

The Structure of α -Keto-1,5-tetramethyleneferrocene

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The structure of α -keto-1,5-tetramethyleneferrocene has been determined by three-dimensional X-ray diffraction analysis. This compound, $C_{14}H_{14}FeO$, crystallized in the centrosymmetric triclinic space group $P\bar{1}$. The unit cell, containing two molecules, has the dimensions

$$\begin{aligned} a &= 6.76 \pm 0.02, & b &= 7.71 \pm 0.01, & c &= 13.72 \pm 0.01 \text{ \AA}, \\ \alpha &= 65^\circ 47' \pm 10', & \beta &= 118^\circ 22' \pm 20', & \gamma &= 108^\circ 21' \pm 20' \end{aligned}$$

A trial structure was obtained by fully computerized symbolic addition methods. Refinement was carried out by a combination of Fourier summation and three-dimensional least-squares methods yielding a final R value of 0.039.

The planes of the cyclopentadienyl rings are essentially parallel and their deviation from an eclipsed configuration is 8.9° . The average cyclopentadienyl carbon-carbon bond distance is $1.433 \pm 0.015 \text{ \AA}$ and the average iron-carbon bond distance is $2.053 \pm 0.011 \text{ \AA}$. The unsubstituted cyclopentadienyl ring shows no distortion from pentagonal symmetry.

Introduction

The configuration of α -keto-1,5-tetramethyleneferrocene (I) (Fig. 1), $C_{14}H_{14}FeO$, has been of some interest recently with respect to certain predictions which could be made on the basis of circular dichroism measurements (Schlögl, 1966). The 'sandwich' system itself is also of interest because of the possibility of different configurations (eclipsed and staggered) of one cyclopentadienyl relative to another. In the present case, the unsubstituted cyclopentadienyl ring could possibly be fully staggered relative to the substituted ring, a configuration found in ferrocene (Dunitz, Orgel & Rich, 1956) but not in certain of its derivatives studied recently:

Biferrocenyl (Macdonald & Trotter, 1964),
Diethyldiferrocenyl (Struchkov & Kaluski, 1965),
1,1'-Tetramethylethyleneferrocene (Laing & Trueblood, 1965),
 α -Keto-1,1'-trimethyleneferrocene (Jones, Marsh & Richards, 1965),
Dibenzoylferrocene (configuration not substantially discussed; Struchkov & Khotsyanova, 1957).

We have studied the structure of (I) in order to reveal more fully the exact configuration present in this compound.

Experimental

A crystalline sample of (I) was supplied by Dr K. Schlögl of the Institute for Organic Chemistry, University of Vienna. α -Keto-1,5-tetramethyleneferrocene crystallizes from hexane in the form of red-orange needles. A small, approximately cubical crystal was aligned on a precession camera (equipped with a

Polaroid film cassette) and preliminary photographs of several layers indicated the space group to be either $P\bar{1}$ or $P\bar{1}$.

The crystal was transferred to a General Electric XRD 5 Spectrogoniometer with single-crystal orienter, using a scintillation counter and $Cu K\alpha$ ($\lambda = 1.5418$) radiation (nickel filter and pulse height analyzer). The cell data obtained for the triclinic unit cell are

$$\begin{aligned} a &= 6.67 \pm 0.02, & b &= 7.71 \pm 0.01, & c &= 13.72 \pm 0.01 \text{ \AA} \\ \alpha &= 65^\circ 47' \pm 10', & \beta &= 118^\circ 22' \pm 20', & \gamma &= 108^\circ 21' \pm 20' \end{aligned}$$

All data were collected at ambient room temperature. The density calculated on the basis of two molecules of $C_{14}H_{14}FeO$ per unit cell is 1.55 g.cm^{-3} .

Approximately a hemisphere of data was collected by the stationary-crystal stationary-counter technique. Peak heights were corrected by subtracting the minimum background average for both sides of the intensity peaks. The maximum 2θ angle of observed peaks was $< 80^\circ$, which was chosen to insure the ratio of intensity-of-peak to integrated-intensity to be approximately unity (Alexander & Smith, 1962). There were

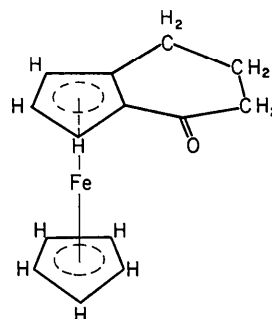


Fig. 1. The molecular formula.

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668 accessible reflections of which 629 were independent.

Absorption corrections were not applied since at $\chi=90^\circ$ the variation in intensity with φ was less than $\pm 6\%$ and the variation of symmetry related intensities ($\Delta\varphi=180^\circ$) was within counter error (Furnas, 1957). The Lorentz and polarization corrections, appropriate to XRD-5 geometry, were applied.

As a test for the symmetry of the space group the $N(z)$ test (Rogers, 1965) was applied to all 668 reflections. The agreement with the theoretical centrosymmetric distribution is shown in Fig. 2. As a further confirmation of $P\bar{1}$, rather than $P1$, no significant differences in intensity between reflections hkl and $\bar{h}\bar{k}\bar{l}$, attributable to anomalous dispersion effects due to the iron atom ($f''=3.45$) (Cromer, 1965), were observed.

The intensities were placed on an absolute scale and E 's (normalized structure factors) were calculated by FAME (Computer program written by A. Stone and R. Dewar). The resulting distribution of E 's is shown in Table 1. In subsequent calculations the renormalized E 's were used since they seemed, in general, to have a distribution more closely resembling the theoretical centric distribution.

Table 1. Distribution of calculated E 's compared with theoretical values

	E	Rescaled* E	Theoretical	
			Centric	Acentric
$\langle E \rangle$	0.792	0.821	0.798	0.886
$\langle E^2 \rangle$	0.931	1.000	1.000	1.000
$\langle E^2 - 1 \rangle$	0.836	0.875	0.968	0.736
$\% E > 1$	33.0	35.0	32.0	37.0
> 2	2.4	3.3	5.0	1.80
> 3	0.0	0.0	0.3	0.01

* E 's were rescaled so that $\langle E^2 \rangle \equiv 1$.

Determination and refinement of the structure

The phases of the observed structure factors were assigned by the symbolic addition method (Hauptman & Karle, 1953) using MAGIC (program written by A. Stone and R. Dewar). There were 443 phases determined with a high probability (>0.990) and of the 186 not determined, 73 were unobserved reflections ($<$ two times background).

There were four very consistent assignments of signs to the symbols (four symbols were used) of which the second set tried gave a Fourier E -map which seemed most reasonable on chemical grounds. (This set of signs proved to be 96% correct on the basis of signs calculated from the final least squares cycle.) This three-dimensional map showed all the atoms in the molecule plus a few spurious peaks of much lower height.

Since the methylene carbon atoms were not extremely well resolved, only the ferrocene fragment of the molecule was used to calculate the phases of the observed structure factors. At this point the R value (calculated without unobserved reflections) was 0.38. A new three-dimensional Fourier map was calculated

and all sixteen atoms were well resolved. From the new positions (located in 1/60 grid) R was 0.194.

Three cycles of (full-matrix) least-squares refinement of positional and isotropic temperature parameters and a scale factor reduced R to 0.072. The 100 reflection was omitted in this refinement since a scan of this peak showed it to be very broad and hence the peak height observed was not a good indication of the actual intensity.

A difference Fourier map was next computed to examine the anisotropic behavior of the atoms and if possible to locate the hydrogen atom positions. This difference map showed a substantial amount of anisotropic vibration about the refined atomic positions. In addition sixteen peaks not involved in anisotropic vibration were found. Of these, the fourteen highest peaks were assigned as hydrogen atom positions with the aid of a three dimensional model.

With the hydrogen atoms included the R value dropped to 0.055. One cycle of least-squares refinement using isotropic temperature parameters (hydrogen atom temperature factors fixed at $B=3.0 \text{ \AA}^2$) brought R to 0.049. Individual anisotropic temperature factors were introduced for all the atoms at this point. Two more cycles of least-squares refinement of all parameters, except those of the hydrogen atoms, brought the final R value to 0.039 (or 0.051 including unobserved reflections).

During the final stages of refinement the atomic positional parameters shifted less than one-half their e.s.d. It should be noted that during the anisotropic refinement the temperature factors of C(10) shifted to give a not-positive definite test and so the temperature factors of C(13) [which were most nearly like those of C(10)] were substituted in the final calculation of R . The final observed and calculated $|F|$'s are listed in Table 2.

Unit weights were assigned to all the reflections and the unobserved reflections (set equal to zero) were included during all stages of refinement. Scattering factors used, and the real part of the anomalous dispersion correction for iron, were taken from *International Tables for X-ray Crystallography* (1962). All calculations were performed on the IBM-7090 computer. Programs used during the refinement were the (full-matrix) least-squares program ORFLS (Busing, Martin & Levy, 1962) and the Fourier summation program ERFR2 (Sly, Shoemaker & Van den Hende, 1962).

Table 3 shows the final positional parameters and their e.s.d.'s (as estimated by the least-squares program) as well as the isotropic temperature factors taken after the last cycle of isotropic temperature refinement. The individual anisotropic temperature factors are given in Table 4. The hydrogen atom positions after a single cycle of refinement are given in Table 5. Their e.s.d.'s are not given since the positional parameters were not sufficiently well refined. The configuration of the atoms and the labeling used is shown in Fig. 3.

Table 2. Observed and calculated structure factors

H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c			
1	-2	-5	15.2410	15.9315	2	-4	-2	53.4110	53.0200	1	0	5	26.2090	26.4713	1	5	1	3.8280	3.4957			
2	-2	-5	19.5220	20.4490	2	-4	-2	19.2171	20.1009	1	0	6	4.1260	4.0113	0	4	1	0.5743	0.5743			
4	-2	-5	23.5980	22.2157	2	-2	-1	5.4750	5.4991	1	0	3	25.8610	24.9633	2	4	1	14.4350	13.5536			
5	-2	-5	0	2.3967	4	-4	-2	5.3710	6.1659	2	0	6	26.2630	26.0153	4	4	1	15.6440	15.1061			
2	-3	-8	4.4960	4.7110	4	-4	-2	21.1100	21.0546	1	0	3	21.1100	21.0546	2	4	1	13.8430	13.8430			
1	-3	-8	7.2400	7.8723	5	-2	-1	14.9200	15.0570	1	0	2	19.0510	19.7441	0	6	2	12.0540	10.9336			
1	-3	-8	12.7510	12.6134	1	-5	-3	9.8300	9.4360	2	0	4	5.8420	5.1234	1	3	1	10.1570	9.7273			
4	-3	-8	16.1820	15.1188	2	-5	-3	7.6120	8.8541	3	0	5	9.1960	5.1022	3	1	2	32.0700	31.6023			
5	-3	-8	10.1570	11.5244	3	-5	-3	5.3120	5.3120	2	0	3	4.1260	4.2661	3	2	1	10.5750	9.3510			
1	-2	-6	3.9550	2.3452	4	-5	-3	9.8340	9.8439	3	0	4	4.5950	10.5664	0	5	2	21.6630	21.4004			
1	-1	-3	51.1770	50.2092	1	-3	-2	17.6300	18.2525	1	0	1	29.1230	29.1665	1	5	2	16.0000	15.5455			
2	-2	-6	0	2.5060	2	-6	-4	15.0000	20.9576	2	0	2	18.0320	18.4352	0	2	1	22.5310	22.7527			
3	-2	-6	29.4560	22.5532	1	-6	-4	13.2500	13.3179	3	0	3	30.4360	29.2262	0	4	2	22.7010	23.1172			
2	-1	-3	27.1110	26.4700	3	-6	-4	16.9970	17.4054	4	0	3	0	0	0	6	3	6.5920	6.5920			
4	-2	-6	38.4190	36.7636	2	-3	-2	18.8510	15.2374	3	0	2	3.7260	3.5225	1	4	2	27.7650	29.0640			
5	-2	-6	16.1810	15.2925	3	-3	-2	24.9490	24.9581	2	0	1	47.2650	46.3041	1	2	1	2.9450	3.2476			
3	-1	-3	11.5840	12.7995	4	-3	-2	6.2330	5.6491	3	0	1	15.5220	15.1616	2	4	2	12.3640	11.9463			
4	-1	-3	11.3980	12.3614	3	-3	-2	0	0	3	0	1	37.2920	34.4702	2	1	1	8.2300	8.2300			
5	-1	-3	5.7130	4.6555	1	-4	-3	9.4300	8.8103	4	0	1	20.3030	19.5036	3	2	1	16.2560	17.4323			
2	-2	-7	16.5340	17.2775	2	-4	-3	6.1600	6.0573	0	-1	8	17.5950	17.3000	4	2	1	12.7000	12.4002			
1	-2	-7	9.5350	9.9649	4	-4	-3	11.0940	11.9941	1	-1	8	18.2420	18.5222	0	5	0	2.7334	2.7334			
4	-2	-7	17.9420	16.9272	1	-4	-3	12.1030	12.0030	2	0	3	21.6750	20.2150	3	2	1	3.2160	3.2160			
4	-2	-7	14.0630	13.1742	1	-4	-4	6.5940	7.1503	1	-1	7	7.0160	7.3362	0	3	2	26.4020	26.2721			
5	-2	-7	8.2000	8.3127	2	-5	-4	23.5400	24.1109	0	-1	6	41.7600	39.3322	0	6	4	2.3770	2.4955			
1	-1	-4	35.6930	33.7316	2	-5	-4	28.8930	29.1195	1	-1	6	42.0750	42.5575	1	3	2	10.5660	11.4725			
2	-1	-4	11.5840	11.5216	3	-5	-4	9.2910	9.2910	1	-1	6	41.7600	41.7600	2	2	1	11.4725	11.4725			
1	-2	-8	8.7210	8.9995	2	-6	-5	7.3400	6.6857	0	-1	5	34.7290	34.6237	3	2	1	5.2700	5.2700			
3	-2	-8	0	2.4954	1	-6	-5	10.6080	8.8846	1	-1	5	34.9800	33.2680	4	3	1	14.6850	20.5300			
2	-1	-4	31.3860	32.8247	3	-6	-5	4.5500	4.4332	2	-1	5	12.9440	13.4075	4	3	2	36.2800	35.4745			
3	-1	-4	16.5340	16.4927	4	-6	-5	10.6080	10.6080	2	-1	5	15.6830	15.6830	3	2	1	18.2560	18.2560			
4	-2	-8	9.2450	9.6841	2	-6	-6	11.1650	11.4418	1	-1	4	0	0	4	12.4720	11.5174	4	1	-3	5.5640	5.5640
3	-1	-4	13.5920	13.7829	2	-5	-5	10.9550	9.4205	2	-1	4	0	0	5	4.2820	6.2707	5	1	-3	19.2370	15.4340
1	-1	-4	26.4210	26.7529	1	-4	-4	13.5490	11.4213	3	-1	4	11.3610	11.1600	0	1	1	12.6040	11.3352			
2	-1	-4	23.7470	23.7470	1	-5	-4	10.5910	16.6890	1	-2	2	5.2320	6.0445	2	2	2	28.3900	28.3900			
1	-1	-5	25.5650	25.3186	1	-6	-6	0	0	2	-2	6	15.7100	15.7100	0	3	3	16.5840	16.4393			
2	-1	-5	17.3690	16.7460	1	-2	-2	28.9500	26.3820	1	-1	3	27.1160	27.0117	0	4	4	27.5690	27.1731			
3	-1	-5	22.7670	21.0900	2	-4	-4	21.8700	21.2631	2	-2	6	5.2640	4.0229	0	5	5	15.1480	13.1991			
4	-1	-5	4.6390	4.6390	3	-5	-6	8.9300	8.1324	3	-1	3	45.6800	45.6777	1	5	5	17.3120	17.2237			
5	-1	-5	0	2.7110	3	-5	-6	5.3120	5.3120	2	-2	3	25.8610	25.8610	4	4	2	24.3170	24.3170			
1	-1	-6	28.1340	26.2652	3	-3	-3	10.3040	10.5543	4	-1	3	8.7790	8.3753	3	3	3	46.0640	45.2830			
1	-1	-6	3.0590	1.4837	3	-4	-4	10.1120	15.9126	1	-2	5	10.5160	11.0873	1	2	2	20.8430	20.5349			
3	-1	-6	10.6210	10.6210	1	-5	-5	5.3500	4.9411	2	-2	5	7.5290	8.0897	2	2	2	5.6640	6.1106			
4	-1	-6	18.4510	15.4416	1	-5	-5	19.2920	19.2920	1	-3	3	15.7576	15.7576	3	3	2	29.4572	29.4572			
5	-1	-6	21.0390	21.8138	2	-2	-2	15.2970	15.6752	1	-2	4	5.1070	5.5447	1	1	1	40.7220	40.5544			
2	-1	-7	14.9370	16.5636	3	-3	-3	14.8300	15.5014	1	-1	2	23.8400	24.2621	2	2	2	0	1.9661			
3	-1	-7	9.5750	10.4511	4	-4	-4	10.1400	10.4800	2	-2	4	10.1870	10.6856	3	3	3	5.6600	6.1102			
3	-1	-7	14.5620	15.1776	4	-4	-4	5.1520	5.1520	1	-2	3	10.6270	10.6270	1	2	2	17.5820	17.5820			
4	-1	-7	15.0420	14.6334	4	-3	-3	4.6740	4.6052	2	-1	2	0	0	1	4.4890	5.2887					
5	-1	-7	8.0420	7.6479	3	-2	-2	34.6070	34.5275	3	-1	2	18.0590	18.6517	3	1	1	7.4780	6.7003			
1	-1	-8	8.1570	8.9452	5	-3	-3	13.4200	13.3228	4	-1	2	14.2790	15.0481	1	1	1	15.9370	15.6310			
1	-1	-8	8.9500	9.6927	4	-3	-3	10.2670	10.2670	3	-1	3	17.9510	17.9510	4	4	3	10.5260	10.5260			
3	-1	-8	8.8560	10.3630	4	-2	-2	17.7800	17.5573	2	-3	5	0	0	3	3.0200	3.8301					
4	-1	-8	0	2.2391	5	-2	-2	12.4400	14.6887	1	-2	3	32.2130	32.1535	4	5	5	27.3860	28.1155			
1	0	-5	3.9130	6.4953	3	-1	-1	25.9300	25.9288	2	-2	3	29.1450	29.1450	1	4	5	19.4790	20.4868			
1	0	-5	46.8240	46.8240	1	-5	-5	6.0600	6.4410	1	-2	3	6.4410	6.4410	2	-3	2	11.7500	11.7500			
1	0	-6	6.8900	6.2645	5	-1	-1	11.9490	11.8532	1	-3	4	0	0	3	3.2200	3.1578					
2	0	-6	3.2600	3.2600	2	-6	-6	0	0	2	-3	4	13.4120	13.3254	3	4	4	10.5060	10.1552			
2	0	-8	17.1520	17.9378	3	-6	-7	0	0	6	-7	4	10.3610	11.0466	2	3	4	3.4080	3.8117			
1	0	-8	36.3510	36.3510	4	-6	-7	0	0	5	-7	6	11.0670	11.0670	3	-2	3	3.4080	3.8117			
1	0	-8	25.8780	25.4562	2	-5	-6	14.5020	14.5997	1	-2	2	6.6210	7.1627	0	7	7	27.3500	27.2123			
2	0	-7	25.0310	24.9010	1	-5	-6	3.4850	3.3090	3	-3	3	13.0390	13.1355	0	3	4	45.0400	43.8225			
1	0	-3	38.7760	39.0235	3	-5	-6	19.9730	20.7555	1	-1	1	11.5520	12.9255	4	6	4	4.0740	3.4582			
2	0	-8	0	0.0640	4	-6	-7	6.4100	6.4100	6	-2	2	5.1650	5.1650	1	6	6	6.9520	6.9520			
3	0	-8	0	1.9132	4	-5	-4	24.3340	23.7692	3	-3	3	0	0	8	8.7600	8.7600					
3	0	-8	0	23.7390	24.5181	1	-4	-5	23.4380	22.5674	3	-2	2	7.4480	8.2271	2	3	4	10.0020	9.4763		
1	0	-2	15.8830	15.8830	4	-5	-4	16.3990	16.8322	1	-1	1	32.7280	30.1155	3	3	2	22.0090	21.8223			
1	0	-2	11.6470	11.6470	5	-4	-5	5.5500	7.3466	6	-5	6	4.4890	4.4890	0	1	1	5.1120	5.1120			
3	0	-2	9.5450	5.3821	5	-4	-5	10.3500	10.1850	3	-1	1	6.4300	6.0931	0	5	3	31.8760	32.7364			
4	0	-8	0	1.4876	1	-3	-4	32.1520	31.5184	4	-1	1	21.6250	21.5590	1	3	5	26.7070	26.3305			
4	0	-7	18.3910	18.8844	2	-6	-8	0	0	2	-2	3	23.0480	22.6648	2	3	5	13.0000	12.8050			
4	0	-7	6.6150	6.6150	4	-4	-4	13.5620	12.5777	2	-1	3	6.6160	6.6160	4	7	4	30.4650	30.4650			
2	0	-3	8.7660	9.0676	3	-3	-4	24.1000	23.3557	3	-2	0	0	0	1	4.7400	4					

Table 3. *Final positional parameters* ($X, Y, Z \times 10^4$)
The number in parentheses after each parameter is its e.s.d.
Labelling of the atoms is illustrated in Fig. 2.

	X	Y	Z	$B(\text{\AA}^2)$
Fe	4497 (2)	180 (2)	1956 (1)	3.20 (0.07)
O	2828 (16)	1502 (11)	3834 (7)	4.3 (0.2)
C(1)	1879 (19)	1637 (14)	1408 (14)	3.1 (0.3)
C(2)	2417 (22)	1991 (15)	461 (11)	3.6 (0.3)
C(3)	4748 (23)	2774 (14)	703 (12)	3.4 (0.3)
C(4)	5724 (21)	3014 (13)	1845 (13)	2.8 (0.3)
C(5)	3984 (22)	2309 (13)	2288 (15)	2.6 (0.3)
C(6)	7262 (19)	-1243 (13)	2907 (13)	3.0 (0.3)
C(7)	5802 (24)	-1927 (13)	3515 (10)	3.0 (0.3)
C(8)	3600 (20)	-2660 (14)	2766 (14)	3.4 (0.3)
C(9)	3707 (20)	-2466 (14)	1730 (13)	3.5 (0.3)
C(10)	5958 (22)	-1596 (14)	1807 (12)	4.4 (0.4)
C(11)	8140 (18)	3847 (13)	2552 (10)	3.3 (0.3)
C(12)	8670 (17)	3042 (14)	3860 (11)	4.0 (0.3)
C(13)	6762 (20)	3036 (14)	4157 (9)	3.7 (0.3)
C(14)	4313 (22)	2186 (14)	3457 (15)	3.2 (0.3)

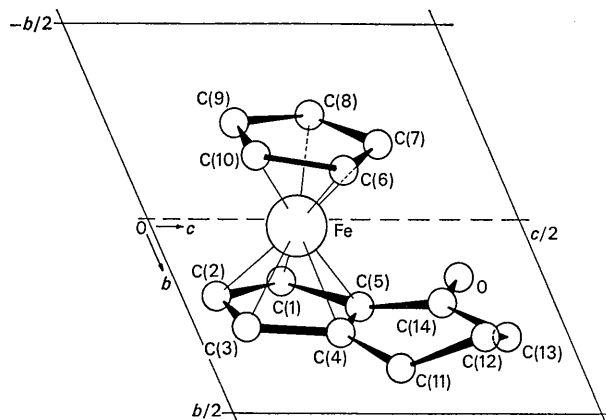


Fig. 3. [100] projection of the molecule showing labeling of the atoms.

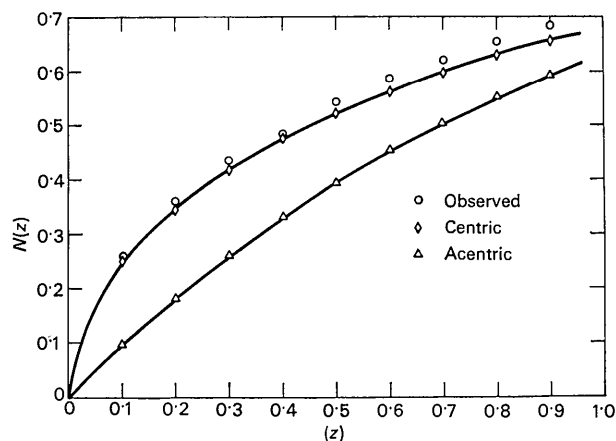


Fig. 2. Results of the $N(z)$ test.

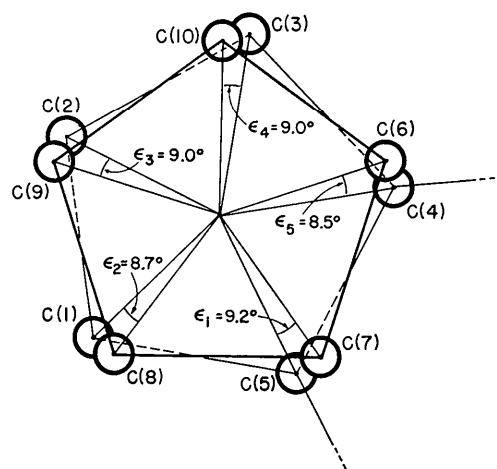


Fig. 4. View along the normal to the five-membered rings.

Table 4. *Final anisotropic temperature factors* ($\times 10^4$)

The number in parentheses after each parameter is its e.s.d. The temperature factors are expressed in the form
 $T = \exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl)$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	238 (6)	162 (4)	55 (2)	36 (4)	37 (2)	-34 (2)
O	308 (35)	345 (24)	78 (10)	48 (23)	90 (15)	-84 (11)
C(1)	231 (51)	182 (29)	49 (15)	97 (29)	13 (24)	-47 (17)
C(2)	237 (57)	220 (32)	38 (15)	92 (32)	-14 (21)	-53 (16)
C(3)	314 (58)	171 (30)	37 (14)	107 (31)	23 (23)	-17 (15)
C(4)	271 (60)	80 (26)	66 (19)	52 (31)	100 (30)	10 (16)
C(5)	340 (63)	82 (26)	43 (18)	98 (30)	26 (34)	-34 (16)
C(6)	343 (50)	85 (26)	56 (15)	49 (28)	79 (26)	-27 (15)
C(7)	428 (58)	77 (25)	39 (13)	109 (30)	59 (28)	-6 (15)
C(8)	289 (58)	162 (30)	70 (16)	16 (31)	79 (24)	-17 (17)
C(9)	257 (57)	126 (29)	79 (16)	-2 (30)	26 (22)	-47 (16)
C(10)*	451	168	61	107	52	-78
C(11)	221 (51)	156 (28)	65 (15)	-3 (30)	65 (20)	-31 (17)
C(12)	236 (46)	248 (32)	79 (16)	47 (28)	42 (20)	-72 (17)
C(13)	321 (54)	228 (31)	54 (12)	95 (32)	32 (22)	-48 (15)
C(14)	265 (69)	135 (30)	69 (19)	107 (34)	36 (31)	-34 (18)

* Temperature factor is not positive-definite. This atom was also calculated to have the greatest isotropic temperature factor.

Table 5. Hydrogen atom positional parameters ($X, Y, Z \times 10^4$) after a single cycle of isotropic refinement with $B = 3.0 \text{ \AA}^2$ held fixed

	Bonded to	X	Y	Z
H(1)	C(1)	347	1096	1479
H(2)	C(2)	1420	1613	-172
H(3)	C(3)	5541	3259	324
H(4)	C(13)	9169	3944	2134
H(5)	C(13)	8024	5191	2231
H(6)	C(6)	9018	-555	3181
H(7)	C(7)	6258	-1607	4248
H(8)	C(8)	2514	-2984	3135
H(9)	C(9)	2340	-2695	883
H(10)	C(10)	6560	-1386	1356
H(11)	C(12)	601	3734	4404
H(12)	C(12)	8915	2098	4064
H(13)	C(13)	7046	2415	5006
H(14)	C(13)	6748	4084	4079

Results and discussion

The bond angles and interatomic distances were calculated from the final refined atomic coordinates and are listed in Table 6 along with e.s.d.'s calculated with the program ORFFE (Busing, Martin & Levy, 1964). The average iron-carbon bond distance is $2.053 \pm 0.011 \text{ \AA}$ and the average carbon-carbon bond distance in the cyclopentadienyl rings is $1.433 \pm 0.015 \text{ \AA}$. These values are in good agreement with those found in ferrocene and some of its derivatives (Laing & Trueblood, 1965). The average carbon-hydrogen bond distance calculated was 0.97 \AA with an average mean deviation of 0.12 \AA . This suggests that the hydrogen atoms are not quite positioned correctly.

Table 6. Bond distances and angles

	Distance	e.s.d.
Fe-C(1)	2.063 \AA	0.011 \AA
Fe-C(2)	2.069	0.011
Fe-C(3)	2.056	0.011
Fe-C(4)	2.047	0.011
Fe-C(5)	2.036	0.012
Fe-C(6)	2.049	0.011
Fe-C(7)	2.062	0.011
Fe-C(8)	2.051	0.011
Fe-C(9)	2.054	0.010
Fe-C(10)	2.041	0.011
Average	2.053	
C(1)-C(2)	1.411	0.014
C(2)-C(3)	1.424	0.015
C(3)-C(4)	1.450	0.014
C(4)-C(5)	1.434	0.015
C(5)-C(1)	1.472	0.016
C(6)-C(7)	1.429	0.014
C(7)-C(8)	1.444	0.015
C(8)-C(9)	1.402	0.014
C(9)-C(10)	1.428	0.015
C(10)-C(6)	1.431	0.014
Average	1.433	
C(4)-C(11)	1.539	0.016
C(11)-C(12)	1.533	0.014
C(12)-C(13)	1.525	0.015
C(13)-C(14)	1.554	0.016
C(14)-C(15)	1.477	0.016
Average	1.526	
C(14)-O	1.221	0.014

Table 6 (cont.)

	Angle	e.s.d.
C(5)-C(1)-C(2)	105.7°	1.0°
C(1)-C(2)-C(3)	111.4	1.0
C(2)-C(3)-C(4)	106.6	1.1
C(3)-C(4)-C(5)	107.9	1.2
C(4)-C(5)-C(1)	108.3	1.3
C(6)-C(7)-C(8)	107.6	1.1
C(7)-C(8)-C(9)	108.7	1.0
C(8)-C(9)-C(10)	107.8	1.0
C(9)-C(10)-C(6)	108.8	1.1
C(10)-C(6)-C(7)	107.1	1.1
C(3)-C(4)-C(11)	130.7	1.3
C(1)-C(5)-C(14)	126.5	1.3
C(4)-C(5)-C(14)	125.2	1.2
C(4)-C(11)-C(12)	110.9	0.9
C(11)-C(12)-C(13)	113.8	0.9
C(12)-C(13)-C(14)	117.8	1.0
C(13)-C(14)-C(15)	112.5	1.2
C(5)-C(14)-O	124.0	1.2
C(13)-C(14)-O	123.5	1.6

Contrary to the suggestion of Macdonald & Trotter (1964) that there might be significant distortion from pentagonal symmetry in cyclopentadienyl rings bound to iron, the unsubstituted cyclopentadienyl ring of this molecule shows no significant distortion whatever. The substituted ring does show some distortion from pentagonal symmetry, but this might be expected owing to bonding to the tetramethylene group.

The best planes through the cyclopentadienyl rings were calculated by a least-squares program (Schmidt & Davis, 1962). The equations of the normals to these planes as well as out of plane distances of certain atoms are given in Table 7. The largest out of plane distance of the methylene carbon atoms is -0.55 \AA for C(12), all others deviate less than 0.06 \AA . The average separation between carbon atoms defining these planes is 3.309 \AA compared to the average distance between the planes of 3.304 \AA . The dihedral angle between the rings is 1.5° . Thus the rings are parallel to within experimental error.

Table 7. Least-squares planes (referred to triclinic coordinates) through the five membered rings and certain out of plane distances

Plane defined by C(1), C(2), C(3), C(4), C(5):	
$-2.563X + 6.994Y + 0.905Z = 0.800$	
Out of plane deviations (\AA):	
C(1)	-0.009
C(2)	0.014
C(3)	-0.013
C(4)	0.008
C(5)	0.0005
Fe	-1.650
Plane defined by C(6), C(7), C(8), C(9), C(10):	
$-2.741X + 6.980Y + 1.081Z = -2.549$	
Out of plane deviations (\AA):	
C(6)	0.005
C(7)	-0.006
C(8)	0.005
C(9)	-0.001
C(10)	-0.003
Fe	1.654

It is interesting to examine the configuration of one cyclopentadienyl ring relative to the other. A view of these rings along the normal to their planes is shown in Fig. 4. The average angle of deviation from fully eclipsed configuration is $\varepsilon=8.9^\circ$. The angle ε was defined as the angle between the lines passing through the nearly superimposed atoms and the midpoint of the opposite sides of the rings. This can be compared to ferrocene where $\varepsilon=36^\circ$ (fully staggered configuration).

This configuration can be understood by considering the H---H van der Waals contacts in a three-dimensional model of the structure. The shortest intermolecular H---H distances calculated were H(13)---H(7') at 2.68 Å and H(13)---H(8') at 2.63 Å. If more reasonable carbon-hydrogen bond distances of 1.1 Å are assumed these contact distances are reduced to 2.5 Å. This symmetrical arrangement suggests that the unsubstituted five-membered ring may be constrained to its conformation by such H---H contacts.

Another interesting H---H contact is seen in the intramolecular distances H(12)---H(6) at 2.8 Å and H(12)---H(7) at 2.9 Å. Again if normal carbon-hydrogen distances are assumed, the contacts are reduced to 2.5 and 2.4 Å, respectively. Thus it seems most reasonable to suggest that the conformation found can be explained primarily by these H---H interactions.

As a final note there seems to be no evidence for the existence of C-H---O hydrogen bonds (Sutor, 1963). The closest O---C distance is 3.43 Å for O---H(9)-C(9) which is slightly larger than the sum of the van der Waals radii of 3.40 Å.

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