

The Crystal and Molecular Structure of 1,1'-Tetramethylethylenferrocene*

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1,1'-Tetramethylethylenferrocene forms monoclinic plates of space group $P2_1/c$, and four molecules in the unit cell with $a_0=7.756$, $b_0=10.97$, $c_0=15.41$, and $\beta=92.63^\circ$. The structure was solved from three-dimensional Patterson and Fourier syntheses, and was refined by block-diagonal least squares. The two five-membered rings are tilted 23° with respect to one another, but because of the bridge linking them are staggered only by about 9° , in contrast to ferrocene. The strain in the molecule is apparent also in the fact that the dihedral angles in the bridge are only about 26° , and that the exocyclic bonds are bent about 11° from the ring planes. The bond distances in the bridge are slightly greater than normal. The bond distances in the ring and to the iron atom appear normal.

1,1'-Tetramethylethylenferrocene (I) [Fig. 1(a)] is an unusual derivative of ferrocene with a two-carbon bridge between the cyclopentadiene rings. The shortness of this bridge would be expected to force the rings, which are parallel in ferrocene itself, to be appreciably tilted relative to one another, and, in fact, the differing chemical shifts observed for the ring protons in the NMR spectrum of (I) have been interpreted in terms of such a tilt (Rinehart, Frerichs, Kittle, Westman, Gustafson, Pruett & McMahon, 1960). Ballhausen & Dahl (1961) predicted that the cyclopentadiene rings in metallocenes could be tilted by as much as 45° (*i.e.* that the angle ω in Fig. 1(b) could be as small as 135°) without affecting the energy of the metal-ring bonding. We have studied the crystal structure of (I) in order to learn the exact angle of tilt of the rings and other details of the arrangement of the rings with respect to one another. The structure is also of interest because the high-amplitude oscillation of one ring relative to the other that appears characteristic of ferrocene (Dunitz, Orgel & Rich, 1956) is not possible here.

Experimental

A sample of (I) was obtained from Dr K. L. Rinehart; sublimation *in vacuo* produced orange-red, diamond-shaped plates whose surface became coated with a faint yellow film when exposed to air. This slight surface

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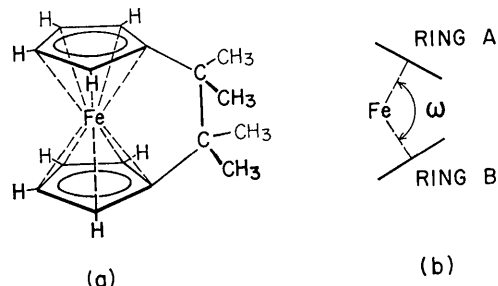


Fig. 1. (a) The molecular formula. (b) The angle between the ring normals, ω .

decomposition did not increase even after many hours in an X-ray beam. Rotation and Weissenberg photographs with Cu K radiation showed the crystals to be monoclinic. The systematic extinctions, $0k0$ absent with k odd and $h0l$ absent with l odd, indicate that the space group is $P2_1/c$. Unit-cell dimensions were determined from zero-layer Weissenberg photographs about **a** and **b**, calibrated with superimposed ceric oxide ($a_0=5.411$ Å) powder photographs ($\lambda(\text{Cu } K\alpha)=1.5418$ Å). They are: $a_0=7.756$, $b_0=10.97$, $c_0=15.41$ Å, and $\beta=92.63^\circ$. The estimated standard deviations are about 0.1% and 0.1° . A density of 1.35 g.cm⁻³ was obtained by flotation in a mixture of chlorobenzene and bromobenzene. The calculated density for four molecules in the unit cell is 1.36 g.cm⁻³.

Photographs taken with molybdenum radiation were very poor because of the large cell dimensions and also because the crystals fluoresced very strongly. The fluorescence in copper radiation was also strong but the wave length was more compatible with the cell dimensions of the crystals so multiple-film Weissenberg intensity data were collected with unfiltered Cu K radiation. A brass shim placed in front of the films cut out the fluorescent radiation satisfactorily. A chunky crystal mounted about **a** with dimensions of $0.17 \times 0.18 \times 0.06$ mm was used for collection of four layers of unintegrated data, which were estimated visually by comparison with a calibrated intensity strip. Another irregularly shaped crystal of maximum dimensions $0.18 \times 0.18 \times 0.12$ mm. was mounted around **b** and six layers of data were collected with an integrating Nonius camera. These intensities were estimated partly with a densitometer (Baird-Atomic, Inc., model CB) and partly by visual comparison with a calibrated integrated intensity strip. Of the 3133 independent reflections within the copper sphere, 1219 were observed, 930 were too weak to be measured, and the rest were inaccessible experimentally.

In spite of the small size of the crystals, there were variations in absorption of as much as 45% from the mean due to the large absorption coefficient of 96.5 cm⁻¹. This means that there may be absorption errors as large as 22% in a few of the structure factors, but no absorption corrections were made. Consequently

the 'temperature factors' derived here are probably lower than the true ones for this structure; on the other hand, we believe that the positional parameters will not be greatly affected (Donohue, Dunitz, Trueblood & Webster, 1963; Christofferson, Sparks & McCullough, 1958; Jellinek, 1958), so significant errors in the observed geometry of the molecule due to absorption are unlikely.

The intensities were converted to F^2 's and placed on the same relative scale by a least-squares process (Rollett & Sparks, 1960) using 589 reflections common to the a -axis and b -axis photographs. The b -axis data were weighted more heavily because the integrated intensities were considered more reliable and also the variation in absorption was smaller for this crystal. Independent F^2 values for the same reflection showed an average deviation from their mean of about 10%; thus the average deviation of the corresponding structure factors from the mean value is about 5%.

McWeeny's (1954) atomic scattering factors for graphite were used for carbon; the hydrogen curve was taken from the exact quantum-mechanical calculation results quoted in *International Tables for X-ray Crystallography* (1962). Freeman & Watson's (1961) form factor for iron was used after being corrected for the effects of anomalous dispersion (Dauben & Templeton, 1955). All calculations were done on an IBM 7090 computer.

Determination and refinement of the structure

The iron atom was easily located by inspection of unsharpened Patterson projections along a and b . A three-dimensional Fourier map with phases determined by the iron atom showed all sixteen carbon atoms clearly. Four isotropic and four anisotropic cycles of least-squares refinement reduced R from 25% to 9.2%. The block-diagonal least-squares program used was a modified version of ACA 317 (Gantzel, Sparks & Trueblood, unpublished), which minimizes the function $\sum w(|F_o| - |F_c|)^2$; the weighting system was that of Hughes (1941) with $4F_{\min}$ taken as 18.3.

A three-dimensional difference Fourier synthesis was then calculated in an attempt to locate the 20 hydrogen atoms. The estimated standard deviation of the electron density (Cruickshank, 1949) was about $0.15 \text{ e.}\text{\AA}^{-3}$ and 23 peaks above $0.30 \text{ e.}\text{\AA}^{-3}$ appeared in the map. Twenty of these peaks corresponded to fairly reasonable hydrogen positions; the C-H bond distances ranged from 0.88 \AA to 1.37 \AA with an average of 1.09 \AA . However, some of the H-C-H and H-C-C angles were distorted from the usual values and some of the C...H and H...H intermolecular packing distances seemed too short. To see if short distances were an essential feature of the molecular packing, it was decided to fix the C-H distances arbitrarily at about 1.08 \AA and choose more reasonable angles. A calculation of all distances less than 3.5 \AA showed no abnormally close contacts so these assumed hydrogen positions were used in all re-

maining calculations, the data being apparently insufficiently precise for getting more meaningful positions for the hydrogens. Isotropic B 's ranging from 4.0 to 6.0, approximately equal to the B 's of adjacent carbon atoms, were assigned to the hydrogen atoms.

Two least-squares cycles, with the hydrogen atoms included only in the structure factor calculations and eleven reflections for which secondary extinction seemed important removed, reduced R to 7.9%. A similar set of least-squares calculations was done with the unobserved reflections included in the data. The 930 unobserved reflections had previously been given the value $\frac{1}{3} I_{\min}$ (Hamilton, 1955), and had been scaled along with the rest of the data although not used in any calculation of the scale factors. R converged to 14.8% after four cycles; the final parameter shifts were all less than one-third of their standard deviations calculated from the inverse matrix of the last least-squares cycle.

Table 1. Final parameters*

Final parameters*				
Atom	x	y	z	B^\dagger
1	1419(12)	3877(10)	2661(5)	3.6 \AA^2
2	363(13)	4252(12)	3366(6)	4.4
3	1059(15)	3765(11)	4165(11)	4.4
4	2433(16)	2998(11)	3970(7)	4.6
5	2693(15)	3059(9)	3048(6)	4.2
6	1416(13)	4444(9)	1741(6)	3.5
7	3075(13)	5266(9)	1643(6)	3.5
8	3712(16)	5716(11)	2550(6)	4.9
9	2773(20)	6554(11)	3096(8)	5.6
10	3620(27)	6468(14)	3931(10)	8.4
11	5127(16)	5724(14)	3938(8)	5.5
12	5167(18)	5267(13)	3059(7)	5.7
13	1313(17)	3383(13)	1074(7)	5.3
14	-323(15)	5153(15)	1583(8)	5.6
15	4572(17)	4523(15)	1264(8)	6.0
16	2741(17)	6377(12)	1036(8)	5.4
Fe	2889(2)	4768(1)	3531(1)	3.7
Assumed hydrogen parameters				
H	x	y	z	B
2	-81	476	328	4.0 \AA^2
3	62	390	480	4.5
4	321	250	445	5.0
5	368	262	268	5.0
9	161	708	290	5.0
10	325	700	451	6.0
11	614	570	445	5.5
12	616	465	284	5.0
13	247	276	118	5.0
13'	13	282	115	5.0
13''	134	371	41	5.0
14	-35	548	94	5.5
14'	141	456	168	5.5
14''	-32	588	203	5.5
15	422	419	61	5.0
15'	488	373	167	5.0
15''	573	506	123	5.0
16	171	694	128	5.0
16'	232	607	39	5.0
16''	388	692	99	5.0

* $x, y, z, \times 10^4$ for carbon and iron atoms, $\times 10^3$ for hydrogen. The number in parentheses after each such parameter is their e.s.d. The hydrogen atoms are numbered to correspond with the carbon to which they are attached (Fig. 3).

† The e.s.d. of B is at least 10%.

Only thirteen of the unobserved reflections calculated greater than $1.5 F_{\min}$ and of these only three were (slightly) larger than $2.0 F_{\min}$. The final observed and calculated structure factors are listed in Table 8. A final difference Fourier map, calculated with the observed data and with phases determined by the parameters corresponding to $R=7.9\%$ contained no positive or negative areas greater than three times the e.s.d. of the electron density except in the region of the iron atom where the maximum variation was about $1 e.\text{\AA}^{-3}$, presumably due to inaccuracies in the iron scattering factor.

Table 1 gives the final positional parameters and their e.s.d.'s, from the last least-squares cycle with the observed and unobserved data; the temperature parameters are given in Table 2. These e.s.d.'s are slightly larger than those calculated from the refinement of the observed data only, but they are more realistic since e.s.d.'s are underestimated by a few per cent in the block diagonal least-squares approximation. An isotropic temperature factor is also given for each atom; although anisotropic thermal parameters were used in

the final refinement, they do not seem warranted in view of the likelihood of absorption errors. Table 1 gives as well the assumed hydrogen parameters.

Crystal and molecular structure

The arrangement of the molecules in the unit cell is shown in Fig. 2. The packing is determined by $H \cdots H$ and $H \cdots C$ contacts (Table 4) none of which is significantly smaller than the sum of the accepted van der Waals radii (about 2.4 and 2.9 Å, respectively). There are no $C \cdots C$ intermolecular distances less than 3.61 Å. The average isotropic temperature factor of the carbon atoms is about 5.0, which is relatively high, particularly since absorption should have reduced the temperature factors somewhat. This seems to indicate that the molecules may be undergoing a fair amount of librational motion, but the data did not warrant any detailed analysis.

The molecular geometry is illustrated in Figs. 3, 4 and 5; the hydrogen atoms have been omitted from the drawings. The angle of tilt, *i.e.* the angle between the least-squares planes of the two cyclopentadiene rings, is 23.2° . This corresponds to an ω angle (Fig. 1) of 156.8° , which is well within the limit set by Ballhausen & Dahl (1961). The pairs of $C \cdots C$ distances between the rings (Fig. 4), C(2)–C(9), C(5)–C(12), and C(3)–C(10), C(4)–C(11) show no particular trend of the rings to be skewed to one side, *i.e.* there is no additional tilt of one ring relative to the other about the exocyclic C–C bonds. This additional tilt is present in the three-carbon bridged ferrocene, α -keto-1,1'-trimethyleneferrocene (Jones, Marsh & Richards, 1965), where the carbons on one side of the rings are about 0.15 Å closer to each other. The angle of tilt between the rings in this compound is 9.8° , corresponding to an ω of 170.2° .

Table 2. Final thermal parameters and estimated standard deviations ($\times 10^4$)*†

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	134 (15)	92 (9)	34 (4)	-81 (24)	43 (12)	-29 (9)
C(2)	132 (16)	136 (13)	36 (4)	12 (29)	15 (12)	-11 (12)
C(3)	199 (20)	95 (10)	40 (4)	-120 (29)	29 (15)	3 (11)
C(4)	244 (24)	92 (10)	42 (4)	-45 (31)	-1 (16)	35 (11)
C(5)	228 (22)	69 (8)	40 (4)	-12 (28)	-26 (15)	8 (10)
C(6)	156 (17)	63 (7)	39 (4)	56 (24)	-26 (13)	6 (9)
C(7)	135 (16)	79 (9)	36 (4)	15 (24)	-2 (12)	21 (9)
C(8)	272 (26)	89 (10)	34 (4)	-120 (31)	59 (16)	11 (10)
C(9)	352 (34)	83 (10)	49 (5)	-108 (36)	54 (21)	-21 (12)
C(10)	546 (56)	121 (14)	65 (7)	-396 (56)	59 (32)	-39 (16)
C(11)	188 (22)	138 (14)	58 (6)	-230 (36)	-41 (18)	22 (15)
C(12)	264 (26)	140 (14)	42 (5)	-214 (37)	-34 (18)	85 (14)
C(13)	268 (26)	123 (13)	40 (5)	-88 (36)	-48 (18)	-47 (13)
C(14)	137 (18)	183 (19)	55 (6)	35 (34)	-21 (16)	51 (17)
C(15)	197 (22)	173 (18)	53 (6)	38 (38)	43 (18)	5 (17)
C(16)	241 (25)	102 (11)	58 (6)	-9 (33)	-12 (19)	81 (14)
Fe	199 (2)	71 (1)	29 (1)	-85 (3)	-2 (1)	-2 (1)

* According to the expression for the temperature factor: $\exp[-\beta]$, where $\beta = B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl$.

† The e.s.d. is given below each value.

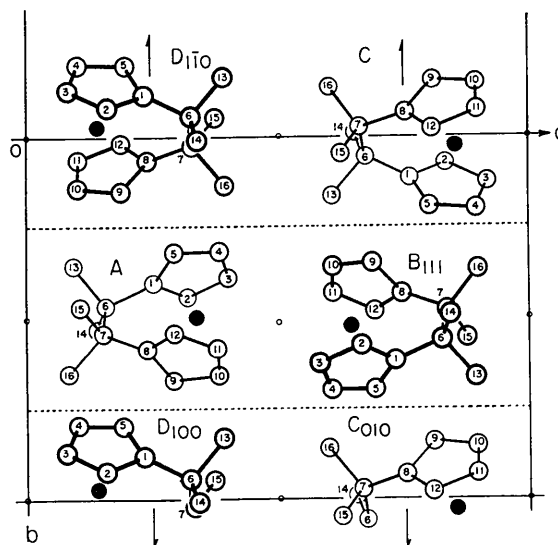


Fig. 2. A view of the structure down a^* ; no hydrogen atoms are shown.

In crystalline ferrocene the angle of rotation of one ring with respect to the other about their mutual normal is $2\pi/10$ (36°), *i.e.* the rings are staggered. In α -keto-1,1'-trimethyleneferrocene this angle is only 12° and in the present two-carbon bridged ferrocene, where

Table 3. Bond distances and bond angles*†

Atoms	Distance	e.s.d.	Atoms	Distance	e.s.d.
1-2	1.450 Å	0.013	Fe-1	1.978 Å	0.009
2-3	1.425	0.014	Fe-2	2.044	0.011
3-4	1.401	0.017	Fe-3	2.075	0.011
4-5	1.445	0.015	Fe-4	2.092	0.012
5-1	1.443	0.015	Fe-5	2.020	0.010
8-9	1.464	0.017	Fe-8	1.965	0.011
9-10	1.420	0.020	Fe-9	2.071	0.012
10-11	1.425	0.023	Fe-10	2.036	0.016
11-12	1.447	0.017	Fe-11	2.099	0.013
12-8	1.431	0.017	Fe-12	2.017	0.013
1-6	1.548	0.014			
7-8	1.543	0.014			
6-13	1.552	0.016			
6-14	1.567	0.016			
7-15	1.554	0.017			
7-16	1.551	0.016			
6-7	1.584	0.014			

Atoms	Angle	Atoms	Angle
1-2-3	110°	1-6-14	108°
2-3-4	108	13-6-14	104
3-4-5	109	1-6-7	110
4-5-1	108	13-6-7	112
5-1-2	105	14-6-7	114
8-9-10	105	6-7-15	111
9-10-11	113	6-7-16	113
10-11-12	104	6-7-8	109
11-12-8	110	15-7-8	107
12-8-9	108	16-7-8	110
5-1-6	127	15-7-16	107
2-1-6	126	7-8-12	127
1-6-13	108	7-8-9	125

* Carbon atoms are identified by number.

† The e.s.d. of angles involving carbon atoms vary from 1° to nearly 2°.

Table 4. Some intermolecular C...H and H...H distances*

Distance	From atom at x, y, z	To atom	At position†	In adjacent unit cell
3.0 Å	H(11)	C(3)	B	111
3.0	H(16)	C(3)	D	
3.0	H(11)	C(4)	B	111
3.0	H(14')	C(5)	D	
2.9	C(8)	H(5)	D	100
2.9	C(9)	H(13')	D	
3.0	C(9)	H(15')	D	100
2.9	C(10)	H(15')	D	100
2.9	C(11)	H(13)	D	100
3.0	C(12)	H(5)	D	100
3.0	H(10)	C(16)	C	010
2.4	H(12)	H(2)	A	100
2.5	H(16'')	H(3)	D	100
2.5	H(4)	H(13'')	C	
2.2	H(9)	H(13')	C	
2.4	H(14)	H(13'')	C	010
2.4	H(15'')	H(14')	A	100

* All C...H of 3.0 Å or less and all H...H of 2.6 Å or less. Hydrogen positions are assumed (see text).

† Position A is x, y, z; position B is -x, -y, -z; position C is x, $\frac{1}{2}$ -y, $\frac{1}{2}$ +z; position D is -x, $\frac{1}{2}$ +y, $\frac{1}{2}$ -z. See Fig. 2.

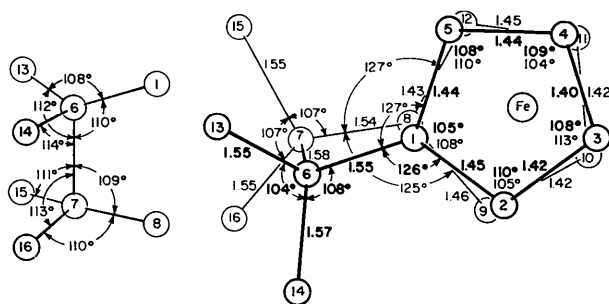


Fig. 3. Bond distances and angles. The molecule is viewed along the average of the normals to the planes of the rings. Darker numbers refer to the nearer ring. Some bridge angles are shown to the left.

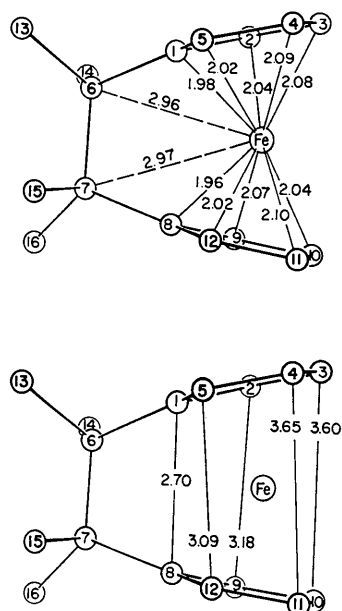


Fig. 4. Side views of the molecule showing Fe-C distances and inter-ring distances.

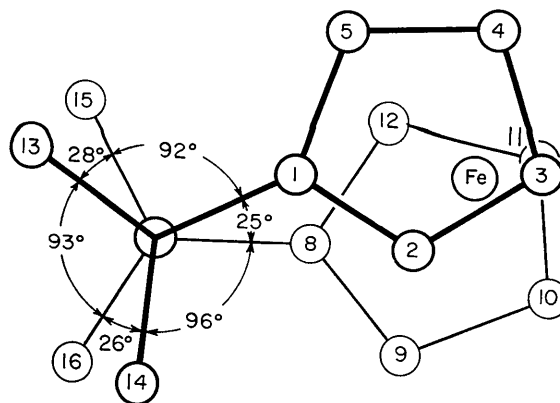


Fig. 5. View of the molecule along the C(6)-C(7) bond, showing dihedral angles in the bridge.

this angle is between 9° and 10° , the rings are even closer to being eclipsed (Fig. 3). This eclipsing of the rings and resulting small dihedral angles of 25° , 26° and 28° in the bridge (Fig. 5) are unavoidable when the rings are joined by such a short bridge. The eclipsing of the rings probably does not interfere with the Fe-C bonding since the rings apparently rotate freely in ferrocene at higher temperatures (Seibold & Sutton, 1955). X-ray studies of ruthenocene (Hardgrove & Templeton, 1959) and osmocene (Jelinek, 1959) have

shown that eclipsing of the rings is the preferred orientation in these compounds in the solid state.

It is noteworthy that because the molecule has no symmetry element of the second kind, as a result of the non-zero dihedral angles in the bridge, two enantiomorphous forms of it are present in the crystal. Presumably they are readily interconverted, since only conformational equilibria are involved if one assumes no great intrinsic ferrocene barrier to rotation of the rings past the eclipsed position.

Table 5. Comparison of average interatomic distances in ferrocene and some ferrocene derivatives (\AA)*

Compound	Method	Fe-ring C	Ring C-C†	Inter-ring C...C‡	Reference
1,1'-Tetramethylethylenferrocene	X-ray	2.04 (1)	1.44 (2)		This work
α -Keto-1,1'-trimethylenferrocene	X-ray	2.04 (1)	1.43 (1)		Jones, Marsh & Richards (1965)
Ferrocene	e.d.	2.06 (1)	1.44 (3)	3.32 (6)	Berndt (1957)
Ferrocene	e.d.	2.03 (2)	1.43 (3)	3.25 (3)	Seibold & Sutton (1955)
Ferrocene	X-ray	2.05 (1)	1.40 (2)	3.32 (3)	Dunitz, Orgel & Rich (1956)
Dibenzoylferrocene	X-ray	2.05 (2)	1.41 (3)		Struchkov & Khotsyanova (1957)

Numbers in parentheses are standard deviations ($\times 10^2$) of individual values quoted in references cited.

† No corrections for thermal libration have been made. Thus, some of the C-C distances are too small (perhaps by 0.02-0.03 \AA) in compounds where there may be high amplitudes of vibration parallel to rings.

‡ Spacing between best planes through the two rings.

Table 6. Some intramolecular non-bonded C...C and H...H distances

Type of interaction	Atoms	Distance	Type of interaction	Atoms	Distance
Atoms joined to the same atom (separated by two C-C bonds)					
CH ₃ ...CH ₃	13-14	2.47 \AA	CH ₃ ...C _{bridge}	13-7	2.61 \AA
	15-16	2.50		14-7	2.64
CH ₃ ...C _{ring}	13-1	2.50	C _{bridge} ...C _{ring}	15-6	2.59
	14-1	2.52		16-6	2.62
	15-8	2.49		6-2	2.68
	16-8	2.53		6-5	2.68
				7-9	2.67
		7-12	2.66		
		6-8	2.54		
		7-1	2.57		
Atoms separated by two bonded atoms (by three C-C bonds)					
CH ₃ ...C _{ring}	13-5	3.20	CH ₃ ...CH ₃	13-15	2.82
	14-2	2.95		14-16	2.89
	13-8	3.85		14-15	3.91
	14-8	3.46		13-16	3.47
	15-12	2.90			
	16-9	3.18			
	15-1	3.41			
	16-1	3.88			
Some H...H distances $\leq 2.6 \text{\AA}$ *					
	Atoms	Distance	Atoms	Distance	
	H(2)-H(14')	2.5	H(12)-H(15'')	2.5	
	H(2)-H(14'')	2.3	H(13)-H(15)	2.3	
	H(5)-H(13)	2.5	H(13)-H(15')	2.3	
	H(5)-H(15')	2.2	H(13'')-H(15)	2.3	
	H(9)-H(14')	2.4	H(14)-H(16)	2.3	
	H(9)-H(16)	2.5	H(14)-H(16')	2.4	
	H(12)-H(15')	2.3	H(14'')-H(16)	2.3	
			H(15)-H(16')	2.5	
			H(15'')-H(16'')	2.5	
			H(13')-H(14')	2.4	
			H(13'')-H(14)	2.5	

* Hydrogen positions are assumed (see text).

The geometry of the rings seems fairly normal; the average C–C bond distance is 1.44 Å with the average individual e.s.d. about 0.02 Å, which is comparable to the values observed in ferrocene, dibenzoylferrocene and α -keto-1,1'-trimethyleneferrocene (Table 5). The distortions of some bond angles in the rings from 108° are not considered significant, although those at C(10) and C(11) border on significance. The average Fe–C distance, 2.04 Å, is the same as the average value found in ferrocene and its derivatives (Table 5) but C(1) and C(8) are pulled a little closer (0.07 Å) to the iron atom while the carbons on the opposite sides of the rings are farther away.

The bond distances from the methyl groups to the carbons in the bridge are within 2σ of Bartell's tetrahedral single-bond distance, 1.533 Å (1959). The angles around C(6) and C(7), which vary from 104° to 114°, show some self-consistent and perhaps significant distortions from the usual tetrahedral angle of 109.5°. The intramolecular C...C distances (Table 6) show that C(1), C(13) and C(14), each bonded to C(6), are all about 2.50 Å apart in an equilateral triangle arrangement. Carbon atoms 8, 15 and 16, each bonded to C(7), can be similarly described. This situation is in accord with the simple steric model (Bartell, 1960) which assigns an intramolecular van der Waals radius of 1.25 Å to carbon atoms bonded to the same atom (ignoring the difference between methyl and aromatic carbons). This 'hard sphere' treatment emphasizes the importance of non-bonded repulsions between the carbon atoms more than the effects of hybridization in determining bond angles around C(6) and C(7); the angles will be unequal when the bond distances are unequal.

However, the fact that angles 6-7-15, 6-7-16, 7-6-13 and 7-6-14 are all increased (to 111°, 113°, 112° and 114°, respectively) may also result from otherwise short contacts between methyl groups 13 and 15 and methyl groups 14 and 16. The projection down the C(6)–C(7) bond (Fig. 5) shows that the dihedral angles involving these methyl groups are decreased from the most favorable 60° to 28° and 26°, respectively. The corresponding C...C distances are 2.82 and 2.89 Å, whereas if the dihedral angle were 60°, the distances would be about 3.07 Å as in gauche n-butane (Bonham & Bartell, 1959). There are three fairly close H...H contacts of about 2.3 Å between each pair of methyl groups. A decrease of 3° in all the bond angles mentioned above would further shorten the components of any separation along the direction of the C(6)–C(7) bond by about 0.16 Å. Although few of the actual contacts are parallel to this bond, they do have significant components parallel to it, and since they are already short, any decrease of these angles to the usual tetrahedral value would be energetically costly. The increase of these angles above the tetrahedral value thus seems a direct consequence of the smallness of the dihedral angle in the bridge, which is itself the result of the shortness of the C–C bridge.

The internal angles of the bridge, 7-6-1 and 6-7-8, are not significantly different from the tetrahedral angle 109.5°, in spite of the fact that the repulsion between carbon atoms 1 and 8, forced together by the bridge, might have been expected to increase the angles at C(6) and C(7). The C(1)–C(8) interatomic distance of 2.70 Å is even shorter than the closest contacts between the aromatic rings in the highly strained diolefin of [2.2]paracyclophane (Coulter & Trueblood, 1963), and is of course very far below the observed 3.4 Å separation of parallel aromatic rings in unstrained compounds (Robertson, 1953). One can only conclude that the considerable repulsion between two aromatic carbon atoms which is normally expected at this distance is counterbalanced by the attraction of each to the iron atom, so that the two C–C–C angles in question have the normal value.

The question also arises whether the bridge bonds, especially between tetrahedral carbon atoms 6 and 7 but also from the trigonal carbon atoms 1 and 8 to the tetrahedral carbon atoms 6 and 7, have been lengthened in order to avoid even closer approach of carbon atoms 1 and 8. Since 2σ for these three bonds is about 0.03 Å, the apparent lengthening of bonds 1–6 and 7–8 by 0.03–0.04 Å, from the expected value of 1.51 Å (Bartell & Bonham, 1960; Keidel & Bauer, 1956) is scarcely significant, and similarly the apparent lengthening of bond 6–7 from the expected 1.544 Å (Bartell, 1959) to 1.58 Å is only on the border of significance, although it is certainly suggestive. However, if the latter effect really arose from C(1)–C(8) repulsion, it is hard to see why the aforementioned C–C–C angles in the bridge would not be enlarged.

The out-of-plane deformation of aromatic rings found in the paracyclophanes (Coulter & Trueblood, 1963; Gantzel & Trueblood, 1965) is not observed in these rings, which are planar within the standard deviations (Table 7). C(1) and C(8) are not significantly out of the four-carbon planes, 2-3-4-5 and 9-10-11-12, as they would be if the bridge were disrupting the

Table 7. *Least-squares planes of the rings*†

Direction cosines with respect to a, b, c*	Atom	Deviations of atoms from plane
	1	0.02 Å
	2	–0.03
0.6097	3	0.03
0.7792	4	–0.01
0.1456	5	–0.01
	*6	0.34
	*Fe	1.64
–0.5736	8	0.03
–0.7784	9	–0.03
0.2551	10	0.02
	11	–0.01
	12	–0.02
	*7	0.30
	*Fe	1.63

† Atoms with (*) were not included in calculation of the plane.

STRUCTURE OF 1,1'-TETRAMETHYLETHYLENEFERROCENE

Table 8 (cont.)

10 1.70U -1.83	4 27.99 -30.02	11 11.30 11.47	7 7.08U -1.42	-8 2.95U -0.12	10 18.23 14.82	-12 6.65U 3.16	6 2.08U -1.42
11 6.04 -0.76	5 6.21U -0.90	12 2.96U 4.96	8 7.14U 1.28	-9 2.13U -2.66	11 22.27 -21.32	-13 5.76U -7.26	7 1.97U -0.71
12 2.12U 1.76	-1 21.94 -20.96	13 16.00 -1.08	9 19.76 -1.36	-10 2.45U 0.10	12 7.47 7.47	8 7.85U 3.26	8 7.51 6.91
13 6.72U 4.96	-2 20.04 -14.95	14 2.00U -1.01	10 19.20 18.93	-11 10.93 -11.75	13 7.85U 3.26	9 6.31U -11.07	-2 2.60U 5.36
14 6.02U -2.00	3 4.90U 3.01	15 1.73U -1.06	11 6.10U -7.80	-12 2.25U 5.82	14 7.05U 3.16	10 1.12U 11.73	-2 2.60U 5.36
-1 16.46 15.19	-5 49.26 44.84	16 7.14U -4.14	-2 5.17 5.09	13 5.87U -0.02	15 1.07U 0.35	11 2.15U 20.08	7 11.26 11.25
-2 6.52U 6.14	-6 6.02U 0.16	17 7.09U 11.98	-3 16.25 16.91	-4 5.01U 9.21	16 7.40U 3.07	12 6.26U 4.90	-7 11.17 10.07
-3 6.35U -0.81	-7 10.96 9.55	18 12.00 -9.42	-4 8.47 7.07	-5 11.52 14.14	17 7.62U 10.57	13 6.26U 4.90	-8 9.79 9.35
-4 12.28 12.84	-8 20.75 -20.40	19 15.16 -17.95	-5 5.64 -5.53	-6 6.48U 4.39	18 7.82U 10.57	14 6.04U -0.04	-9 9.79 9.35
-5 6.93U -2.80	-9 15.26 14.10	20 15.26 14.10	-6 19.86 20.67	-7 19.86 20.67	19 8.71U 3.35	15 6.62U -6.93	-10 2.02U 4.87
-6 11.41 11.82	-10 16.15 15.75	21 16.42 15.96	-7 9.94 9.76	-8 16.01 15.37	20 7.85U 3.61	16 6.04U -0.04	-11 1.87U 2.38
-7 10.15U 4.15	-11 4.36 7.42	22 17.10 4.36	-8 2.47U 0.54	-9 2.47U 0.54	21 5.29U -3.91	17 5.29U -3.91	-12 1.72U 2.38
-8 4.95U -1.09	-12 15.16 -17.95	23 22.00 -25.42	-9 2.50U -25.42	-10 2.50U -25.42	22 7.85U 3.61	18 6.81U 6.26	-13 6.81U 6.26
10 1.33 14.49	-13 2.00U 4.90	-5 6.05U 5.77	-10 23.24 26.49	-11 23.24 26.49	23 6.15U 17.12	-11 18.10 18.36	10 5.83U 5.86
1 6.23U -0.62	-14 1.71U 5.36	-6 6.05U 5.77	-11 6.08U -10.05	-12 6.08U -10.05	24 14.05 -13.01	-12 19.34 -20.09	-1 6.23U -0.62
2 7.95 6.86	11 21.85 20.21	-7 16.04 -17.04	-12 10.33 12.38	-13 10.33 12.38	25 9.41U 1.24	-13 12.22 -12.68	1 7.95 6.86
3 6.07U 2.66	12 20.85 19.85	-8 6.94U -4.74	-13 6.27U -6.30	-14 6.27U -6.30	26 8.83U 0.33	-14 9.65 11.48	2 6.07U 2.66
4 17.08 19.00	13 21.46 21.50	-9 10.33 12.38	-14 12.64 12.64	-15 12.64 12.64	27 9.10U 1.24	-15 11.48 11.48	3 17.08 19.00
5 7.74U 2.82	14 21.46 21.50	-10 10.33 12.38	-15 12.64 12.64	-16 12.64 12.64	28 8.83U 0.33	-16 11.48 11.48	4 7.74U 2.82
6 7.44U 5.05	15 21.46 21.50	-11 10.33 12.38	-16 12.64 12.64	-17 12.64 12.64	29 8.83U 0.33	-17 11.48 11.48	5 7.44U 5.05
7 7.16U 7.15	16 21.46 21.50	-12 10.33 12.38	-17 12.64 12.64	-18 12.64 12.64	30 8.83U 0.33	-18 11.48 11.48	6 7.16U 7.15
8 4.74U 10.73	17 21.46 21.50	-13 10.33 12.38	-18 12.64 12.64	-19 12.64 12.64	31 8.83U 0.33	-19 11.48 11.48	7 4.74U 10.73
9 4.20U 9.52	18 21.46 21.50	-14 10.33 12.38	-19 12.64 12.64	-20 12.64 12.64	32 8.83U 0.33	-20 11.48 11.48	8 4.20U 9.52
10 1.25U 2.30	19 21.46 21.50	-15 10.33 12.38	-20 12.64 12.64	-21 12.64 12.64	33 8.83U 0.33	-21 11.48 11.48	9 1.25U 2.30
11 2.49U 4.59	20 21.46 21.50	-16 10.33 12.38	-21 12.64 12.64	-22 12.64 12.64	34 8.83U 0.33	-22 11.48 11.48	10 2.49U 4.59
12 6.13U 5.03	21 21.46 21.50	-17 10.33 12.38	-22 12.64 12.64	-23 12.64 12.64	35 8.83U 0.33	-23 11.48 11.48	11 6.13U 5.03
13 6.01U 5.76	22 21.46 21.50	-18 10.33 12.38	-23 12.64 12.64	-24 12.64 12.64	36 8.83U 0.33	-24 11.48 11.48	12 6.01U 5.76
14 5.85U 5.10	23 21.46 21.50	-19 10.33 12.38	-24 12.64 12.64	-25 12.64 12.64	37 8.83U 0.33	-25 11.48 11.48	13 5.85U 5.10
15 5.34U 2.39	24 21.46 21.50	-20 10.33 12.38	-25 12.64 12.64	-26 12.64 12.64	38 8.83U 0.33	-26 11.48 11.48	14 5.34U 2.39
16 4.98U 4.88	25 21.46 21.50	-21 10.33 12.38	-26 12.64 12.64	-27 12.64 12.64	39 8.83U 0.33	-27 11.48 11.48	15 4.98U 4.88
17 4.74U 5.05	26 21.46 21.50	-22 10.33 12.38	-27 12.64 12.64	-28 12.64 12.64	40 8.83U 0.33	-28 11.48 11.48	16 4.74U 5.05
18 4.61U 5.76	27 21.46 21.50	-23 10.33 12.38	-28 12.64 12.64	-29 12.64 12.64	41 8.83U 0.33	-29 11.48 11.48	17 4.61U 5.76
19 4.50U 6.48	28 21.46 21.50	-24 10.33 12.38	-29 12.64 12.64	-30 12.64 12.64	42 8.83U 0.33	-30 11.48 11.48	18 4.50U 6.48
20 4.40U 7.19	29 21.46 21.50	-25 10.33 12.38	-30 12.64 12.64	-31 12.64 12.64	43 8.83U 0.33	-31 11.48 11.48	19 4.40U 7.19
21 4.30U 7.90	30 21.46 21.50	-26 10.33 12.38	-31 12.64 12.64	-32 12.64 12.64	44 8.83U 0.33	-32 11.48 11.48	20 4.30U 7.90
22 4.20U 8.61	31 21.46 21.50	-27 10.33 12.38	-32 12.64 12.64	-33 12.64 12.64	45 8.83U 0.33	-33 11.48 11.48	21 4.20U 8.61
23 4.10U 9.32	32 21.46 21.50	-28 10.33 12.38	-33 12.64 12.64	-34 12.64 12.64	46 8.83U 0.33	-34 11.48 11.48	22 4.10U 9.32
24 4.00U 10.03	33 21.46 21.50	-29 10.33 12.38	-34 12.64 12.64	-35 12.64 12.64	47 8.83U 0.33	-35 11.48 11.48	23 4.00U 10.03
25 3.90U 10.74	34 21.46 21.50	-30 10.33 12.38	-35 12.64 12.64	-36 12.64 12.64	48 8.83U 0.33	-36 11.48 11.48	24 3.90U 10.74
26 3.80U 11.45	35 21.46 21.50	-31 10.33 12.38	-36 12.64 12.64	-37 12.64 12.64	49 8.83U 0.33	-37 11.48 11.48	25 3.80U 11.45
27 3.70U 12.16	36 21.46 21.50	-32 10.33 12.38	-37 12.64 12.64	-38 12.64 12.64	50 8.83U 0.33	-38 11.48 11.48	26 3.70U 12.16
28 3.60U 12.87	37 21.46 21.50	-33 10.33 12.38	-38 12.64 12.64	-39 12.64 12.64	51 8.83U 0.33	-39 11.48 11.48	27 3.60U 12.87
29 3.50U 13.58	38 21.46 21.50	-34 10.33 12.38	-39 12.64 12.64	-40 12.64 12.64	52 8.83U 0.33	-40 11.48 11.48	28 3.50U 13.58
30 3.40U 14.29	39 21.46 21.50	-35 10.33 12.38	-40 12.64 12.64	-41 12.64 12.64	53 8.83U 0.33	-41 11.48 11.48	29 3.40U 14.29
31 3.30U 15.00	40 21.46 21.50	-36 10.33 12.38	-41 12.64 12.64	-42 12.64 12.64	54 8.83U 0.33	-42 11.48 11.48	30 3.30U 15.00
32 3.20U 15.71	41 21.46 21.50	-37 10.33 12.38	-42 12.64 12.64	-43 12.64 12.64	55 8.83U 0.33	-43 11.48 11.48	31 3.20U 15.71
33 3.10U 16.42	42 21.46 21.50	-38 10.33 12.38	-43 12.64 12.64	-44 12.64 12.64	56 8.83U 0.33	-44 11.48 11.48	32 3.10U 16.42
34 3.00U 17.13	43 21.46 21.50	-39 10.33 12.38	-44 12.64 12.64	-45 12.64 12.64	57 8.83U 0.33	-45 11.48 11.48	33 3.00U 17.13
35 2.90U 17.84	44 21.46 21.50	-40 10.33 12.38	-45 12.64 12.64	-46 12.64 12.64	58 8.83U 0.33	-46 11.48 11.48	34 2.90U 17.84
36 2.80U 18.55	45 21.46 21.50	-41 10.33 12.38	-46 12.64 12.64	-47 12.64 12.64	59 8.83U 0.33	-47 11.48 11.48	35 2.80U 18.55
37 2.70U 19.26	46 21.46 21.50	-42 10.33 12.38	-47 12.64 12.64	-48 12.64 12.64	60 8.83U 0.33	-48 11.48 11.48	36 2.70U 19.26
38 2.60U 19.97	47 21.46 21.50	-43 10.33 12.38	-48 12.64 12.64	-49 12.64 12.64	61 8.83U 0.33	-49 11.48 11.48	37 2.60U 19.97
39 2.50U 20.68	48 21.46 21.50	-44 10.33 12.38	-49 12.64 12.64	-50 12.64 12.64	62 8.83U 0.33	-50 11.48 11.48	38 2.50U 20.68
40 2.40U 21.39	49 21.46 21.50	-45 10.33 12.38	-50 12.64 12.64	-51 12.64 12.64	63 8.83U 0.33	-51 11.48 11.48	39 2.40U 21.39
41 2.30U 22.10	50 21.46 21.50	-46 10.33 12.38	-51 12.64 12.64	-52 12.64 12.64	64 8.83U 0.33	-52 11.48 11.48	40 2.30U 22.10
42 2.20U 22.81	51 21.46 21.50	-47 10.33 12.38	-52 12.64 12.64	-53 12.64 12.64	65 8.83U 0.33	-53 11.48 11.48	41 2.20U 22.81
43 2.10U 23.52	52 21.46 21.50	-48 10.33 12.38	-53 12.64 12.64	-54 12.64 12.64	66 8.83U 0.33	-54 11.48 11.48	42 2.10U 23.52
44 2.00U 24.23	53 21.46 21.50	-49 10.33 12.38	-54 12.64 12.64	-55 12.64 12.64	67 8.83U 0.33	-55 11.48 11.48	43 2.00U 24.23
45 1.90U 24.94	54 21.46 21.50	-50 10.33 12.38	-55 12.64 12.64	-56 12.64 12.64	68 8.83U 0.33	-56 11.48 11.48	44 1.90U 24.94
46 1.80U 25.65	55 21.46 21.50	-51 10.33 12.38	-56 12.64 12.64	-57 12.64 12.64	69 8.83U 0.33	-57 11.48 11.48	45 1.80U 25.65
47 1.70U 26.36	56 21.46 21.50	-52 10.33 12.38	-57 12.64 12.64	-58 12.64 12.64	70 8.83U 0.33	-58 11.48 11.48	46 1.70U 26.36
48 1.60U 27.07	57 21.46 21.50	-53 10.33 12.38	-58 12.64 12.64	-59 12.64 12.64	71 8.83U 0.33	-59 11.48 11.48	47 1.60U 27.07
49 1.50U 27.78	58 21.46 21.50	-54 10.33 12.38	-59 12.64 12.64	-60 12.64 12.64	72 8.83U 0.33	-60 11.48 11.48	48 1.50U 27.78
50 1.40U 28.49	59 21.46 21.50	-55 10.33 12.38	-60 12.64 12.64	-61 12.64 12.64	73 8.83U 0.33	-61 11.48 11.48	49 1.40U 28.49
51 1.30U 29.20	60 21.46 21.50	-56 10.33 12.38	-61 12.64 12.64	-62 12.64 12.64	74 8.83U 0.33	-62 11.48 11.48	50 1.30U 29.20
52 1.20U 29.91	61 21.46 21.50	-57 10.33 12.38	-62 12.64 12.64	-63 12.64 12.64	75 8.83U 0.33	-63 11.48 11.48	51 1.20U 29.91
53 1.10U 30.62	62 21.46 21.50	-58 10.33 12.38	-63 12.64 12.64	-64 12.64 12.64	76 8.83U 0.33	-64 11.48 11.48	52 1.10U 30.62
54 1.00U 31.33	63 21.46 21.50	-59 10.33 12.38	-64 12.64 12.64	-65 12.64 12.64	77 8.83U 0.33	-65 11.48 11.48	53 1.00U 31.33
55 0.90U 32.04	64 21.46 21.50	-60 10.33 12.38	-65 12.64 12.64	-66 12.64 12.64	78 8.83U 0.33	-66 11.48 11.48	54 0.90U 32.04
56 0.80U 32.75	65 21.46 21.50	-61 10.33 12.38	-66 12.64 12.64	-67 12.64 12.64	79 8.83U 0.33	-67 11.48 11.48	55 0.80U 32.75
57 0.70U 33.46	66 21.46 21.50	-62 10.33 12.38	-67 12.64 12.64	-68 12.64 12.64	80 8.83U 0.33	-68 11.48 11.48	56 0.70U 33.46
58 0.60U 34.17	67 21.46 21.50	-63 10.33 12.38	-68 12.64 12.64	-69 12.64 12.64	81 8.83U 0.33	-69 11.48 11.48	57 0.60U 34.17
59 0.50U 34.88	68 21.46 21.50	-64 10.33 12.38	-69 12.64 12.64	-70 12.64 12.64	82 8.83U 0.33	-70 11.48 11.48	58 0.50U 34.88
60 0.40U 35.59	69 21.46 21.50	-65 10.33 12.38	-70 12.64 12.64	-71 12.64 12.64	83 8.83U 0.33	-71 11.48 11.48	59 0.40U 35.59
61 0.30U 36.30	70 21.46 21.50	-66 10.33 12.38	-71 12.64 12.64	-72 12.64 12.64	84 8.83U 0.33	-72 11.48 11.	

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The Crystal Structure of the Serpentine Mineral, Lizardite $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$

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Lizardite from Kennack Cove, Cornwall, England, is an unusual serpentine in being sufficiently coarse-grained for single-crystal X-ray analysis. The basic layered serpentine structure is confirmed for this specimen but the crystals are found to be disordered in three different ways. (1) The crystals are macroscopically bent about more than one axis. (2) Some of the layers are displaced by $\pm b/3$. (3) Some of the layers are rotated by 180° . The broadened reflexions resulting from each of these factors have been examined and, within the limits imposed by them, the structural detail has been refined. The inter-layer repeat is $c=7.3 \text{ \AA}$ and individual layers have trigonal symmetry with $a=5.3 \text{ \AA}$.

Two types of serpentine mineral have been well characterized, chrysotile by its fibrous habit with fibre repeat distance 5.3 \AA , and antigorite with its super-period in the a direction. Much massive serpentine has neither of these features and has been termed lizardite (Whittaker & Zussman, 1956). Electron microscopic examination of lizardite shows essentially platy particles in which the intra-layer orthogonal repeat distances are simply $a=5.3$, $b=9.2 \text{ \AA}$, and the X-ray powder patterns in general show no evidence of other than a single-layered cell with $c \simeq 7.3 \text{ \AA}$ and $\beta=90^\circ$. The detailed structure of individual serpentine layers (Fig. 1) has been assumed, by virtue of the chemical formula, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, and cell parameters, to be a trioctahedral analogue of the single kaolinite layer; complex distorted versions of this have been shown to comprise the structures of chrysotile (Whittaker, 1956a) and antigorite (Kunze, 1956, 1958, 1961), but no direct evidence of the simple structure has hitherto been presented for lizardite, because of the difficulty of obtaining single crystals large enough for X-ray diffraction work. One specimen of lizardite, however, offers the possibility of single-crystal X-ray work, namely that from Kennack Cove, Cornwall (Midgley, 1951; Whittaker & Zussman, 1956), since its crystallite size, though small, is manageable from this point of view. It has

emerged after study of this specimen that the extent to which the structure can be determined in detail is limited even in this case because of the existence of different kinds of imperfections, the most obvious of which is that the crystals are considerably bent.

Experimental

X-ray powder pattern

The powder pattern given in Table 1 is more complete than that given by Whittaker & Zussman (1956) and is indexed with an ortho-hexagonal unit cell having $a=5.31$, $b=9.2$ ($\simeq \sqrt{3}a$), $c=7.31 \text{ \AA}$, $\beta=90^\circ$.

Table 1. *Lizardite powder pattern*

Cu $K\alpha$ radiation, 11.46 cm diameter camera
 Indices on basis of cell with $a=5.31$, $b=9.20$, $c=7.31 \text{ \AA}$, $\beta=90^\circ$

$d_{\text{obs.}}$	$d_{\text{calc.}}$	hkl	I
7.4 \AA	7.31 \AA	001	<i>vs</i>
4.6	4.60	020	<i>s</i>
3.9	3.89	021	<i>m</i>
3.67	3.66	002	<i>s</i>
2.875	2.862	022	<i>vw</i>
2.663	2.655	200	<i>mw</i>
2.505	2.496	201	<i>vs</i>
2.410	2.437	003	<i>vvw</i>
2.307	2.300	040	<i>vvw</i>
2.156	2.148	202	<i>s</i>
1.945	1.947	042	<i>vvw</i>
1.835	1.828	004	<i>vw</i>
1.799	1.795	203	<i>m</i>
1.743	1.738	310	<i>mw</i>

* This work was begun while the authors were at the Department of Geology, University of Manchester.