The Crystal Structure of Ferrocene*

By J. D. Dunitz†, L. E. Orgel‡ and Alexander Rich§

The Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.

X-ray analysis of crystals of ferrocene shows that the molecule has approximate D_{5d} symmetry, with Fe–C, 2.045 ± 0.01 Å; C–C, 1.403 ± 0.02 Å.

Introduction

The 'sandwich' structure of bis-*cyclo*pentadienyl iron (Wilkinson, Rosenblum, Whiting & Woodward, 1952; Fischer & Pfab, 1952) has already been confirmed by preliminary crystal-structure studies (Eiland & Pepinsky, 1952; Dunitz & Orgel, 1953). We have now carried out a more detailed analysis, utilizing three-dimensional data, and have obtained a somewhat more precise description of the structure.

Experimental

The cell constants were re-determined from ($hk0$) and ($h0l$) Weissenberg photographs on which sodium chloride powder lines had been superimposed. Least-squares analysis of the observed spacings leads to the values

$$a = 10.561, \ b = 7.597, \ c = 5.952 \text{ Å}, \ \beta = 121.02°$$

for the cell constants, with estimated standard error of about 0.1%. The space group is $P2_1/a$ and there are two centrosymmetric molecules of Fe $(C_5H_5)_2$ in the unit cell, so that the iron atoms must lie at symmetry centres.

For the intensity estimation, two principal sets of photographs were taken about the b and c crystal axes, with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The crystals were sealed in thin-walled glass tubes to prevent loss by sublimation and the layers, $hk0$–$hk7$, and $h0l$–$h3l$, were recorded by the Weissenberg equi-inclination technique with several films, separated by thin sheets of copper, in the camera. A few reflexions of very large spacing were recorded with Cu $K\alpha$ radiation ($\lambda = 1.542$ Å). The $|F|$ values of almost 1200 reflexions were obtained from visual estimates of the intensities.

Our intensity estimates are subject to two main

sources of error, apart from those inherent in the visual method. Absorption errors of up to about 35% are possible for individual reflexions, although the mean absorption error is much less than this. Extinction errors are likely to be more serious. Since the iron atoms occur in a C-centred arrangement, reflexions with $h+k$ even show almost normal decline, and are therefore almost all strong and so subject to extinction. Reflexions with $h+k$ odd are, on the other hand, mainly weak. The extinction error thus occurs in a rather systematic fashion. We shall return to this point in a later section.

Scale and temperature factors

The temperature factors for the iron atoms and for the carbon atoms could be estimated independently. The iron atom does not contribute to reflexions with $h+k$ odd. The temperature factor for the carbon atoms could therefore be obtained by Wilson's (1942) method, where the averaging is taken only over odd reflexions. For reflexions with $h+k$ even, an average over the F values, rather than the F^2 values, yields the temperature factor for the iron atom alone. In this way, the temperature factors are found to be exp $(-5.5 \sin^2 \theta/\lambda^2)$ for the carbon atoms and exp $(-3.2 \sin^2 \theta/\lambda^2)$ for the iron atom. The scale factors determined by the two methods were in good agreement.

Refinement of coordinates

The approximate structure based on the first projections down the b and c axes was used as a starting point for a series of least-squares refinements. Four refinement stages were first carried out on $h+k$ odd reflexions. Two more stages were then done on all reflexions. Coefficients of off-diagonal terms were not computed and were taken as zero, with the exception of those involving products of the type $(\partial F/\partial x_i)$ $(\partial F/\partial z_i)$. The final coordinates (Table 1, column (A)) have a standard error of 0.024 Å, determined from the internal consistency of the least-squares results.

At the end of the least-squares refinement the quantity $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ was still as high as 0.175, which led us to compute a three-dimensional

Table 1. *Atomic coordinates*

	$(A)*$			$(B)*$		
	x/a	y/b	z/c	x/a	y/b	z/c
C_1	0·0169	0·2592	0·0306	0·0169	0·2613	0·0306
C_2	0·0444	0·1777	0·2115	0·0447	0·1767	0·2103
C_3	0·1614	0·0576	0·0889	0·1612	0·0590	0·0873
C_4	0·2186	0·0788	0·1737	0·2183	0·0787	0·1733
C_5	0·1349	0·1978	0·2278	0·1352	0·1963	0·2267
Fe	0	0	0	0	0	0

* (A) As found by final least-squares calculation.
  (B) Corrected on basis of difference synthesis.

Fourier series in the hope that this might show systematic differences from the least-squares model. The signs of the Fourier-series coefficients were taken from the final structure-factor calculation of the least-squares analysis (in fact, all reflexions with $h+k$ even had positive sign); about 10 weak $h+k$ odd reflexions were omitted because of ambiguity of sign. The calculations were done on I.B.M. machines. The resulting function showed a considerable accumulation of electron density between the calculated positions of the carbon atoms. This is evident from Fig. 1(a), in which relevant sections at constant y are superimposed to give a composite representation of the molecule, and also from Fig. 1(b), which shows a section through the mean plane of the *cyclo*pentadienyl ring.

Such an accumulation of electron density also appears in the three-dimensional difference synthesis in which the Fourier coefficients are F_o-F_c; but in addition, smaller although quite definite accumulations occur at positions related by rotation around the b axis. The difference synthesis has strongly negative troughs at every atomic centre; and again, although less marked, at positions related to these by rotation around b. It is clear that the low values of the electron-density function at the atomic centres and the high values between the atoms of the ring are only in part attributable to rotational disorder; the presence of corresponding features at symmetry-related regions which are, in general, not close to any of the atoms must arise from some systematic error in our intensity estimations.

The most likely cause of these effects would seem to be extinction errors. The very strongest reflexions, those most seriously reduced by extinction, have the carbon contribution in phase with the iron contribution, and are therefore positive. Now the Fourier component corresponding to such a reflexion will, in general, be positive at the atomic positions, and the effect of extinction is therefore predictable. Since F_o is measured too small, the electron density near atomic positions is diminished. And moreover, since only reflexions with $h+k$ even are affected, the diminution will occur not only at atomic positions but also at positions related by rotation about the b axis. This follows from the trigonometric form, $\cos 2\pi(hx+lz)$ $\times \cos 2\pi ky$, of these terms in the Fourier-series expression. The extinction error integrated over any appreciable part of the unit cell must be close to zero, so that the diminution at the atomic positions will tend to be compensated by an accumulation of spurious electron density between the atoms.

In our case we have a means of making a rough correction for the extinction effects. In adjusting the coordinates from the gradient of the difference synthesis (Cochran, 1951), the shift term is taken as $\partial/\partial r[D(x,y,z)-D(\bar{x},y,\bar{z})]$ instead of simply $\partial/\partial r D(x,y,z)$, for an atom at (x, y, z). For C_1, of course, which has $x \sim 0$, $y \sim \frac{1}{4}$, $z \sim 0$, the correction cannot be applied, and this is unfortunate because, owing to the rather special character of the coordinates, the extinction error is particularly severe for this atom.

Table 2. *Bond distances*

Bond distances are calculated from the coordinates of Table 1, columns (A) and (B). The standard deviation quoted is that of the individual results from the mean. The standard deviation of the mean itself is $\sigma/\sqrt{5}$

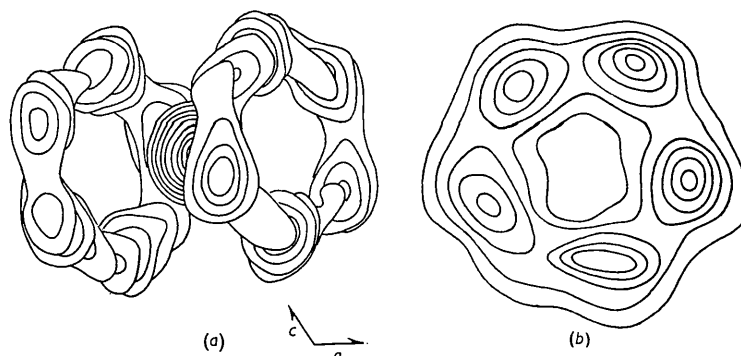|	(A)	(B)		(A)	(B)
Fe–C_1	1·994 Å	2·010 Å	C_1–C_2	1·396 Å	1·403 Å
Fe–C_2	2·059	2·050	C_2–C_3	1·400	1·386
Fe–C_3	2·078	2·069	C_3–C_4	1·365	1·352
Fe–C_4	2·074	2·070	C_4–C_5	1·413	1·399
Fe–C_5	2·034	2·024	C_5–C_1	1·471	1·476
Mean	2·048	2·045		1·409	1·403
S.d.	0·031	0·024		0·035	0·040

Fig. 1. (a) Superposition of relevant sections of three-dimensional Fourier series to give composite picture of $Fe(C_5H_5)_2$ molecule. (b) Section of three-dimensional Fourier synthesis through plane of *cyclo*pentadienyl ring.

Adjustment of the least-squares coordinates (Table 1, column (A)), as described above, leads to the co-ordinates listed in Table 1, column (B), and the bond distances in Table 2, columns (B). The Fe–C distances become somewhat more regular, the C–C distances slightly less so. Another criterion is the deviation of individual atoms from the mean plane of the ring. The least-squares coordinates give, for these devia-tions, -0.012, -0.010, -0.076, $+0.039$, $+0.058$ Å, $\sigma = 0.047$ Å, while the adjusted coordinates lead to -0.007, $+0.013$, -0.046, $+0.023$, $+0.017$ Å, $\sigma = 0.025$ Å, a significant improvement.

Discussion of results

The coordinates of Table 1, columns (B), lead to a molecule which still departs quite considerably from D_{5d} symmetry. The standard deviation from the mean of the Fe–C distances is 0.024 Å, of the C–C distances 0.040 Å, and from the mean plane, 0.025 Å. Further-more, this mean plane is inclined at $3° 30'$ to the line from the iron atom to the mean centre of the ring. Because of the systematic nature of the extinction errors, it is difficult to estimate the standard error of the carbon atom positions from the mean slope of the difference synthesis. The least-squares analysis gives 0.024 Å, and if this figure is even of the right order of magnitude the deviations from strict D_{5d} symmetry are of rather doubtful significance. The Fe–C distance is 2.045 Å $(\sigma \sim 0.01$ Å$)$ and the C–C distance 1.403 Å $(\sigma \sim 0.02$ Å$)$ if strict D_{5d} symmetry is assumed.

The difference map, even after correcting for ex-tinction by subtracting $D(\bar{x}, y, \bar{z})$ from $D(x, y, z)$, still shows an accumulation of electron density between the atoms of the ring and a corresponding deficit at the atoms themselves, as would result from libration of the ring about its mean position. Free rotation, either of the molecule as a whole, or of the cyclo-pentadienyl rings with respect to one another, is, however, quite excluded by the X-ray results. The (010) projection (Dunitz & Orgel, 1953), in which the sign of every reflexion is determined by the iron contri-bution, is independent of any assumptions concerning the carbon atom positions, and shows moderately good resolution of four of the five carbon atoms; free rota-tion of the rings would lead to complete smearing of the electron density around the circle formed by the rotating group.

That free or only slightly hindered rotation of the cyclopentadienyl rings occurs in isolated molecules is shown by recent electron-diffraction studies of the vapour (K. Hedberg, private communication) and by dipole-moment studies of mono- and di-substituted ferrocene derivatives (Richmond & Freiser, 1955). No appreciable barrier is to be expected, moreover, from molecular-orbital considerations (Dunitz & Orgel, 1953, 1955; Moffitt, 1954). The D_{5d} configuration found in the crystal is, however, slightly stabilized because of the staggering of the carbon atoms in opposite cyclopentadienyl rings, separated by 3.32 Å in ferrocene. Freezing of the molecules in this configur-ation must arise from the interaction of neighbouring molecules in the crystal. The hydrogen atoms cannot, of course, be located from our data, but if the C–H bonds are taken as about 1.05 Å in length and lying in or nearly in the plane of the ring, it is found that free rotation of the rings would lead to H $\cdots$ H ap-proaches of about 2.2 Å.

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