ON THE MOLECULAR STRUCTURE OF FERROCENE, Fe(C$_5$H$_5$)$_2$

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INTRODUCTION

The main features of the molecular structure of ferrocene have been firmly established through a series of studies[1]. However, the position of the hydrogen atoms and the shape and height of the barrier to internal rotation of the ligand rings in the *free* molecule remain unknown.

X-ray studies have demonstrated that the rings assume a staggered position in the crystal. But since other studies have shown that in crystalline biferrocenyl the rings are rotated 17° from the eclipsed position[2], and that the closely analogous compound ruthenocene is eclipsed[3], it is possible that the barrier to internal rotation in all these compounds, including ferrocene, is so low that the relative orientation of the rings in the crystal is determined by intermolecular packing forces.

Indeed, an early electron diffraction study of gaseous ferrocene indicated that at 400° all relative orientations of the rings are essentially equally probable[4], *i.e.*, that the height of the barrier is small compared to the thermal energy at this temperature.

There is additional evidence supporting this observation: no frequency corresponding to a torsional vibration has been found[5]. The proton nuclear magnetic resonance spectrum of ferrocene in the solid exhibits one sharp line[6], showing that the rings must shift rapidly from one equilibrium position to the next.

The X-ray investigations of ferrocene and related compounds have given no information on the position of the hydrogen atoms[1], and in the absence of contradictory evidence they have been assumed to be lying in the plane of the carbon ring. The symmetry of the isolated C$_5$H$_5$ ligand, or the *local* symmetry, is then D_{5h}, and four ring normal vibrations should be infrared active, while seven are actually observed[5]. This may be explained through a breakdown of the selection rules due to the perturbing presence of the metal atom, or through an actual deformation of the ligand into C_{5v} symmetry by bending the C–H bonds out of the plane of the carbon ring.

A recent electron diffraction study of dibenzene chromium, where the infrared spectrum suggests a similar asymmetry, indicated that the hydrogen atoms are bent about 5° out of the plane towards the metal atom[7]. Another study of cyclopentadienyl-indium, showed that the hydrogen atoms in this molecule may be bent about 5° *away* from the metal atom[8]. No interpretation of the infrared spectrum of this compound has been published.

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EXPERIMENTAL*

Ferrocene (puriss.) was obtained from L. Light & Co., Ltd., England, and used without further purification. The electron diffraction pattern from the gas was recorded on the Oslo apparatus with a nozzle temperature of about 140°. Exposures were made with two nozzle to plate distances, 48 and 19 cm, covering the scattering ranges $s = 1.5$ Å^{-1} to 20 Å^{-1} and $s = 7$ Å^{-1} to 45 Å^{-1}, respectively. Four apparently perfect plates covering each range were used in this study. The plates were photometered and optical densities were converted into intensities in the usual way. The intensities were then corrected for plate flatness and the screening effect of the rotating sector. The total intensity was multiplied with s^4, and the background was subtracted. The resulting molecular intensity was modified through multiplication with

$$s_{\mathcal{T}}(s) = s \ [Z_C - F_C(s)]^2$$

Z_C denotes the atomic number and $F_C(s)$, the atomic scattering factor of carbon. The latter were taken from Berghuis et al.[9].

STRUCTURE ANALYSIS

The modified molecular intensity is shown in Fig. 1. Fourier inversion yielded the radial distribution (RD) curve shown in Fig. 2. In this curve every interatomic distance, R_{ij}, in the molecule is represented by a peak centered at $r = R_{ij}$. The area
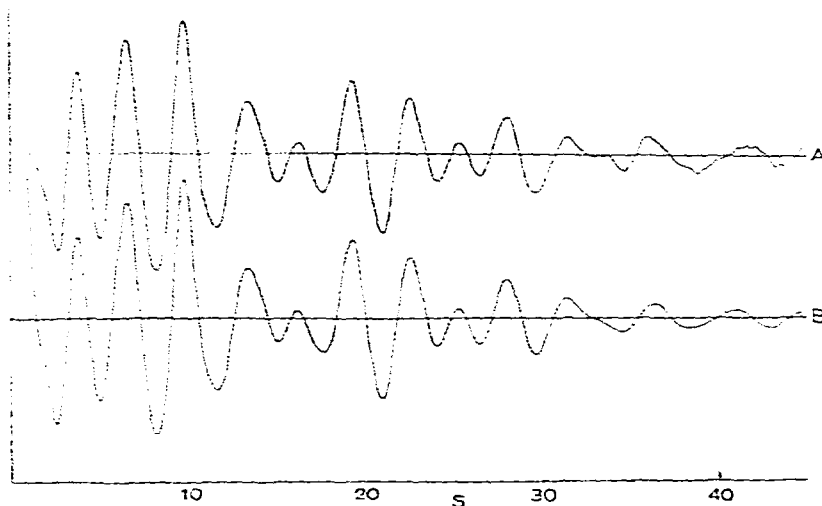

Fig. 1. Modified molecular intensity curves for ferrocene: A, experimental; B, theoretical curve for an eclipsed model.

under the peak is approximately proportional to $Z_i Z_j n_{ij}/R_{ij}$, where n_{ij} is the number of times the distance occur in the molecule. The width of each peak is determined mainly by the root mean square amplitude of vibration, u_{ij}.

* For a discussion of the electron diffraction method for determination of molecular structure see O. BASTIANSEN AND P. N. SKANCKE, Advances in Chem. Phys., 3 (1961) 323.

Using the results of earlier investigations the interpretation of the RD curve was straightfoward: The peak at 1.1 Å corresponds to the C–H bond length, the peak at 1.43 to the C–C bond length, and the peak at 2.05 to the Fe–C distance. The peak at 2.3 Å is composite, it contains a $C_1 \ldots C_3$ peak at 2.3 and a smaller $C_1 \ldots H_2$ peak at
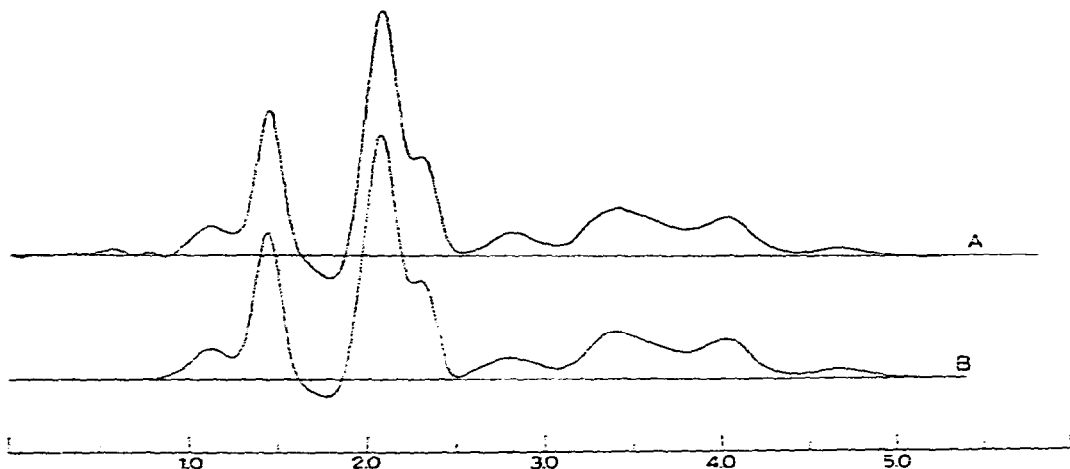

Fig. 2. Radial distribution (RD) curves for ferrocene with damping constant $k = 0.0015$ Å^2: A, experimental; B, theoretical curve for an eclipsed model.

2.25 Å. The peak at 2.8 Å corresponds to the Fe...H distance, and the complex of unresolved peaks at r > 3.3 Å arises from the distances between atoms in different ligand rings.

The analysis of the structure was carried out assuming the C_5 rings to be regular pentagons parallel to each other. Except for the relative orientation of the rings, the structure is then completely defined by four parameters, the C_1–C_2, C_1–H_1, Fe–C, and Fe...H distances. (See Fig. 3.) These were refined through a least squares calculation on the modified molecular intensity curve using a program written by
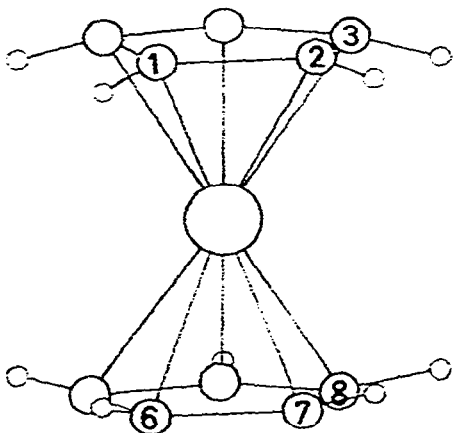

Fig. 3. Molecular structure of ferrocene in the gas phase

Seip[10]. The theoretical molecular intensity was calculated from

$$I_{theor}(s) = \sum_{i>j} n_{ij} A_{ij}(s) \sin (R_{ij}s) \exp \left(- \tfrac{1}{2} u^2_{ij}s^2\right) \cdot 1/R_{ij}$$

The functions

$$A_{ij}(s) = \varphi(s)[Z-F(s)]_i [Z-F(s)]_j \cos [\eta_i(s)-\eta_j(s)]$$

were assumed to be constants except for the Fe–C and Fe...H distances when they were computed from the values for $F_{Fe}(s)$ and $\eta(s)$, the phaseshifts, given by Ibers and Hoerni[11]. The refinement converged to give the values listed in Table 1. They are in agreement with most previously reported values to within the rather large (0.01 to 0.02 Å) error limits of the latter, and we believe them to be the most accurate values now available. The parameters obtained through the least squares refinement, $r_g(1)$, can be converted into the center of gravity of the distance distribution curve, $r_g(0)$, by adding u^2/r (ref. 12). If anharmonicity is disregarded $r_g(0) = r_e$, the equilibrium distance. The Fe...H equilibrium distance calculated under this assumption is 2.814 Å with a standard deviation of 0.009 Å. The same distance can be computed from the other equilibrium parameters under the assumption that the hydrogen atoms lie in the plane of the carbon ring: $R' = 2.868$ Å, st. dev. $= 0.006$ Å. The observed shortening is then $\Delta = 0.054$ with a standard deviation of 0.011 Å. This corresponds to a bending of the C–H bonds $4.6° \pm 0.9°$ out of the plane of the carbon ring towards the metal atom. Since the present calculation has not considered anharmonicity or shrinkage effects, the result should be taken as an indication rather than a demonstration that a deformation of the ligand has taken place*.

TABLE 1

STRUCTURAL PARAMETERS FOR FERROCENE

Distance[a]	$r_g(1)$[b] (Å)	$r_g(0)$[c] (Å)	u[b] (Å)
C_1–C_2	1.429 ± 0.003	1.431 ± 0.005	0.047 ± 0.003
Fe–C	2.056 ± 0.002	2.058 ± 0.005	0.062 ± 0.003
C_1–H_1	1.116 ± 0.012		0.084 ± 0.012
Fe...H	2.805 ± 0.026		0.157 ± 0.027
$\angle$ H–C–C_5-plane		$4.6 \quad \pm 2.7$[d]	
C_1...C_3	2.312		0.058 ± 0.007
C_1...H_2	2.270		0.063 ± 0.016
C_1...H_3	3.388		0.121 ± 0.039
Inter-ring distance		3.319 ± 0.015	
C_1...C_6	3.316		0.097 ± 0.022
C_1...C_7	3.361		0.150 ± 0.024
C_1...C_8	4.042		0.119 ± 0.014
C_1...H_6	3.412		0.133 ± 0.041[e]
C_1...H_7	3.943		0.133 ± 0.048
C_1...H_8	4.677		0.133 ± 0.041[e]

[a] Labels for the atoms are shown in Fig. 3. [b] The error limits are 3 times the standard deviations resulting from the least squares analysis. [c] $r_g(0) = r_g(1) + u^2/r_g(1)$. If anharmonicity is neglected, $r_g(0) = r_e$, the equilibrium distance. The error limits include estimates of the proportionality (see text). [d] The error limit does not take into account shrinkage or anharmonicity (see text). [e] $u(C_1...H_6)$ and $u(C_1...H_3)$ were assumed to be equal.

* Note added in proof: A study of $Mn(C_5H_5)$, where distortion of the C–H bonds is not to be expected, indicate that these effects are negligible (A. ALMENNINGEN, A. HAALAND AND T. MOTZFELDT, to be published).

The distances between atoms in different rings were computed for a staggered and an eclipsed model, and the corresponding amplitudes were refined through a least squares calculation as before. The inter-ring distance distribution for a freely rotating model was obtained by calculating the distances between a carbon atom in one ring and carbon atoms distributed at 15 degree intervals in the other ring. An RD curve calculated for a model with 5 degree intervals showed no significant difference from that calculated with 15 degree intervals. The vibrational amplitudes were refined under the assumption that C...C distances within each range 3.30 to 3.50, 3.51 to 4.00, and 4.01 to 4.11 Å have identical u-values. The weighting function used in the least squares analysis was $W = \exp[-0.1(s - 4.0)^2]$ in the range $1.5 < s < 4.0$ Å^{-1}, $W = 1.0$ in the range $4.0 \leqslant s < 32.0$ Å^{-1}, and $W = \exp[-0.006(s - 32.0)^2]$ in the range $32.0 < s < 44.75$ Å^{-1}. The error sums resulting from the least squares refinement were

Eclipsed model: $\sum W[I_{obs}(s)-I_{th}(s)]^2 = 4.46 \times 10^3$

Free rotation model: $\sum W[I_{obs}(s)-I_{th}(s)]^2 = 4.90 \times 10^3$

Staggered model: $\sum W[I_{obs}(s)-I_{th}(s)]^2 = 6.10 \times 10^3$.

Fig. 4 shows RD curves over the range 3.0 to 5.0 Å. The shape of the curve in this region is determined by the relative orientation of the two rings. The eclipsed model gives an extremely good fit over the whole range (see Fig. 2). In particular, it is the only model that reproduces the broad maximum due to inter-ring C...H distances at 4.7 Å. The freely rotating model gives a slightly less satisfactory fit and does not yield a maximum at 4.7 Å. The staggered model is clearly unsatisfactory and can be ruled out.
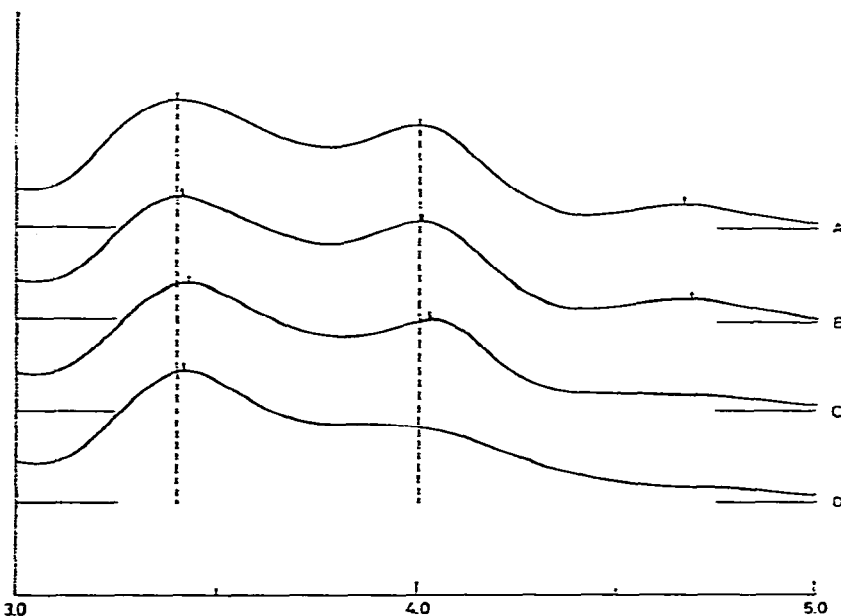

Fig. 4. Radial distribution curves for ferrocene in the region $3.0 \leqslant r \leqslant 5.0$ Å with damping constant $k = 0.0036$ Å^2: A, experimental; B, eclipsed model; C, freely rotating model; and D, staggered model.

The eclipsed model, then, seems most probable, while a freely rotating one cannot be excluded. However, the change of the interatomic distances of the eclipsed molecule when the rings are rotated into the staggered position are comparable to the corresponding root mean square variations, u-values. Hence a molecule may spend a considerable fraction of the time in the staggered conformation. The difference between the "eclipsed" and the "freely rotating" models is therefore one of degree. Both predict a distribtion of ligand rings over all rotation angles. They differ in the fraction of molecules they assume to be momentarily staggered, that is in the height of the barrier to internal rotation which for the "freely rotating" model is zero.

An estimate of the barrier height can be obtained from the u-values of the "eclipsed" model: Keeping C_1 fixed, the relative motion of the atoms on the other ring may be broken down into components tangential, radial, and perpendicular to the ring. If each motion is assumed to be harmonic, the root mean square amplitude of each may be computed from the three observed u-values:

$$u_{tan} = 0.37 \text{ Å}$$

$$u_{rad} = 0.11 \text{ Å}$$

$$u_{perp} = 0.10 \text{ Å}$$

The ratio between the number of molecules in the staggered and in the eclipsed conformation can be computed from u_{tan}, and a barrier height of

$$\Delta E \sim 1.1 \text{ kcal/mole}$$

is found by Boltzmann statistics.

The standard deviations obtained through a least squares refinement do not include proportionality errors in the s-scale of the observed intensity[13]. Such errors lead to a scaling up or down of the entire molecule, without change of geometry. Analysis shows (Ref) that such errors lead to a standard deviation of $1 \cdot 10^{-3} \cdot R_{ij}$ in the assumed bond lengths. Three times this amount has been included in the error limits of the second column in Table 1.

SUMMARY

Electron diffraction studies of ferrocene vapor at $140°$ show that the free molecule has an eclipsed (D_{5h}) equilibrium configuration with a small barrier to internal rotation. The barrier is estimated to be about 1.1 kcal/mole. The principal molecular parameters are: C–C, 1.431 ± 0.005 Å; Fe–C, 2.058 ± 0.005 Å, and C–H, 1.122 ± 0.020 Å. The C–H bonds seem to be bent about $5°$ out of the plane of the C_5 ring towards the iron atom.

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