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The Neutron Diffraction Stucture of $[C_5H_4\text{-}(CH_2)_3\text{-}C_5H_4]TiCl_2$*

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The crystal structure of 1,1′-trimethylene-di-π-cyclopentadienyl titanium dichloride, $[C_5H_4\text{-}(CH_2)_3\text{-}C_5H_4]$-$TiCl_2$, was determined from three-dimensional neutron diffractometry data in order to obtain accurate information for those structural parameters involving hydrogen atoms. Also, we were interested in the effect on the C-C bond lengths of shifting electron density from the C atoms and accumulating it in the regions of the π-bonds of the Cp rings. The substance crystallizes as deep red-brown parallelepipeds in the monoclinic space group $P2_1/n$ with $a = 8.490(2)$, $b = 14.209(4)$, $c = 10.185(2)$ Å, and $\beta = 90.43(2)°$. The cell volume is 1228.6 $Å^3$ while the measured and calculated densities are 1.566(8) and 1.572 $gm\text{-}cm^{-3}$, respectively. The molecule consists of a planar $TiCl_2$ fragment sandwiched equidistantly between two eclipsed rings which are canted such that their normals make an angle of 133.1° and linked by a ($-CH_2\text{-}CH_2\text{-}CH_2-$) chain. The entire propyl chain is to one side of the vector bisecting the Cl-Ti-Cl angle and the ring carbons connected to the terminal $-CH_2-$ groups of the propyl chain do not occupy the position of nearest approach between the two rings. The normal to the plane of each of the rings does not coincide with the Ti-(ring centroid) vector, the angle between the two being 0.80° for ring 1 and 0.70° for ring 2. The two Ti-Cl distances are 2.368(8) and 2.365(9) Å and the Cl(1)-Ti-Cl(2) angle is 93.2(3)°. The average C-C distance for rings 1 and 2 are 1.416(7) and 1.402(7) Å, respectively. The average Cp C-H distance is 1.05(2) and 1.12(2) Å for rings 1 and 2. The average C-C-C and C-C-H angles are 108.0(5) and 126.0(8)° for ring 1 and 107.9(5)° and 125.6(9)° for ring. 2. The average C(cp)-C(H_2) distance is 1.494(7) Å while the average C(H_2)-C(H_2) distance is 1.509(8) Å. The average aliphatic C-H distance is 1.06(2) Å. Finally, the average values of the C-C-C, C-C-H, and H-C-H angles at the aliphatic chain are 115.1(5), 109.9(8), and 105.7(9)°, respectively.

The normals to rings 1 and 2 make angles of 23.9 and 22.9° with the normal to the $TiCl_2$ plane. The Cl atoms 1 and 2 lie 1.703 and 1.736 Å, respectively, above and below the plane defined by (ring 1 centroid)-Ti-(ring 2 centroid). The angles between the vectors (ring 1 centroid)-Ti and (ring 2 centroid)-Ti with the normal to the plane defined by the $TiCl_2$ fragment are 23.4 and 23.5°, respectively. The perpendicular distances between the ring centroids and the $TiCl_2$ plane are 1.89 and 1.89 Å, respectively, for rings 1 and 2. Finally, the angles between the Ti-Cl(1) and Ti-Cl(2) vectors with the normal to the (ring 1 centroid)-Ti-(ring 2 centroid) plane are 135.9 and 137.1°.

The maximum deviation of any carbon from planarity in rings 1 and 2 is 0.01 and 0.05 Å, respectively. The maximum deviation from planarity of any hydrogen from the plane defined by the hydrogens of rings 1 and 2 is 0.03 and 0.02 Å. The planes defined by the hydrogens do not coincide with the planes defined by the five carbons of the same Cp ring. There is a slight, very possibly insignificant, but consistent displacement of the ring hydrogens towards the Ti atom in both rings. A measure of this effect can be obtained from the following distances:

Ti-(Plane of Carbons, Ring 1) = 2.06 Å
Ti-(Plane of Hydrogens, Ring 1) = 2.04
Ti-(Plane of Carbons, Ring 2) = 2.06
Ti-(Plane of Hydrogens, Ring 2) = 2.04

For each ring, the difference in pairs of these quantities probably do not exceed two standard deviations and, except for the consistency of the results for the two rings, are of doubtful significance.

All distances and angles involving heavy atoms are in excellent agreement with the results of an X-ray study reported elsewhere. The C-C distances in the rings obtained by neutron diffraction are slightly larger than those obtained in the X-ray study, as expected. The final values of the discrepancy indices for the present study are $R_1 = 0.053$ and $R_2 = 0.048$, with an error of fit of 1.04.

Introduction

The crystal structure of 1,1′-trimethylene-di-π-cyclopentadienyl titanium dichloride, $[C_5H_4\text{-}(CH_2)_3\text{-}C_5H_4]$-$TiCl_2$, was obtained from three-dimensional neutron diffraction data in order to determine accurately bond lengths and angles involving hydrogen atoms with an accuracy that is not accessible from the X-ray data. We were also interested in comparing the C-C distances of the Cp rings with the values obtained by X-ray diffraction in order to gauge the effect of shifting electron density from the carbon atoms into the region of the π-bonds. Finally, his substance offered an opportunity to compare the length of the (ring carbon)-H distance with the (aliphatic carbon)-H distance as

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obtained from the same set of data.

The particular choice of compound for this study was dictated by our experience with another titanium cyclopentadienyl derivative-Cp_2TiS_5. An analysis of the structural parameters for the pentasulfide[3] indicated that the C-C distances of the two rings (about 1.34 and 1.38 Å) varied inversely as the degree of librational freedom of the given ring. The ring with the smaller C-C distance was found (using a Schomaker-Trueblood[4] analysis of the motion) to librate approximately 12° about the mid-point. A similar analysis for the second ring indicated the motion was only 8°. Therefore, it is clear that to obtain accurate C-C and C-H bond lengths it is necessary to immobilize the rings as much as possible. Rather than resorting to the technique of reducing thermal motion by lowering the sample temperature, we secured samples of the title compound with the hope that ring motion would be minimized by the linkage across the two Cp rings. After encouraging results became available from an X-ray study,[5] and in view of the fact that suitable crystals were available, we decided to undertake a neutron diffraction analysis which would permit full characterization of the structural parameters of this molecule. As it is well-documented[6] by now, the positional parameters of hydrogen atoms obtained from X-ray data are not as reliable as those obtained from neutron diffraction; therefore, since no cyclopentadienyl compound had previously been subjected to neutron diffraction analysis, we have carried such a study to accurately determine the structural parameters involving hydrogen atoms. Among the questions we wanted to answer is the following: Do the hydrogen atoms of the cyclopentadienyl moiety deviate from coplanarity with the ring carbons, and if so, in which direction?

Crystal Data. The crystals were given to us by Dr. M. Hillman of Brookhaven National Laboratory. The details of the synthesis and physical properties of this substance will be reported elsewhere by Hillman and Weiss.[7] 1,1′-trimethylene-di-π-cyclopentadienyl titanium dichloride has composition $C_{13}H_{14}TiCl_2$, a molecular weight of 289.05 gm-mole^{-1}, a measured density of 1.566(8) gm-cm^{-3} (obtained by flotation in aqueous zinc bromide solution) and a melting point of 228-229°C (corr.). Systematic absences in both the X-ray[5] and neutron diffraction studies are: 0k0, for $k \neq 2n$; $h0\ell$, for $h+\ell \neq 2n$, which uniquely determines the space group as $P2_1/n$. From the manual centering of 20 reflections in the X-ray study,[5] cell constants were determined by least-squares fitting of the angular settings to be $a = 8.490(2)$, $b = 14.209(4)$, $c = 10.185(2)$ and $\beta = 90.43(2)°$. The cell volume is 1228.6 Å^3 which accommodates four molecules if d(calc) = 1.562 gm-cm^{-3}.

Neutron Diffraction Measurements. From the same crystallization process one one is able to obtain crystals suitable for X-ray and neutron diffraction studies, both having a narrow mosaic spread (the width at half-height for an omega scan was about 0.2° for the crystal used in the neutron diffraction measurements). The crystals used in this study were beautiful red-brown parallelepipeds bound by the (1,0,1), ($\bar{1}$,0,$\bar{1}$), ($\bar{1}$,0,1), (1,0,$\bar{1}$), (0,1,0) and ,0,1,0) faces, the distance between the pairs of faces being 1.75, 1.75 and 0.90 mm respectively. The specimen chosen was mounted along the [101] direction on a Cd-plated brass rod, which was in turn mounted on a Y-814 Enraf-Nonius goniometer head. The crystal was aligned by optical goniometry and transferred to a computer-controlled neutron diffractometer which is part of the Brookhaven Multiple Spectrometer System.[8] Neutrons were provided by the Brookhaven National Laboratory High Flux Beam Reactor which has an approximate flux of 8×10^6 neutrons-cm^{-2} sec^{-1} at the specimen. Monochromatization was achieved by diffracting the neutron beam by the (311) face of a Ge crystal and the flux of neutrons was monitored throughout the course of data collection. The wavelength used was 0.9958 Å and data was collected using a θ-2θ step scan technique in which the width of the step was $\Delta(2\theta) = 0.04°$. A couting time of 4 seconds was used at each point of the scan whose total width in 2θ was 3° for all reflections. The minimum and maximum values of $\sin\theta/\lambda$ were 0.06 and 0.34, respectively. Two standard reflections were monitored periodically in order to keep track of either decay, local fluctation in the electronics or crystal alignment changes. The two standards were checked every 30 reflections and during the period of data collection their integrated intensities did not vary by more than 6% from the mean value. The data were reduced to structure amplitudes, corrected for absorption and averaged where necessary. The absorption coefficient of this substance for neutrons was esitmated to be 1.223 cm^{-1}. This value was calculated using the following mass absorption coefficients:[9] Ti, 0.044 cm^2-gm^{-1}; Cl, 0.33 cm^2-gm^{-1}; C, 0.00015 cm^2-gm^{-1} and H, 23.16 cm^2-gm^{-1}. Of the 1072 independent data recorded a total of 831 reflections were found to have $F_o^2 > 2\sigma(F_o^2)$. Since the X-ray analysis[5] had converged at this point to residuals of $R_1 = 2.9\%$, $R_2 = 4.0\%$ and a error-of-fit or 1.20, we used the positions of the Ti, Cl, C and H atoms derived from the X-ray study as trial parameters for the least-squares refinement of the neutron diffraction data.

The values of the neutron scattering lengths used in the refinement of the data were:[10] $b(Ti) = -0.34 \times 10^{-12}$ cm; $b(Cl) = 0.961 \times 10^{-12}$ cm; $b(C) = 0.665 \times 10^{-12}$ cm and $b(H) = -0.378 \times 10^{-12}$ cm. The heavy atom positions and thermal parameters were held fixed while the positional and isotropic thermal parameters of the hydrogen atoms were varied. After two cycles of refinement the residuals were $R_1 = 0.10$ and $R_2 = 0.10$, where R_1 and R_2 are defined as $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ $R_2 = \{\Sigma\omega(| F_o | - | F_c |)^2 / \Sigma\, \omega F_o^2\}^{1/2}$, with $\omega = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) =$

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[4] V. Schomaker and K.N. Trueblood, *Acta Cryst.*, *B24*, 63 (1968).

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[8] D.R. Beaucaga, M.A. Kelly, D. Ophir, S. Rankowitz, R.J. Spinrad, and R. van Norton, *Nucl. Instr. and Methods*, *40*, 26 (1966).

[9] « International Tables for X-ray Crystallography », The Kynoch Press, Birmingham, Vol. III, 1968, Table 3.2.5, p. 197.

[10] The Neutron Difraction Commission, *Acta Cryst.*, *A25*, 391 (1969).

Table I. Positional and Thermal Parameters. The positional and thermal parameters were multiplied by 10^4, their estimated standard deviations are given in parentheses and the form of the thermal ellipsoid used was $\exp\text{-}[\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}hl]$. Root-mean-square components of thermal motion are also listed for all atoms.

ATOM	X/A	Y/B	Z/C	B11	B22	B33	B12	B13	B23
TI	-2378(9)	0761(6)	2174(6)	0070(15)	0029(6)	0060(8)	-0014(14)	0005(11)	-0006(7)
CL1	-2911(4)	-0586(3)	0875(3)	0176(8)	0050(3)	0076(3)	0003(5)	0013(5)	-0014(3)
CL2	0107(4)	0185(3)	2887(3)	0133(7)	0068(3)	0110(4)	0007(6)	-0025(5)	0025(3)
C1	-6166(6)	1725(4)	2681(5)	0119(12)	0050(4)	0128(9)	0008(9)	0040(9)	-0005(6)
C2	-5706(7)	2648(5)	2073(5)	0145(14)	0062(6)	0129(8)	0027(11)	0011(11)	0017(6)
C3	-4814(6)	2548(4)	0800(5)	0129(11)	0060(6)	0102(7)	0051(9)	0000(9)	-0003(6)
C1-1	-4801(6)	1141(4)	3202(4)	0087(9)	0045(4)	0074(5)	0004(8)	0008(7)	0016(4)
C1-2	-4729(7)	0175(4)	3185(5)	0152(15)	0039(4)	0100(7)	-0027(9)	0039(9)	0006(5)
C1-3	-3401(7)	-0130(4)	3954(4)	0158(13)	0045(4)	0079(6)	-0006(9)	0024(8)	0021(5)
C1-4	-2686(7)	0692(3)	4498(4)	0183(14)	0042(4)	0054(5)	-0004(9)	-0017(7)	0007(4)
C1-5	-3553(7)	1481(4)	4023(4)	0128(12)	0052(4)	0054(5)	-0036(9)	-0012(8)	-0025(4)
C2-1	-3240(6)	2110(3)	0892(4)	0130(11)	0034(4)	0094(6)	0047(8)	0024(8)	0025(5)
C2-2	-2611(7)	1438(4)	0048(4)	0203(13)	0048(4)	0067(5)	0043(9)	-0002(9)	0005(4)
C2-3	-1041(8)	1313(4)	0316(5)	0211(15)	0054(6)	0138(8)	0051(10)	0110(10)	0034(6)
C2-4	-0595(7)	1914(4)	1317(6)	0115(12)	0055(5)	0155(8)	-0031(9)	-0013(9)	0053(6)
C2-5	-1949(6)	2384(4)	1772(4)	0126(11)	0038(4)	0102(6)	0011(9)	0004(8)	0006(4)
H11	-0694(1)	0180(1)	0345(1)	0232(27)	0114(12)	0192(19)	0039(19)	0117(21)	0066(14)
H12	-0681(1)	0131(1)	0196(1)	0141(23)	0150(16)	0168(15)	-0010(18)	-0096(16)	0067(14)
H21	-0503(2)	0306(1)	0276(1)	0286(32)	0061(8)	0122(13)	-0031(20)	0023(19)	-0036(9)
H22	-0682(2)	0309(1)	0184(1)	0246(30)	0089(12)	0221(18)	0081(21)	-0037(22)	0022(13)
H31	-0464(1)	0319(1)	0036(1)	0192(24)	0099(11)	0194(18)	0050(19)	-0006(20)	0092(12)
H32	-0553(1)	0214(1)	0014(1)	0188(26)	0105(12)	0122(12)	-0016(18)	-0050(16)	-0035(12)
H1-2	-0547(1)	-0206(1)	0261(1)	0186(25)	0086(10)	0124(13)	-0043(18)	0035(17)	-0069(9)
H1-3	-0298(2)	-0080(1)	0407(1)	0322(34)	0054(8)	0180(15)	-0016(19)	0050(22)	0001(10)
H1-4	-0171(1)	0069(1)	0513(1)	0182(22)	0087(9)	0107(12)	0035(17)	0004(14)	0003(10)
H1-5	-0334(1)	0221(1)	0424(1)	0227(29)	0067(7)	0130(12)	0041(18)	-0023(18)	-0031(9)
H2-2	-0335(2)	0106(1)	-0072(1)	0578(50)	0068(8)	0071(10)	0040(23)	-0056(21)	-0020(8)
H2-3	-0016(2)	0001(1)	-0022(1)	0380(40)	0130(16)	0237(21)	0148(24)	0218(25)	0073(16)
H2-4	0057(1)	0193(1)	0180(2)	0128(25)	0097(13)	0434(38)	-0030(20)	-0032(25)	0077(18)
H2-5	-0200(1)	0290(1)	0252(1)	0314(34)	0057(9)	0203(18)	-0052(19)	-0038(25)	-0011(10)

R.M.S. Amplitudes of Vibration Along the Three Principal Axes of the Thermal Ellipsoid (Å). The first entry gives the neutron and the second the x-ray result for $[C_5H_4{-}(CH_2)_3{-}C_5H_4]TiCl_2$. The third entry is for Cp_2TiS_5 (see ref. 3). The numbers *have been multiplied by 10^3.*

Atom	Axis 1	Axis 2	Axis 3
Ti	136	170	209
	165	169	194
	148	167	173
Cl(1) or S(1)[a]	185	243	256
	175	229	267
	169	211	331
Cl(2) or S(2)[a]	191	244	286
	184	233	284
	173	224	279
C1-1	168	180	234
	163	212	223
	148	222	323
C2-1	156	226	272
	166	195	272
	151	235	311
C3-1	171	239	254
	158	209	273
	151	248	297
C4-1	162	208	263
C4-1	169	231	249
	169	207	279
C5-1	103	209	276
	166	213	226
	162	216	292
C1-2	111	199	286
	169	199	226
	172	249	410
C2-2	177	195	301
	168	214	299
	174	260	442
C3-2	163	193	375
	163	204	367
	158	222	406
C4-2	142	214	338
	161	208	376
	154	232	461
C5-2	186	220	236
	161	244	256
	179	215	444

[a] This comparison is made to show the motion of the TiX_2 moiety in the two compounds. S and Cl have about the same mass and number of electrons.

Table II. Observed Structure Amplitudes, Their Estimated Standard Deviations and the Calculated Structure Amplitudes.

K	L	FO	SIG	FC
*** H= -3 ***				
-2	7	26	2	27
-2	9	21	3	26
-1	7	61	2	60
-1	8	10	3	7
-1	9	9	6	12
*** H= -2 ***				
-5	5	42	2	38
-3	5	24	3	30
-3	6	32	2	33
-2	5	50	2	47
-2	6	75	2	71
-2	7	22	2	18
-2	8	17	3	13
-2	9	20	3	25
-1	5	65	2	59
-1	6	13	4	12
-1	7	19	3	27
-1	8	41	2	39
-1	9	50	2	50
0	6	33	2	31
*** H= -1 ***				
12	4	39	2	38
11	4	33	3	33
11	5	29	3	30
10	5	22	3	19
10	6	41	2	42
10	7	10	6	15
-9	4	47	2	45
-9	5	30	2	32
-9	6	46	2	45
-8	4	46	2	45
-8	5	12	4	11
-8	6	7	7	8
-8	7	11	5	1
-8	8	12	4	11
-7	3	27	3	28
-7	4	65	2	65
-7	8	48	2	44
-6	4	25	2	22
-6	5	18	2	17
-6	5	17	3	17
-6	6	13	3	9
-6	8	17	3	15
-6	9	22	2	21
-5	3	54	2	51
-5	4	17	2	14
-5	5	45	2	49
-5	7	15	3	11
-5	9	17	3	15
-4	3	28	2	25
-4	5	20	2	20
-4	6	15	4	13
-4	6	17	2	13
-4	7	83	2	87
-4	8	8	6	2
-3	3	56	2	53
-3	4	68	2	66
-3	6	11	3	7
-3	7	51	2	51
-3	8	11	4	7
-3	9	12	6	17
-2	3	43	2	40
-2	4	14	3	14
-2	6	58	2	55
-2	5	18	3	17
-2	9	18	3	17
-1	3	19	3	18
-1	4	15	2	11
-1	5	39	2	38
-1	6	11	5	17
-1	7	55	2	54
-1	7	51	2	54
-1	8	25	2	27
-1	8	22	3	27
-1	9	52	2	52
-1	9	54	2	52
0	3	158	4	153
0	3	161	4	153
0	5	16	4	16
0	7	42	2	44
0	9	8	6	2
*** H= 0 ***				
-13	3	11	4	6
-13	4	34	2	32
-12	3	45	2	44
-12	4	15	3	8
-11	3	13	4	9
-11	4	90	3	88
-11	6	34	3	31
-10	2	34	2	32
-10	3	33	2	32
-10	4	18	4	22
-10	5	22	2	31
-10	6	15	6	19
-10	7	19	3	22
-9	3	22	3	24
-9	4	32	2	33
-9	5	13	4	16
-9	6	18	3	19
-9	7	17	3	17
-8	2	35	2	33
-8	3	51	2	47
-8	4	41	2	43
-8	5	31	2	32
-8	6	58	2	59
-8	8	16	3	13
-7	2	52	2	48
-7	4	10	4	3
-7	5	83	2	82
-7	6	65	2	66
-7	7	29	3	32
-7	8	26	3	29
-6	2	13	3	13
-6	3	83	2	76
-6	4	20	3	20
-6	5	9	5	13
-6	7	10	4	9
-6	8	52	2	50
-6	9	15	4	14
-5	1	21	2	19
-5	2	23	2	22
-5	3	10	5	6
-5	4	34	2	36
-5	5	40	2	37
-5	6	25	2	24
-5	7	5	5	7
-5	8	26	2	27
-5	9	61	2	60
-4	1	50	2	46
-4	2	47	2	48
-4	3	16	2	12
-4	4	63	2	60
-4	6	25	3	25
-4	6	27	2	25
-4	6	26	2	25
-4	7	80	3	83
-4	7	81	3	83
-4	8	52	2	56
-4	8	56	2	56
-4	9	10	5	14
-4	9	12	5	14
-3	2	165	4	164
-3	4	15	2	18
-3	5	24	2	21
-3	6	49	2	46
-3	7	25	2	30
-3	7	30	2	30
-3	8	57	2	60
-3	8	61	2	60
-3	9	13	4	5
-2	1	93	2	88
-2	2	9	3	9
-2	3	41	2	41
-2	4	6	5	5
-2	5	59	2	56
-2	6	9	4	5
-2	7	28	2	27
-2	7	26	2	27
-2	7	25	3	27
-2	8	20	3	20
-2	8	14	4	20
-2	8	21	3	20
-2	9	17	3	10
-2	9	11	5	10
-2	9	10	4	10
-2	10	11	4	4
-2	10	9	5	4
-1	2	46	1	44
-1	3	99	3	94
-1	4	25	2	25
-1	5	54	2	54
-1	6	13	4	13
-1	7	63	2	63
-1	7	64	2	63
-1	7	63	2	63
-1	9	16	3	8
-1	9	14	4	8
-1	10	14	4	13
-1	10	17	3	13
-1	10	12	5	13
0	2	9	2	8
0	4	78	2	80
0	4	84	2	80
0	4	82	2	80
0	4	81	2	80
0	4	81	2	80
0	4	83	2	80
0	4	82	2	80
0	4	78	2	80
0	4	82	2	80
0	4	82	2	80
0	4	79	2	80
0	4	79	2	80
0	4	80	2	80
0	4	79	2	80
0	4	79	2	80
0	4	80	2	80
0	4	78	2	80
0	4	79	2	80
0	4	78	2	80
0	4	81	2	80
0	4	80	2	80
0	4	80	2	80
0	4	80	2	80
0	4	79	2	80
0	4	80	2	80
0	4	79	2	80
0	4	80	2	80
0	4	80	2	80
0	4	78	2	80
0	4	80	2	80
0	4	79	2	80
0	4	81	2	80
0	4	82	2	80
0	4	79	2	80
0	4	80	2	80
0	6	30	2	29
0	6	30	2	29
0	8	44	2	43
0	8	41	2	43
0	8	45	2	43
0	10	60	2	58
0	10	56	2	58
0	10	56	2	58
1	1	5	3	7
1	2	42	1	44
1	3	94	3	94
1	3	93	2	94
1	3	93	2	94
1	3	94	3	94
1	3	95	3	94
1	3	96	3	94
1	3	93	3	94
1	3	96	3	94
1	3	94	3	94
1	3	95	3	94
1	3	93	2	94
1	3	94	3	94
1	3	94	3	94
1	3	93	2	94
1	3	95	3	94
1	3	98	3	94
1	3	94	3	94
1	3	93	3	94
1	3	93	3	94
1	3	93	3	94
1	3	93	3	94
1	3	95	3	94
1	3	97	3	94
1	3	93	3	94
1	3	93	3	94
1	3	94	3	94
1	3	94	3	94
1	3	93	3	94
1	3	94	3	94
1	3	95	3	94
1	3	93	2	94
1	3	95	3	94
1	3	94	3	94
1	3	92	2	94
1	3	96	3	94
1	4	22	2	25
1	5	55	2	54
1	5	56	2	54
1	6	15	3	13
1	6	13	3	13
1	7	59	2	63
1	7	63	2	63
1	7	62	2	63
1	9	16	3	8
1	9	10	6	8
1	10	14	3	13
1	10	11	4	13
2	2	10	2	9
2	3	41	2	41
2	4	7	5	5
2	5	55	2	56
2	7	25	2	27
2	7	28	2	27
2	7	25	2	27
2	8	21	3	20
2	8	18	3	20
2	8	15	2	20
2	9	13	4	10
2	9	13	4	10
2	9	12	4	10
3	4	13	3	18
3	6	49	2	46
3	7	30	2	30
3	7	31	2	30
3	7	32	2	30
3	8	62	2	60
3	8	61	2	60
3	8	58	2	60
3	9	9	5	5
4	1	47	1	46
4	3	12	3	12
4	4	56	2	60
4	6	23	3	25
4	6	24	2	25
4	6	27	2	25
4	7	78	2	83
4	7	75	2	83
4	8	56	2	56
4	8	57	2	58
4	9	5	6	14
4	9	17	3	14
5	1	17	2	19
5	2	21	2	22
5	4	34	2	36
5	5	39	2	37
5	6	24	2	24
5	7	11	4	7
5	8	26	2	27
5	9	59	2	60
5	9	59	2	60
6	0	33	2	36
6	2	16	3	13
6	3	72	2	76
6	4	22	3	20
6	5	12	4	13
6	6	11	4	11
6	7	7	5	9
6	8	48	2	50
6	9	19	2	16
7	1	38	2	42
7	2	42	2	48
7	3	102	3	102
7	5	85	3	82
7	6	67	2	66
7	7	33	2	32
7	8	32	2	29
8	1	21	2	26
8	2	29	2	33
8	3	43	2	47
8	4	44	2	43
8	5	29	2	32
8	6	59	2	59
8	7	8	6	4
9	1	31	2	33
9	3	23	2	24
9	4	35	2	33
9	5	10	5	16
9	6	20	2	19
9	7	12	5	17
10	0	75	2	76
10	1	31	2	32
10	2	33	2	32
10	3	34	2	32
10	4	21	3	22
10	5	30	3	31
10	6	22	3	19
10	7	21	3	22
11	-1	37	2	36
11	1	37	2	36
11	2	26	2	26
11	3	14	3	9
11	4	86	3	88
11	5	12	6	22
11	6	30	3	31
12	-1	51	2	52
12	0	14	4	14
12	1	56	2	52
12	2	35	2	34
12	3	44	2	44
12	5	14	3	8
13	-1	11	6	14
13	1	14	4	14
13	2	13	4	11
13	4	29	3	32
14	-1	8	7	8
14	0	15	3	10
14	1	11	5	8
*** H= 1 ***				
0	-1	42	1	44
0	1	139	4	130
0	1	140	4	130
0	3	147	4	150
0	3	146	4	150
0	7	83	3	86
0	9	61	2	61
0	9	60	2	61
1	0	35	1	32
1	1	80	2	78
1	2	18	2	14
1	3	12	2	14
1	4	56	2	53
1	5	64	2	65
1	5	66	2	65
1	6	19	2	22
1	6	19	2	22
1	9	35	2	35
1	9	35	2	35
1	10	31	2	31
1	10	31	2	31
2	-1	9	3	10
2	0	66	2	64
2	1	15	2	14
2	4	17	3	21
2	5	28	2	27
2	6	14	4	21
2	7	43	2	41
2	7	41	2	41
2	8	13	5	12
2	9	16	3	19
3	-1	75	2	80
3	0	25	1	26
3	1	87	2	85
3	2	103	3	98
3	3	24	2	28
3	4	39	2	38
3	5	27	2	25
3	6	56	2	59
3	7	91	3	91
3	7	92	3	91
3	8	10	5	2
3	8	10	6	2
3	9	36	2	34
3	9	33	3	34
4	-1	65	2	63
4	0	93	3	94
4	1	43	2	43
4	2	9	4	12
4	3	26	2	24
4	5	49	2	45
4	6	15	2	15
4	6	19	3	15
4	7	54	2	56
4	8	47	2	44
4	9	15	4	15
5	-1	37	2	39
5	0	18	2	21
5	1	27	2	28
5	2	15	2	19
5	3	34	2	32
5	4	14	3	12
5	6	49	2	49
5	7	31	2	31
6	-2	45	2	49
6	-1	43	2	44
6	0	30	2	36
6	1	73	2	72
6	2	21	2	18
6	3	12	3	13
6	4	12	3	10
6	5	65	2	63
6	5	62	2	63
6	7	53	2	52
6	8	18	3	14
7	-2	65	2	74
7	-1	30	2	31
7	0	16	2	12
7	1	47	2	49
7	2	54	2	55
7	3	34	2	35
7	4	9	6	10
7	6	48	2	47
7	7	16	4	18
7	8	60	2	57
8	-2	30	2	30
8	-1	8	5	4
8	0	19	3	24
8	1	25	2	28
8	2	35	2	33
8	3	56	2	55
8	4	20	2	21
8	5	12	3	3
8	6	30	3	30
8	8	8	8	12
9	-2	14	2	15
9	-1	13	4	15
9	-1	7	6	15
9	0	36	2	38
9	1	56	2	59
9	1	59	2	55
9	2	8	1	15
9	2	5	6	15
9	3	21	2	22
9	4	37	2	35
9	5	17	4	20
10	-2	23	2	23
10	-1	25	2	25
10	0	41	2	40
10	2	36	2	34
10	3	29	3	26
10	4	60	2	56
10	5	9	8	16
11	-2	43	2	42
11	-1	56	2	54
11	0	39	2	40
11	1	41	2	41
11	2	22	2	21
11	3	14	4	14
11	4	19	5	23
11	5	55	3	51
11	6	27	3	24
12	-2	17	4	20
12	-1	10	5	9
12	0	40	2	39
12	1	17	5	16
12	3	9	6	12
12	5	26	3	23
13	-2	14	4	14
13	-1	13	4	12
13	0	12	4	13
13	2	29	3	28
13	3	11	6	18
*** H= 2 ***				
0	0	34	1	33
0	0	33	1	33
0	2	102	3	98
0	2	101	3	98
0	4	60	2	60
0	4	60	2	60
0	6	8	6	4
0	8	27	2	23
1	-3	80	2	79
1	-2	17	2	19
1	-1	10	2	10
1	0	23	1	25
1	1	94	3	90
1	2	38	2	42
1	5	58	2	54
1	5	52	2	54
1	7	21	3	26
1	8	24	2	24
2	-3	29	1	27
2	-2	50	2	50
2	-1	118	3	121
2	0	8	3	4
2	2	49	2	47
2	3	28	2	27
2	4	79	2	74
2	6	74	2	72
2	6	70	2	72
2	8	25	2	21
3	-3	9	3	3
3	-1	64	2	64
3	0	28	1	26
3	1	45	2	44
3	2	16	2	18
3	3	92	2	98
3	4	77	2	75
3	6	42	2	42
3	6	44	2	42
3	7	32	2	31
3	9	11	4	14
4	-3	18	3	15
4	-1	80	2	83
4	0	27	2	25
4	1	26	2	27
4	2	24	2	25
4	3	76	2	73
4	4	35	2	32
5	-3	67	2	68
5	-2	11	3	6
5	-1	30	2	33
5	0	12	4	17
5	1	9	3	3
5	2	54	2	56
5	4	119	3	110
5	5	90	2	92
6	-3	24	2	24
6	-2	71	2	73
6	-1	20	3	23
6	0	15	3	12
6	1	41	2	44
6	2	28	2	30
6	3	44	2	42
6	4	90	2	93
7	-2	17	3	19
7	-1	62	2	60
7	1	9	5	3
8	-3	13	4	11
8	-2	34	2	34
8	-1	74	2	77
8	0	65	2	64
8	1	51	2	52
8	2	48	2	46
9	0	23	3	24
*** H= 3 ***				
0	-5	20	2	20
0	-3	3	5	9
0	-1	24	2	24
0	1	20	2	24
0	1	29	2	24
0	3	35	2	28
0	5	68	2	68
0	5	68	2	68
0	9	21	3	19
1	-5	14	3	12
1	-4	13	2	10
1	-3	8	4	12
1	-2	15	3	15
1	0	51	2	51
1	1	44	2	44
1	2	8	6	3
1	4	9	5	4
1	4	12	4	4
1	5	70	2	70
1	5	67	2	70
1	6	23	2	23
1	7	48	2	47
1	8	42	2	40
1	9	17	4	26
2	-5	23	2	26
2	-4	70	2	69
2	-3	20	2	20
2	-1	57	2	55
2	0	22	2	20
2	1	11	3	7
2	3	112	3	108
2	4	15	3	12
2	6	12	2	9
2	7	9	4	4
2	8	27	3	30
2	9	35	2	33
3	-5	17	3	16
3	-2	22	2	20
3	-4	34	2	32
3	0	55	2	53
3	1	30	2	30
3	2	63	2	65
3	3	31	2	34
3	4	39	2	35
3	5	11	4	10
3	6	12	4	11
3	7	59	2	55
3	8	21	3	19
3	9	18	2	13
4	-5	18	3	21
4	-4	13	3	11
4	-3	55	2	56
4	-2	71	2	72
4	-1	22	2	20
4	0	13	3	13
4	1	21	2	18
4	3	45	2	45
4	4	36	2	37
4	5	24	2	22
5	-3	14	3	14
5	-2	28	2	29
5	0	67	2	64
5	1	75	2	71
5	2	11	5	13
5	3	98	3	98
5	4	43	2	42
6	-4	14	2	12
6	-2	34	2	32
6	-1	13	4	11
6	0	30	4	8
6	1	33	2	34
6	2	31	2	30
6	3	46	2	44
6	4	27	2	27
7	-3	70	2	70
7	-2	13	2	8
7	-1	56	2	57
7	0	10	5	8
7	1	27	3	30
7	2	34	2	35
7	3	38	2	38
8	-1	90	2	91
8	0	14	4	14
8	1	58	2	58
*** H= 4 ***				
0	-2	65	2	68
0	-2	68	2	68
0	0	25	2	24
0	0	25	2	20
0	0	25	2	26
0	2	90	3	95
0	2	95	3	95
0	4	27	2	28
0	4	29	2	26
0	8	75	3	78
1	-6	29	2	28
1	-5	99	3	96
1	-3	50	2	51
1	-2	25	2	24
1	-1	20	2	19
1	0	79	2	80
1	2	28	2	28
1	3	92	3	94
1	6	10	4	10
1	8	30	2	30
2	-6	17	2	13
2	-5	7	5	5
2	-4	46	2	40
2	-3	33	2	32
2	-2	40	2	41
2	-1	12	4	17
2	0	56	2	57
2	1	14	2	16
2	2	51	2	50
2	3	15	3	15
2	4	14	2	14
2	5	34	2	34
2	6	18	3	19
2	7	33	2	31
3	-4	32	2	32
3	-2	24	2	23
3	-1	25	2	24
3	0	14	4	15
3	1	55	2	54
3	2	91	3	96
3	3	14	3	15
3	4	28	2	27
3	4	25	3	27
3	5	25	2	25
3	6	62	2	61
3	7	17	4	20
4	-4	25	2	20
4	-3	23	2	21
4	-1	22	2	21
4	0	45	2	42
4	1	81	2	81
4	2	24	2	22
4	3	26	2	21
4	4	5	5	6
5	-3	20	3	27
5	-2	67	2	66
5	-1	26	2	25
5	0	66	2	66
5	1	8	4	8
5	2	14	3	19
5	3	58	2	60
6	-2	22	2	20
6	-1	10	4	11
6	0	38	2	40
6	1	33	2	31
6	2	38	2	37
*** H= 5 ***				
0	-3	25	2	28
0	-1	59	2	57
0	1	40	2	40
0	1	40	2	40
0	3	28	2	28
0	3	29	2	28
1	-8	26	3	28
1	-7	39	2	34
1	-6	25	2	23
1	-5	43	2	42
1	-4	24	2	29
1	-3	37	2	37
1	-3	38	2	37
1	-2	65	2	67
1	-1	43	2	43
1	0	41	2	42
1	1	24	2	26
1	2	41	2	41
1	3	64	2	65
1	3	61	2	61
1	4	35	2	40
1	5	8	6	14
1	6	38	2	40
2	-7	14	3	17
2	-6	30	2	30
2	-5	40	2	39
2	-4	15	3	15
2	-3	34	2	34
2	-3	34	2	34
2	-2	24	2	24
2	-1	11	4	14
2	0	45	2	43
2	1	19	2	16
2	2	8	5	7
2	3	14	3	14
2	3	17	2	14
2	4	34	2	36
2	5	38	2	41
2	6	37	2	39
3	-2	28	2	30
3	-1	53	2	55
3	2	9	4	11
3	3	35	2	35
3	4	20	3	21
3	5	30	2	27
3	6	18	3	18
3	7	35	3	35
4	-2	90	3	87
4	0	42	2	39
4	1	4	6	1
*** H= 6 ***				
1	-7	22	3	20
1	-6	8	7	1
1	-2	7	6	3
1	-1	25	2	26
1	0	20	2	17
1	1	71	2	72
1	3	49	2	50
1	4	70	2	72
1	5	32	2	35
1	7	14	4	14
2	-7	15	4	15
2	-5	18	3	17
2	-3	55	2	56
2	-2	46	2	47
2	-1	36	2	35
2	0	45	2	44
2	1	14	3	14
2	2	70	2	71
2	3	30	2	29
2	4	29	3	29
2	4	20	3	15
3	3	10	7	14
3	4	15	3	13
3	6	44	2	44
*** H= 7 ***				
1	-5	14	3	13
1	-3	54	2	54
1	-2	12	3	12
1	0	12	3	5
1	1	39	2	39
1	3	10	7	12
1	4	27	3	28
1	5	31	2	26
2	-5	32	2	31
2	-4	44	2	43
2	-2	52	2	53
2	-1	48	2	47
2	0	23	3	25
2	1	13	2	11
2	2	44	2	42
2	3	11	4	8
2	5	33	2	31
3	3	9	6	5
3	5	13	4	15
*** H= 8 ***				
1	-3	13	4	16
1	-2	30	2	30
1	0	36	2	37
1	1	52	2	49
1	2	35	2	35
1	3	32	3	31
2	-3	29	3	30
2	-2	63	2	64
2	-1	20	3	18
2	0	22	3	22
2	1	27	3	27
2	2	17	4	18
3	2	14	3	8

$[\sigma^2_{counting} + (0.05 \times F_o^2)^2]$ and $\sigma_{counting}$ = the counting error, according to Poisson's statistics. It was obvious at this point the heavy atom positions had to be refined also and thus a series of cycles of least squares refinement followed in which all the atoms were refined with anisotropic thermal parameters using block diagonal methods. This block-diagonal refinement procedure was necessary because of the size of the neutron diffraction problem (272 variable parameters). When convergence was achieved, two more cycles of refinement were carried out in which the isotropic extinction parameter was also refined.[11,12] At this point the thermal model was fixed and the positional parameters of *all* the atoms were varied at once to prepare the input tape for the function and error program ORFFE[13] (i.e. standard deviations in the positional parameters were estimated from the inverse of the normal equations matrix). The final values of the residuals are $R_1 = 0.053$ and $R_2 = 0.048$, with an error of fit of 1.04, where the error of fit, or error in an observation of unit weight, is defined as

$$\text{error of fit} = [\Sigma w(|F_o|-|F_c|)^2/\Sigma(NO\text{-}NV)]^{1/2}$$

with NO and NV = the number of observations and the number of variables, respectively. The absolute value of the isotropic extinction parameter was G = 130(37), which depending on whether one uses Zachariasen's[11] type I or type II extinction model implies a mosaic spread of 448 seconds or a domain size of 1.295×10^{-6} centimeters, respectively. The final positional and thermal parameters, together with their estimated standard deviations are given in Table I. Table II gives a comparison between the observed structure amplitudes and those calculated using the positional and thermal parameters listed in Table I.

The programs used were PROCH (for the processing of the raw data);[14] DATAPH (for the absorption correction);[14] SORTH (data sorting and averaging);[14] LINUS (Brookhaven's least-squares refinement program; it also corrects for extinction);[12] ORFFE (BNL's version of Busing, Martin, and Levy's function and error program);[13] ORTEP (Johnson's molecular plotting program);[15] and PLANET (Smith's[16] least-squares planes).

Description of the Structure. The structure of $[C_5H_4\text{-}(CH_2)_3\text{-}C_5H_4]TiCl_2$ consists of a $TiCl_2$ fragment with a Cl-Ti-Cl angle of 93.2° which is symmetrically positioned between two planar cyclopentadienyl rings. The two rings, whose normals make an angle of 133.1°, are linked by a (-CH_2-CH_2-CH_2-) chain which lies entirely to one side of the plane defined by the Ti atom and the centroids of the two rings. The coordi-

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[11] W.H. Zachariasen, *Acta Cryst.*, *23*, 558, (1967).

[12] The extinction correction was performed using program LINUS which is our version of the program originally written by W.R. Busing, K.O. Martin, and H. Levy, « ORFLS, A Fortran Crystallographic Least-Squares Program » ORNL-TM-305, Oak Ridge National Laboratory, 1962. This program contains an extinction correction based on Zachariasen's equations (ref. 11) which were implemented by the procedure described by P. Coppens and W.C. Hamilton, *Acta Cryst.*, *A26*, 71 (1970).

[13] Brookhaven's version of the program « ORFFE, A Fortran Crystallographic Function and Error Program », ORNL-TM-306, Oak Ridge National Laboratory, 1962. Written by W.R. Busing, K.O. Martin, and H. Levy.

[14] PROCH, DATAPH and SORTH are local Brookhaven programs; available on request. The absorption correction performed by DATAPH has been described by P. Coppens, L. Leiserowitz, and D. Rubinovich, *Acta Cryst.*, *18*, 1035 (1965).

[15] C.K. Johnson, « ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations », ORNL-3794-Revised, Oak Ridge National Laboratory 1965.

[16] D.L. Smith, Ph.D. Thesis, University, of Wisconsin, 1962.

nation geometry about the titanium atom may be viewed as a tetrahedron. The symmetric disposition of the rings with respect to the $TiCl_2$ moiety and the nearly staggered configuration of the rings results in an idealized C_{2v} point group symmetry for the molecule, excluding the exocyclic chain. A view of the entire molecule appears in Figure 1. A stereoscopic view of the molecule is given in Figure 2 and the packing in the unit cell is described in Figure 3.

The positions of the non-hydrogen atoms obtained from neutron diffraction data are in close agreement with the positions obtained by Davis and Bernal[5] from x-ray diffraction studies. In Tables III and IV the agreement is summarized by detailed comparisons of

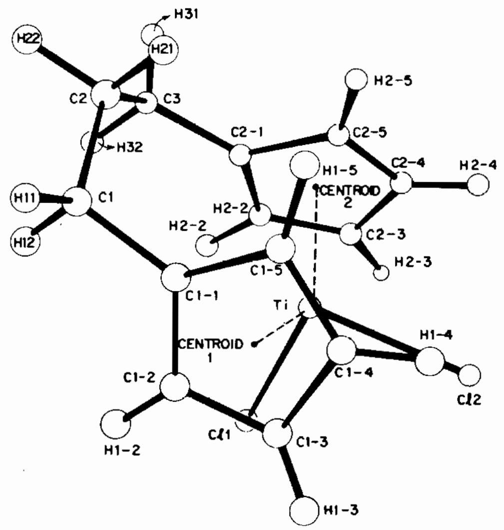

Figure 1. The molecular configuration of $\{(CH_2)_3(C_5H_4)_2\}TiCl_2$. All atoms were made isotropic and of arbitrary magnitude.

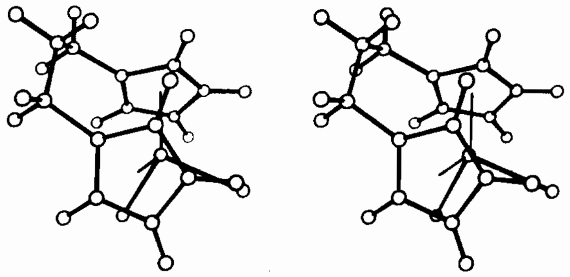

Figure 2. Stereoscopic view of the $\{(CH_2)_3(C_5H_4)_2\}TiCl_2$ molecule.

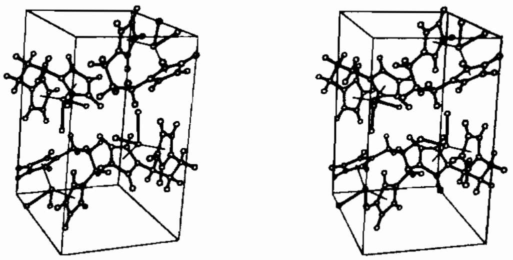

Figure 3. The packing of the molecules in a monoclinic unit cell. The positive b direction is from bottom to top and the positive a axis runs, approximately, from left to right. The cell was rotated + 10° about y and + 20° about x.

Table III. Interatomic Distances (Å) and Angles (Degrees).

A. Interatomic Distances - Neutron vs. X-Ray Results

	neutron	x-ray
Ti...Cl(1)	2.368(8)	2.372(1)
...Cl(2)	2.365(9)	2.364(3)
...(centroid, ring 1)	2.059(—)	2.061(—)
...(centroid, ring 2)	2.056(—)	2.060(—)
Ti...C1-1	2.374(10)	2.400(4)
...C1-2	2.400(10)	2.384(4)
...C1-3	2.381(9)	2.369(4)
...C1-4	2.386(8)	2.385(4)
...C1-5	2.372(9)	2.379(3)
	Av...2.383(9)	2.383(4)
Ti...C2-1	2.428(9)	2.407(3)
...C2-2	2.375(8)	2.390(4)
...C2-3	2.348(9)	2.360(4)
...C2-4	2.397(10)	2.369(3)
...C2-5	2.370(10)	2.367(3)
	Av...2.385(9)	2.379(4)
C1-1...C1-2	1.375(7)	1.401(4)
C1-2...C1-3	1.431(7)	1.398(5)
C1-3...C1-4	1.426(7)	1.396(4)
C1-4...C1-5	1.422(7)	1.397(4)
C1-5...C1-1	1.425(6)	1.419(4)
Ring 1	Av...1.416(7)	1.402(4)
C2-1...C2-2	1.395(6)	1.401(4)
C2-2...C2-3	1.366(8)	1.385(6)
C2-3...C2-4	1.380(8)	1.395(6)
C2-4...C2-5	1.408(7)	1.396(5)
C2-5...C2-1	1.460(7)	1.406(4)
Ring 2 Av.	1.402(7)	1.396(5)
Ring C-C, Overall Av.	1.409(7)	1.399(4)
C1...C1-1	1.515(7)	1.494(4)
C1...C2	1.504(8)	1.505(5)
C2...C3	1.513(7)	1.511(5)
C3...C2-1	1.473(7)	1.495(5)

B. Neutron Results for C-H Bond Lengths

C1-2...H1-2	1.06(2)	C1...H11	1.03(2)
C1-3...H1-3	1.02(2)	C1...H12	1.08(2)
C1-4...H1-4	1.04(1)	C2...H21	1.08(2)
C1-5...H1-5	1.07(2)	C2...H22	1.16(2)
C2-2..H.2-2	1.14(2)	C3...H31	1.03(2)
C2-3...H2-3	1.14(2)	C3...H32	1.07(2)
C2-4...H2-4	1.11(2)	Av. (Ring C)-H-	1.09(2)
C2-5...H2-5	1.08(2)	Av. (Aliph. C)-H-	1.07(2)

C. Bond Angles Between Heavy Atoms (neutron vs. x-ray)

Cl(1)-Ti-Cl(2)	93.20(32)	93.69(5)
R1*-Ti-R2	133.12(—)	132.64(—)
R1-Ti-Cl(1)	106.03(—)	106.20(—)
R1-Ti-Cl(2)	105.68(—)	105.93(—)
R2-Ti-Cl(1)	106.11(—)	105.80(—)
R2-Ti-Cl(2)	105.72(—)	105.87(—)

* Ri = centroid of Ring i.

C1	C1-1	C1-2	125.2(5)	126.1(3)
C1	C1-1	C1-5	125.4(4)	126.8(3)
C1-2	C1-1	C1-5	108.2(5)	106.3(3)
C1-1	C1-2	C1-3	109.3(5)	109.1(3)
C1-2	C1-3	C1-4	107.1(5)	108.0(3)
C1-3	C1-4	C1-5	107.3(4)	107.8(3)
C1-4	C1-5	C1-1	108.1(4)	108.7(3)
C3	C2-1	C2-2	126.9(4)	124.7(3)
C3	C2-1	C2-5	126.8(4)	127.6(3)
C2-2	C2-1	C2-5	105.8(4)	106.9(3)
C2-1	C2-2	C2-3	110.0(5)	109.1(3)
C2-2	C2-3	C2-4	109.0(6)	107.6(3)
C2-3	C2-4	C2-5	108.6(5)	108.4(4)
C2-4	C2-5	C2-1	106.2(4)	107.9(3)

the bond lengths and angles obtained in the two studies. Since detailed comparisons between the results of x-ray[5] and neutron diffraction studies of $[C_5H_4\text{-}(CH_2)_3\text{-}C_5H_4]$ $TiCl_2$ and those of the x-ray study[3] of $(C_5H_5)_2TiS_5$ are significant, the numbering system used in the report of the pentasulfide has been preserved for both the x-ray[5] and neutron diffraction reports of the dichloride.

Table III. (Continued)

C1-1	C1	C2	115.0(5)	116.1(3)
C1	C2	C3	113.9(5)	112.5(3)
C2	C3	C2-1	116.3(4)	116.1(3)
H1-2	C1-2	C1-1	124.5(9)	121(1)
H1-2	C1-2	C1-3	125.9(8)	130(1)
H1-3	C1-3	C1-2	127.9(8)	133(2)
H1-3	C1-3	C1-4	124.9(8)	119(2)
H1-4	C1-4	C1-3	124.5(7)	126(2)
H1-4	C1-4	C1-5	128.2(7)	126(2)
H1-5	C1-5	C1-4	127.1(6)	123(2)
H1-5	C1-5	C1-1	124.8(6)	128(2)
H2-2	C2-2	C2-1	122.8(9)	127(2)
H2-2	C2-2	C2-3	127.2(9)	124(2)
H2-3	C2-3	C2-2	127.8(10)	124(2)
H2-3	C2-3	C2-4	123.1(10)	129(2)
H2-4	C2-4	C2-3	125.7(10)	129(3)
H2-4	C2-4	C2-5	124.8(10)	122(3)
H2-5	C2-5	C2-5	127.1(7)	128(2)
H2-5	C2-5	C2-1	126.2(7)	124(2)
H11	C1	C1-1	106.2(7)	103(3)
H11	C1	C2	112.9(9)	110(3)
H11	C1	H12	104.8(10)	110(3)
H12	C1	C2	108.9(7)	109(2)
H12	C1	C1-1	108.5(8)	109(3)
H21	C2	C1	110.3(7)	108(2)
H21	C2	C3	110.1(8)	111(2)
H21	C2	H22	105.4(10)	103(3)
H22	C2	C1	110.0(9)	111(2)
H22	C2	C3	106.8(8)	111(2)
H31	C3	C2-1	105.4(7)	106(2)
H31	C3	C2	111.8(8)	110(2)
H31	C3	H32	107.0(9)	105(3)
H32	C3	C2	108.3(8)	111(2)
H32	C3	C2-1	107.6(7)	109(2)

C. Non-bonded Intermolecular Contacts Less Than 3.5 Å About the Ti, Cl1 and Cl2 Atoms.

Ti...H1-2	3.03(1)	Cl1...Cl2	3.439(6)
...H1-3	2.99(1)	...C1-2	3.023(6)
...H1-4	3.06(1)	...C1-3	3.232(6)
...H1-5	3.05(1)	...C2-2	3.008(6)
...H2-2	3.09(1)	...C2-3	3.183(7)
...H2-3	3.09(1)	...H1-2	2.84(1)
...H2-4	3.03(2)	...H1-3	3.27(1)
...H2-5	3.08(1)	...H2-2	2.87(1)
		...H2-3	3.27(2)
Cl2...C1-3	3.210(8)	Cl2...H1-3	3.21(1)
...C1-4	2.981(7)	...H1-4	2.87(1)
...C2-3	3.216(6)	...H2-3	3.28(1)
...C2-4	2.983(6)	...H2-4	2.76(1)

D. Intermolecular Contacts Less Than 3.50 Å About the C1 and C2 Atoms

Cl1...H2-3	3.27(2)	000	2[a]
...H12	3.07(1)	$\bar{1}00$	2
...H32	2.76(1)	$\bar{1}00$	2
...H2-2	3.24(2)	$\bar{1}00$	2
...H21	3.43(1)	$\bar{1}\bar{1}0$	3
...H1-5	3.31(1)	$\bar{1}\bar{1}0$	3
...H2-5	2.70(1)	$\bar{1}\bar{1}0$	3
Cl2...H2-3	3.29(1)	000	2
...H31	3.42(1)	000	4
...H21	3.09(1)	$\bar{1}\bar{1}0$	3
...H22	3.32(1)	$\bar{1}\bar{1}0$	3
...H31	3.38(1)	$\bar{1}\bar{1}0$	3

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[a] The notation 000 2 indicates the second atom is in the symmetry position 2 with no cell translations. The symmetry positions 1,2,3 and 4 are: x,y,z; $\bar{x},\bar{y},\bar{z}$; 1/2—x, 1/2+y, 1/2—z and 1/2+x, 1/2—y, 1/2+z.

Table IV. Planes.

A. Equations of Planes and Distances (Å) from These Planes

(a) Plane containing Ti, Cl1 and Cl2

$0.4440x+0.4355y-0.7830z = -2.1585$

centroid, ring 1	—1.89
centroid, ring 2	1.89

(b) Plane containing the five carbons of ring 2

$0.6019x+0.0527y-0.7968z = -4.9852$

C1-1	0.010	C1	—0.211
C1-2	—0.013	H1-2	0.046
C1-3	0.012	H1-3	0.087
C1-4	—0.006	H1-4	—0.032
C1-5	—0.002	H1-5	—0.013
Ti	2.059		

(c) Plane containing the five carbons of ring 2

$0.2195x+0.7326y-0.6443z = 0.9836$

C2-1	0.021	C3	0.228
C2-2	—0.003	H2-2	—0.028
C2-3	—0.017	H2-3	0.024
C2-4	0.031	H2-4	—0.049
C2-5	—0.031	H2-5	0.007
Ti	—2.056		

(d) Plane defined by the Ti and the centroids of rings 1 and 2

$-0.7431x-0.3090y-0.5936z = -0.1369$

C1	1.703	C2	1.327
C12	—1.736	C3	1.575
C1	1.645		

(e) Plane containing the four hydrogens of ring 1

$0.6087x+0.0734y-0.7900z = -4.9413$

H2-1	—0.019	C2-1	—0.057
H3-1	0.030	C3-1	—0.028
H4-1	—0.030	C4-1	—0.014
H5-1	0.018	C5-1	0.005
C1-1	—0.006	Ti	2.039

(f) Plane containing the four hydrogens of ring 2

$0.2280x+0.7272y-0.6474z = 0.9356$

H2-2	—0.010	C2-2	0.015
H3-2	0.017	C3-2	0.012
H4-2	—0.017	C4-2	0.055
H5-2	0.011	C5-2	—0.021
C1-2	0.027	Ti	—2.038

B. Angles in Degrees Between Normals to Planes

a	b	23.9	b	e	1.3
a	c	22.9	b	c	133.2
a	e	23.0	b	d	89.5
a	f	22.3	c	d	89.6
a	d	90.0	c	f	0.6

Table IV. (Continued)

C. Angles (in Degrees) Between Interatomic Vectors and the Normals to Planes

Vector	Plane	Angle
Ti-(centroid, ring 1)	b	0.8
Ti-(centroid, ring 1	a	23.4
Ti-(centroid, ring 2)	c	0.7
Ti-(centroid, ring 2)	a	23.5
C1-C2	d	0.6
C1-C2	b	89.2
C1-C2	c	89.3
C1-C2	d	0.7
C1-C2	e	89.9
C1-C2	f	89.2

[a] The equations of the planes and distances and angles were obtained with the Smith plane program (see ref. 15). The weights used for each atom were given by

$$[(EX)(EY)(EZ)(A)(B)(C)]^{-2/3}$$

where, EX, EY and EZ are the errors in the fractional coordinates of the atom in question (see Table I) and A. B and C are the cell constants. Related to the fractional coordinates x, y and z by the relation:

$$X = zx+cz\cos\beta$$
$$Y = by$$
$$Z = cz\sin\beta$$

Discussion

The Titanium-Chloride Bonds. The Ti-Cl distances of 2.368(8) and 2.365(9) Å obtained from the neutron diffraction data agree well with the values of 2.372(1) and 2.364(3) Å reported in the x-ray study.[5] The average Ti-Cl distance of 2.367(8) Å is significantly longer than Ti-Cl distances reported for compounds which do not contain cyclopentadienyl ligands. These distances range from 2.185(4) Å to 2.32(2) Å in the complexes $TiCl_4$,[17] $[TiCl_2(O\text{-}C_6H_5)_2]_2$,[13] $TiCl_2(C_9H_6NO)_2$ [19] and in $[TiCl(C_5H_7O_2)_2]O^{\cdot}CHCl_3$ [20] in which the coordination number of the titanium ranges from four to six. For the tetrahedral complex $[(C_5H_5)TiClO]_4$,[21] which contains one π-cyclopentadienyl group, the average Ti-Cl bond lengths 2.266(4) Å while in the octahedral complex $TiCl(C_5H_5)\ (C_9H_6NO)_2$ [22] the distance is 2.37(–) Å. The complexes $[POCl_3\text{-}TiCl_4]_2$,[23] $[PCl_4]\ [Ti_2Cl_9]$[24] and $[PCl_4]_2[Ti_2Cl_{10}]$[24] contain chlorine-bridged titanium atoms, the Ti-Cl distances of which are all in the range 2.44(1) to 2.54(1) Å. The average Ti-Cl distance of 2.367(8) Å found in $[C_5H_4\text{-}(CH_2)_3C_5H_4]TiCl_2$ and of 2.37(–) Å found in $TiCl\text{-}C_5H_5)\ (C_9H_6NO)_2$[22] are long compared to the distances found in the four and six coordinate complexes which do not contain π-cyclopentadienyl rings; however, they are short compared to the distances found in the bridged systems. Presumably, (Ti-(π-cyclopentadienyl) bonds result in a weakening of the Ti-Cl bond. Other details of the geometry of this portion of the molecule may be found in the report of the x-ray structural study carried out by Davis and Bernal.[5]

The Cyclopentadienyl Rings. The primary advantage of neutron diffraction over X-ray diffraction, as it affects this study, is that the *magnitude* of the neutron scattering cross-section is approximately the same for all atoms of this compound,[10] the largest difference being a factor of about three. This makes possible the determination of hydrogen atom positions with the same, or better, accuracy as that for heavier elements. The second advantage is that neutrons are scattered by nuclei,[6] not electrons, so that the atomic coordinates of atoms obtained by neutron diffraction studies are not affected by the diffuse distribution of electrons as is in the case of X-ray diffraction. It has been observed[25] that the positions of carbon, hydrogen and nitrogen atoms differ in X-ray and neutron diffraction studies as a result of shifts in electron density from a spherical distribution around the atomic nucleus and into the region of chemical bonds. In our case it was of interest to attempt to determine this effect *via* an expansion in the effective size of the cyclopentadienyl rings when determined by neutrons, as opposed to X-rays. This effect, if observed, should not affect a group estimate based on the Ti-(ring centroid) distances since the shift of electron density in question should occur only in the basal plane of the cyclopentadienyl rings.

The ten Ti... carbon distances, which have a range of 0.08 Å (e.s.d. $\leqslant$ 0.01 Å) for the neutron data, are found to have an average value which is statistically the same as that obtained from X-ray data. This result is valid for the two rings individually. The symmetric displacement of the Ti atom with respect to the carbon atoms of the π-cyclopenadienyl rings is in contrast with the results of Laing and Trueblood[26] who found an asymmetrically disposed Fe in 1,1'tetramethylethylene ferrocene but in agreement with the results of Jones, Marsh, and Richards,[27] whose study of α-keto-1,1'-trimethylene ferrocene showed a homogeneous set of Fe-C distances. Comparison with the latter molecule, with its three atom bridge, is perhaps the more pertinent of the two since in the former substance the molecules are strained by the presence of the short ethylene bridge.[26]

The positions of the hydrogen atoms were the primary object of this work. The average C-H distances for atoms in the π-cyclopentadienyl rings are 1.05(2) and 1.12(2) Å for rings 1 and 2. The average C-H distance for the eight ring carbon atoms bonded to hydrogens is 1.09(2) Å and is the same as the average value of 1.06(2) Å found for the six (methylene carbon)-hydrogen distances. There is a slight, possibly insignificant, displacement of the ring hydrogens toward the titanium. This effect is best demonstrated *not* by the individual displacements of the hydrogens from the best planes of the carbon atoms but rather by the

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(17) « Tables of Interatomic Distance and Configuration in Molecules and Ions », Supplement Special Publication No. 18, The Chemical Society, London, 1965, p. M205.

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difference between the distances of the titanium atom to the best plane through the carbon atoms and the titanium atom to the best plane of the hydrogen atoms These values are

Ti-(plane of carbons, ring 1)	2.06 Å
Ti-(plane of hydrogens, ring 1)	2.04
Ti-(centroid, ring 1)	2.06
Ti-(plane of carbons, ring 2)	2.06
Ti-(plane of hydrogens, ring 2)	2.04
Ti-(centroid, ring 2)	2.06

The maximum deviation of any carbon atom from planarity in rings 1 and 2 is 0.01 and 0.03 Å respectively. The maximum deviation from planarity of any hydrogen from the plane defined by the hydrogens of rings 1 and 2 is 0.03 Å and 0.02 Å. The nearly parallel arrangement of carbon atom and hydrogen atom planes is illustrated by the angles between the normals to these planes which are 0.8° and 0.7° for rings 1 and 2.

The average C-C distances for rings 1 and 2 are 1.416(7) and 1.402(7) Å, respectively (neutron data). The corresponding values obtained from X-ray data are 1.402(4) and 1.396(5) Å. The average C-C distance of 1.408(7) Å (neutron data) in the π-cyclopentadienyl rings is not significantly different than the average value of 1.419 Å cited by Wheatley[28] in his review of metal-(π-cyclopentadienyl) complexes.

The Propyl Chain Bridge. The average methylene carbon-methylene carbon bond length is 1.509(8) Å. This average length is almost insignificantly different from the average value of 1.494(7) Å methylene carbon-ring carbon bond distance. The near identity of these average values is perhaps surprising since the (methylene carbon)-(ring carbon) bond involves atoms with different hybridizations.

The C-C-C bond angles at the three atoms of the propyl chain are in the range 113.9 to 116.3° (e.s.d. = 0.4°). The C-C-C angles at the two terminal carbon atoms of the propyl chain are 115.0(5)° and 116.3(4)° while the angle at the central atom is 113.9(5)°. This chain opening (i.e. C-C-C bond angles all greater than the idealized tetrahedral value) has been observed in the bridged di-π-cyclopentadienyl compounds α-keto-1,1'-trimethyleneferrocene,[17] in [3,3'] paracyclophane[29] and in syn-2,11-dithia [3,3] metacyclophane.[30] For these latter two species, the chain opening effect has been observed although the side chains are of sufficient length that the bridge could be established without distortion. In $[C_5H_4\text{-}(CH_2)_3\text{-}C_5H_4]TiCl_2$ the chain opening is associated with a displacement of the terminal carbon atoms of the propyl chain (C1 and C3) from the plane of the π-cyclopentadienyl group to which they are attached by 0.21 and 0.23 Å, respectively. The direction of these displacements is *away* from the region of the electron density in the ring-Ti bond.

While the C-C-C angles at the methylene carbons are all greater than the tetrahedral value, the three H-C-H angles at the methylene carbon atoms are all less than the tetrahedral value. These angles are in the range 104.8° to 107.0° (e.s.d. ≃0.8°). The reduction in H-C-H angles to values less than tetrahedral we observe in $[C_5H_4\text{-}(CH_2)_3\text{-}C_5H_4]TiCl_2$ is consistent with similar observations in the bridged systems which exhibit chain opening.[17,29,30] These distortions from tetrahedral geometry about the methylene carbons in $[C_5H_4\text{-}(CH_2)_3\text{-}C_5H_4]TiCl_2$ appear *not* to arise from intermolecular interactions since the neutron results confirm the tentative statement made in the report of the X-ray study[5] that there are no meaningful intermolecular or intramolecular hydrogen bonds between the C-H hydrogens and either the Cl or Ti atoms. The distances in question (in the range of 2.8 Å or longer) are of the van der Waals type.

(28) P.J. Wheatley, « Perspectives In Structural Chemistry » J.D. Dunitz, and J.A. Ibers, Eds., John Wiley, and Sons, New York, N.Y., 1967, p. 1.

(29) P.K. Gantzel and K.N. Trueblood, *Acta Cryst.*, *18*, 958 (1965).