  axis of the unit cell, showing the numbering of the atoms.

with their standard deviations for all nonhydrogen atoms. The final anisotropic thermal parameters for all nonhydrogen atoms are listed in Table 2. The atomic parameters for the hydrogen atoms are given

in Table 3. Table 4 lists the observed and calculated structure factors. Table 5 contains the final bond lengths for nonhydrogen atoms, and Table 6 lists the bond angles for nonhydrogen atoms.

Table 4. Observed and calculated structure factors for Ti(OC6H5)4 · HOC6H5

Each group contains k, 10F<sub>o</sub>, and 10F<sub>c</sub>. Unobserved data are asterisked. Extinguished data are marked with an E.

Table with multiple columns of numerical data representing structure factors. The data is organized into groups, each corresponding to a specific (hkl) reflection. Each group contains observed (10F<sub>o</sub>) and calculated (10F<sub>c</sub>) values. Some values are marked with an asterisk to indicate unobserved data. The table is dense and spans most of the page.

Table 5. *Bond lengths*

The number in parentheses is the standard deviation and refers to the least significant digits.

Ti—O(2)	2.200 (10) Å	C(35)—C(36)	1.375 (31) Å
Ti—O(3)	1.842 (11)	C(36)—C(31)	1.372 (24)
Ti—O(4)	2.045 (11)	C(41)—C(42)	1.334 (44)
Ti—O(4')	2.027 (10)	C(42)—C(43)	1.445 (35)
Ti—O(5)	1.884 (10)	C(43)—C(44)	1.397 (34)
Ti—O(6)	1.789 (9)	C(44)—C(45)	1.331 (48)
O(2)—C(21)	1.361 (23)	C(45)—C(46)	1.402 (32)
O(3)—C(31)	1.268 (19)	C(46)—C(41)	1.336 (28)
O(4)—C(41)	1.418 (26)	C(51)—C(52)	1.395 (26)
O(5)—C(51)	1.359 (19)	C(52)—C(53)	1.353 (35)
O(6)—C(61)	1.367 (21)	C(53)—C(54)	1.364 (50)
C(21)—C(22)	1.406 (29)	C(54)—C(55)	1.313 (43)
C(22)—C(23)	1.386 (36)	C(55)—C(56)	1.354 (39)
C(23)—C(24)	1.350 (53)	C(56)—C(51)	1.360 (31)
C(24)—C(25)	1.452 (37)	C(61)—C(62)	1.357 (34)
C(25)—C(26)	1.357 (37)	C(62)—C(63)	1.453 (35)
C(26)—C(21)	1.308 (45)	C(63)—C(64)	1.373 (57)
C(31)—C(32)	1.419 (24)	C(64)—C(65)	1.396 (46)
C(32)—C(33)	1.413 (33)	C(65)—C(66)	1.373 (41)
C(33)—C(34)	1.362 (34)	C(66)—C(61)	1.386 (45)
C(34)—C(35)	1.370 (33)		

Table 6 (*cont.*)

C(34)—C(35)—C(36)	121.6 (19)
C(35)—C(36)—C(31)	120.5 (16)
C(46)—C(41)—C(42)	123.1 (21)
C(41)—C(42)—C(43)	118.6 (18)
C(42)—C(43)—C(44)	116.2 (23)
C(43)—C(44)—C(45)	123.5 (25)
C(44)—C(45)—C(46)	118.0 (19)
C(45)—C(46)—C(41)	120.5 (21)
C(56)—C(51)—C(52)	116.1 (18)
C(51)—C(52)—C(53)	116.9 (22)
C(52)—C(53)—C(54)	126.5 (26)
C(53)—C(54)—C(55)	114.6 (27)
C(54)—C(55)—C(56)	122.1 (28)
C(55)—C(56)—C(51)	123.3 (20)
C(66)—C(61)—C(62)	125.0 (18)
C(61)—C(62)—C(63)	116.9 (23)
C(62)—C(63)—C(64)	117.5 (25)
C(63)—C(64)—C(65)	123.5 (25)
C(64)—C(65)—C(66)	118.8 (26)
C(65)—C(66)—C(61)	118.3 (23)

### Discussion

The molecule consists of dimers, with the titanium atoms bridged by phenoxide oxygen atoms such that the coordination around the titanium is a distorted octahedron (Fig. 1).

There are five distinctly different Ti—O bonds in the structure. Bond lengths to O(3), O(5), and O(6) are 1.842 (11), 1.884 (10), and 1.789 (9) Å, respectively. These three phenoxy oxygen atoms are bonded to only one titanium atom. The bond lengths are in good agreement with other Ti—O bonds of this type. Ibers (1963) reports an average value of 1.77 Å for five Ti—O bonds in tetraethoxytitanium(IV), while Wright & Williams (1968) report a range of 1.745 to 2.072 Å in tetramethoxytitanium(IV). The lone Ti—O interatomic distances in dichlorodiphenoxytitanium(IV) (Caughlan & Watenpaugh, 1966) and dichlorodiethoxytitanium(IV) (Haase & Hoppe, 1968) are 1.744 (10) and 1.77 Å respectively.

The Ti—O length to O(2), which is 2.200 (11) Å, is strikingly long. This is significantly longer than any of the other Ti—O bonds in this compound or the other compounds mentioned above. It is closer in length to that reported for alkoxide oxygen atoms bridging three titanium atoms: 2.23 Å for tetraethoxytitanium(IV) (Ibers, 1963) and 2.13 to 2.20 Å for tetramethoxytitanium(IV) (Wright & Williams, 1968). Because of the large interatomic distance to this oxygen atom, we feel that this is the phenol oxygen atom in the molecule, bonded not only to titanium but also to hydrogen and the phenyl carbon atom.

There is one bridging oxygen atom, O(4), in the molecule, which is bonded to two titanium atoms at the same length within our limits of error: Ti—O(4), 2.045 (11) Å, and Ti—O(4'), 2.027 (10) Å. These values agree well with other reported values for bridging oxygen atoms: 2.03 Å for tetraethoxytitanium(IV) (Ibers, 1963), 1.96 to 2.086 Å for tetramethoxytitanium(IV) (Wright & Williams, 1966), 1.910 (9) and

Table 6. *Bond angles in the  $\text{Ti}(\text{OC}_6\text{H}_5)_4\text{-HOC}_6\text{H}_5$  dimer*

The number in parentheses is the standard deviation and refers to the least significant digits.

Ti—O(4)—Ti'	108.7 (5)°
O(2)—Ti—O(3)	87.4 (4)
O(2)—Ti—O(4)	78.9 (4)
O(2)—Ti—O(5)	162.4 (4)
O(2)—Ti—O(6)	93.0 (4)
O(2)—Ti—O(4')	78.1 (4)
O(3)—Ti—O(4)	160.0 (4)
O(3)—Ti—O(5)	102.4 (5)
O(3)—Ti—O(6)	101.3 (4)
O(3)—Ti—O(4')	91.8 (4)
O(4)—Ti—O(5)	87.7 (4)
O(4)—Ti—O(6)	93.9 (4)
O(4)—Ti—O(4')	71.3 (4)
O(5)—Ti—O(6)	99.2 (4)
O(5)—Ti—O(4')	86.9 (4)
O(6)—Ti—O(4')	163.8 (5)
Ti—O(2)—C(21)	132.2 (10)
Ti—O(3)—C(31)	168.9 (10)
Ti—O(4)—C(41)	125.9 (10)
Ti'—O(4)—C(41)	125.2 (10)
Ti—O(5)—C(51)	126.9 (8)
Ti—O(6)—C(61)	175.1 (11)
O(2)—C(21)—C(22)	115.5 (21)
O(2)—C(21)—C(26)	127.9 (17)
O(3)—C(31)—C(32)	120.7 (15)
O(3)—C(31)—C(36)	120.1 (15)
O(4)—C(41)—C(42)	116.8 (16)
O(4)—C(41)—C(46)	120.1 (24)
O(5)—C(51)—C(52)	119.6 (17)
O(5)—C(51)—C(56)	124.4 (15)
O(6)—C(61)—C(62)	115.0 (25)
O(6)—C(61)—C(66)	120.0 (20)
C(26)—C(21)—C(22)	116.4 (18)
C(21)—C(22)—C(23)	118.9 (24)
C(22)—C(23)—C(24)	121.1 (23)
C(23)—C(24)—C(25)	121.5 (23)
C(24)—C(25)—C(26)	111.5 (26)
C(25)—C(26)—C(21)	130.5 (22)
C(36)—C(31)—C(32)	119.1 (16)
C(31)—C(32)—C(33)	118.4 (16)
C(32)—C(33)—C(34)	120.9 (19)
C(33)—C(34)—C(35)	119.4 (20)

2.122 (9) Å for dichlorodiphenoxytitanium(IV) (Caughlan & Watenpaugh, 1966), 1.96 and 2.03 Å for dichlorodiethoxytitanium(IV) (Haase & Hoppe, 1968).

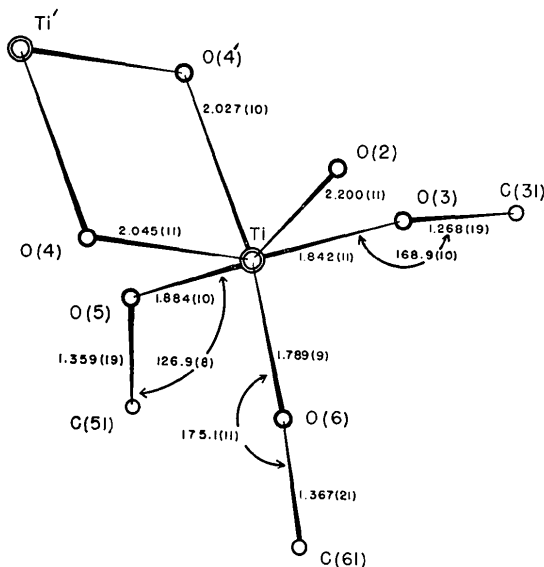


Fig. 2. The titanium octahedron with pertinent lengths and angles in  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{HOC}_6\text{H}_5$ .

Bridging oxygen atoms in bis-[2-methylpentane-2,4-dioxydimethyltitanium(IV)] range from 1.97 to 2.06 Å (Yoshino, Shuto & Itaka, 1970).

The dihedral angle between the plane formed by the Ti-O bridges and the phenyl ring bonded to O(4) is 63.3°. This is less than the corresponding angle of 77.2° calculated for  $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$  from the published coordinates (Caughlan & Watenpaugh, 1966). The fact that these rings are tilted quite far from the Ti-O bridging plane indicates that little  $\pi$ -bonding is introduced into the bridging ring system through delocalization of the electrons within the phenyl ring.

The bond lengths and bond angles in the titanium octahedron are presented in Fig. 2. The Ti-O-C bond angles at O(3) and O(6) are worthy of note. At O(3) the angle is 168.9 (10)°, while at O(6) the value is 175.1 (11)°.  $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$  (Caughlan & Watenpaugh, 1966) has a nearly linear Ti-O-C bond angle of 165.9 (6)°, whereas in the related compound,  $\text{TiCl}_2(\text{OC}_2\text{H}_5)_2$ , 165.5° is reported (Haase & Hoppe, 1968). Tetramethoxytitanium(IV) has a Ti-O-C bond angle of 160.6 (15)° (Wright & Williams 1968). The Ti-O-C bond angle at O(6) is the largest to be reported in titanium alkoxides.

There is a correlation between the Ti-O bond lengths and Ti-O-C bond angles associated with the phenoxy

Table 7. Comparison of the four-membered rings in  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{HOC}_6\text{H}_5$  and related compounds

The number in parentheses is the standard deviation and refers to the least significant digits.

	This work $[\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{HOC}_6\text{H}_5]_2$	Caughlan & Watenpaugh (1966) $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$	Yoshino <i>et al.</i> (1970) $[(\text{CH}_3)_2\text{O}_2\text{TiC}_6\text{H}_{12}]_2$
Ti-Ti'	3.309 (5) Å	3.274 (3) Å	3.225 (7) Å
O-O'	2.372 (14)	2.362 (10)†	2.365 (22)†
Ti-O	2.045 (11)	1.910 (9)	2.02 (2)
Ti-O'	2.027 (10)	2.122 (9)	2.06 (2)
Ti'-O			1.97 (2)
Ti'-O'			1.99 (2)
Ti-O-Ti'	108.7 (5)°	108.5 (3)°	107.9 (7)‡
Ti-O'-Ti'			105.7 (8)‡
O-Ti-O'	71.3 (4)	71.5 (2)	70.8 (6)‡
O-Ti'-O'			73.4 (7)‡

† Calculated from the published coordinates.

‡ Values for standard deviations calculated from the published coordinates.

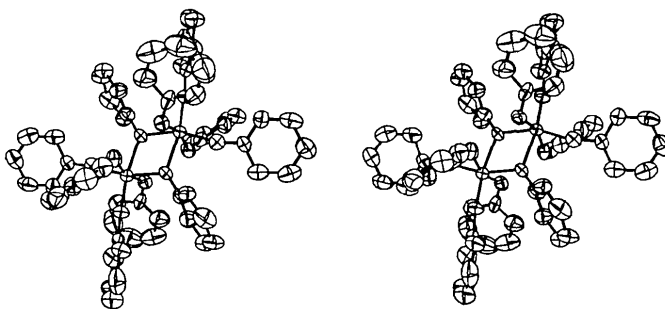


Fig. 3. Stereoview of the  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{HOC}_6\text{H}_5$  dimer along the  $a$  axis of the unit cell.

groups not involved in bridging or the phenol moiety (Fig. 2). The bond length increases significantly with decreasing bond angle. This indicates a decrease in double bond character as the angle at the oxygen atoms decreases.

The O-C bond lengths are also of special interest. The interatomic distances terminating at atoms O(2), O(5), and O(6) are 1.36 (2) Å. These three oxygen atoms are all nonbridging and are distinctly longer than O(3)-C(31), which has a length of 1.268 (19) Å. The shortness of this bond indicates some double bond character in this nearly linear bond.

The four-membered ring formed by Ti(1), Ti(1'), O(4), and O(4') is similar to the four-membered ring in dichlorodiphenoxytitanium(IV) (Caughlan & Watenpaugh, 1966) and bis-[2-methylpentane-2,4-dioxydimethyltitanium(IV)] (Yoshino *et al.*, 1970). The bond lengths and bond angles in the three compounds are compared in Table 7. The Ti-O-Ti and O-Ti-O bond angles are all very similar.

The angle formed by Ti(1')-Ti(1)-O(2) is 75.8°. Angle Ti(1')-Ti(1)-O(5) is 86.7°. The dihedral angle between the planes formed by these two sets of atoms is 1.4°. The interesting feature is that the angles are such that atoms O(2) and O(5') are tilted towards each other. The contact distance between these atoms is 2.671 (13) Å. This is less than the van der Waals distance of 2.80 Å (Pauling, 1960). The oxygen-oxygen distances in phenol range from 2.59-2.70 Å (Gillier-Pandraud, 1967). This suggests hydrogen-bonding be-

tween the phenol oxygen atom, O(2), and phenoxy oxygen atom, O(5'), in the dimer.

It has been suggested (Caughlan & Watenpaugh, 1966) that the red color in  $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$  is due to the  $\pi$ -electron system of the  $\text{TiOC}_6\text{H}_5$  system splitting the titanium  $d$  orbitals.  $[(\text{CH}_3)_2\text{TiO}_2\text{C}_6\text{H}_{12}]_2$  is also colored, being yellow (Yoshino *et al.*, 1970), as is  $(\text{PCl}_4)_2(\text{Ti}_2\text{Cl}_{10})$  (Kistenmacher & Stucky, 1971), which has a very similar structure to the present complex with two bridging chlorine atoms in a dimeric unit. Neither of these two compounds has a  $\pi$ -electron system and it is hard to attribute their color to the splitting of the titanium  $d$  orbitals by delocalized electrons.

A stereo view of the molecule along the  $a$  axis is shown in Fig. 3. The center of the four-membered ring coincides with a center of symmetry in the cell.

The phenyl carbon bond lengths and bond angles are normal. The molecules in the crystal are bonded through van der Waals interactions with no abnormal C-H contact distances. The packing in the unit cell is illustrated in Fig. 4.

All calculations were done on an IBM 360-40 computer in the University of North Dakota Computer Center.

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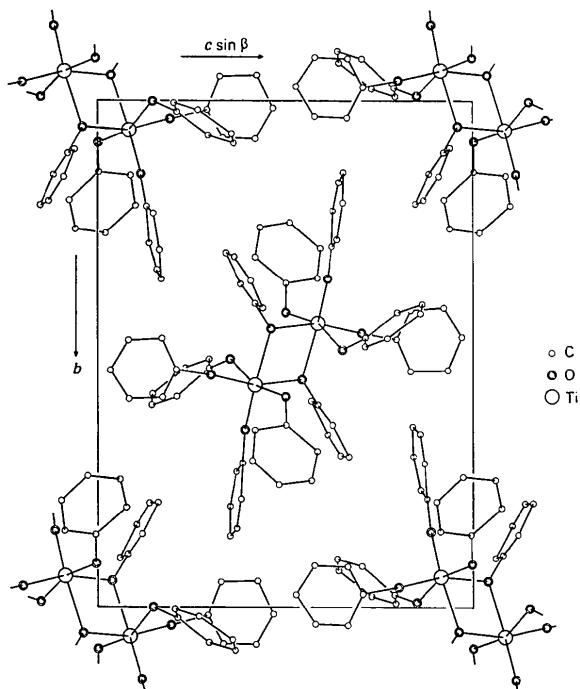


Fig. 4. A packing diagram of the dimer of  $\text{Ti}(\text{OC}_6\text{H}_5)_4\text{-HOC}_6\text{H}_5$  along the  $a$  axis.

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## The Crystal Structure of 6-Histaminopurine Dihydrate

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Crystals of the dihydrate of 6-histaminopurine are monoclinic, space group  $P2_1/c$ , with  $a=5.507$  (5),  $b=31.839$  (9),  $c=7.336$  (4) Å, and  $\beta=105.58$  (4)°. Using X-ray diffractometer data, the structure was solved by symbolic addition and was refined by least-squares methods to  $R_1(\sum||F_o|-|F_c||/\sum|F_o|)=0.136$  and  $R_2(\sum|F_o^2-F_c^2|/\sum F_o^2)=0.112$ . The adenine moiety is in the N(7)-H tautomer form. The structure features hydrogen bonding between purine bases, resulting in ribbons parallel to  $a$  and stacking of adenine moieties along  $c$ . The stacked base planes are approximately parallel and are separated by an interplanar spacing of about 3.4 Å. There are no interactions between histamine imidazole rings or between imidazole and adenine rings.

### Introduction

Many studies have demonstrated that base stacking is an important type of interaction among purine and pyrimidine derivatives in aqueous solution (Chan, Schweizer, Ts'o & Helmkamp, 1964; Broom, Schweizer & Ts'o, 1967; Solie & Schellman, 1968; Ts'o, 1968) and in the solid state (Bugg, Thewalt & Marsh, 1968; Bugg & Thewalt, 1969; Thewalt, Bugg & Marsh, 1970; Bugg & Thewalt, 1970; Bugg, Thomas, Sundaralingam & Rao, 1971; Bugg, 1971). However, in spite of the extensive evidence supporting the importance of base stacking, little is known about the forces involved, or about the geometrical arrangements that result from stacking interactions. We are currently examining base stacking patterns in crystals of purine derivatives to obtain information about the types of interactions responsible for stacking. In this paper we describe the crystal structure and base stacking pattern of 6-histaminopurine (Fig. 1). This and other 6-purinyll derivatives related to the plant-growth hormone, kinetin, have morphological effects on cells in tissue cultures (Lettré, 1960); among these purine derivatives, 6-histaminopurine is outstanding because of its cytotoxic activity against tumor cells (Lettré, 1960; Lettré & Werner, 1968).

### Experimental

Crystals of 6-histaminopurine dihydrate were obtained as clear plates by slowly cooling a hot, saturated aqueous solution. The crystals are stable when stored in a high humidity atmosphere, but rapidly decompose when exposed to room atmosphere, apparently by loss of water of crystallization. Weissenberg and oscillation photographs showed that the crystals are monoclinic; the space group is  $P2_1/c$ , as indicated by the systematic absence of reflections  $0k0$  with  $k$  odd and  $h0l$  with  $l$  odd. A plate, approximately  $0.3 \times 0.1 \times 0.1$  mm, was cut from a larger crystal and was immediately coated with a heavy layer of epoxy in order to retard the rate of decomposition. The crystal was then mounted in an arbitrary orientation on a Picker FACS-1 diffractometer. Approximate cell parameters for use in collecting intensity data were obtained by measuring the angular settings of three high-angle (Cu  $K\alpha_1$ ,  $\lambda=1.54051$  Å) reflections.

Intensity data were collected with the diffractometer, using a scintillation counter, nickel-filtered copper radiation, and a  $\theta-2\theta$  scanning technique. The scanning speed was  $2^\circ \cdot \text{min}^{-1}$ , and a 10 sec background measurement was performed at each terminus of the scans. Measurements were made for the 2075 independent