Acta Cryst. (1979). B35, 1068–1074

A New Interpretation of the Disordered Crystal Structure of Ferrocene

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(*Received* 29 *August* 1978; *accepted* 21 *November* 1978)

Abstract

X-ray analyses of ferrocene [$Fe(C_5H_5)_2$, $C_{10}H_{10}Fe$] at room temperature and at 173 K yield vibrational-ellipsoid patterns that are incompatible with pure rotational disorder of the cyclopentadienyl rings. Below 164 K ferrocene becomes triclinic. Relationships between the diffraction patterns of the monoclinic high-temperature (HT) and triclinic low-temperature (LT) structures suggest that the formally centrosymmetric molecule of the disordered HT phase can be described in good approximation as an averaged superposition of the four molecules present in the primitive LT cell. The molecular centre of symmetry required by the HT space group is thus only statistical in nature, and the crystallographic evidence for the staggered arrangement of the cyclopentadienyl rings in ferrocene and other isomorphous metallocenes has to be revised.

Introduction

The familiar sandwich structure of ferrocene, with the Fe atom centrally placed between two staggered cyclopentadienyl rings, seemed to be established by the early crystal structure analyses (Fischer & Pfab, 1952; Eiland & Pepinsky, 1952; Dunitz & Orgel, 1953). In particular, the choice between eclipsed (D_{5h}) and staggered (D_{5d}) arrangements of the rings appeared to be unequivocal, since only the latter is compatible with the molecular inversion centre required by the space group (C_{2h}^5, $Z = 2$). When the subsequent three-dimensional analysis (Dunitz, Orgel & Rich, 1956; hereinafter DOR) indicated considerable smearing of the electron-density maxima in the planes of the cyclopentadienyl rings, this was attributed to a combination of experimental error in the intensities (based on visual examination of photographic films) and rotational oscillations of the rings about their mean positions in the crystal.

During the intervening years, the presence of disorder in the room-temperature (RT) crystal structure has been indicated by several lines of evidence. Edwards, Kington & Mason (1960) measured the heat capacity C_p of ferrocene in the range 125–200 K and detected a λ-point transition at 163·9 K with a secondary C_p maximum at 169 K; the entropy change for the overall transition was estimated to be $\Delta S = 5{\cdot}31$ J K^{-1} mol^{-1} = R ln 1·89. X-ray measurements down to 95 K failed to reveal any discontinuity in the lattice dimensions. The authors proposed that the low-temperature structure consisted of an ordered arrangement of staggered molecules in the DOR orientation, the λ-point transition corresponding to the onset of rotational disorder. For the structure above the transition, they proposed as the most likely possibilities either a mixture of staggered molecules in two orientations (the DOR orientation and one rotated by 36° about the molecular fivefold axis), or a mixture of staggered and eclipsed molecules.

The occurrence of rotational disorder in RT ferrocene was also detected by Willis (1960, 1961), who carried out a neutron-diffraction analysis based on 215 three-dimensional reflexions. The (010) projection of the nuclear density distribution showed subsidiary negative peaks between the negative peaks corresponding to the H atoms in the DOR orientation. Willis assumed a random mixture of staggered molecules in two orientations (DOR and the one rotated by 36°) and varied the occupancy factors, obtaining the best R for a 2:1 ratio. This implies a 2:1 ratio of DOR and anti-DOR ring orientations, which would also be produced by a random mixture of equal numbers of staggered molecules in the DOR orientation and of eclipsed molecules in each of two orientations rotated by 180° with respect to one another.

According to gas-phase electron-diffraction studies (Bohn & Haaland, 1966; Haaland & Nilsson, 1968), the equilibrium structure of ferrocene is eclipsed rather than staggered; the barrier to internal rotation was estimated to be 3·8 ± 1·3 kJ mol^{-1} (Haaland & Nilsson, 1968). The barrier to reorientation of cyclopentadienyl rings in crystalline ferrocene has been estimated from NMR data (temperature dependence of line width and of spin-lattice relaxation times). Values in the range 7·5–9·6 kJ mol^{-1} have been reported for the LT phase (Holm & Ibers, 1959; Mulay & Attalla, 1963; Campbell, Fyfe, Harold-Smith & Jeffrey, 1976).

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Above the phase transition the barrier appears to become smaller.

In the crystal, the reorientation barrier must be due to a combination of inter- and intramolecular forces. Campbell *et al.* (1976) have used non-bonded potential functions to estimate the intermolecular contribution to the energy profile for reorientation of a single cyclopentadienyl ring in crystalline ferrocene. Since the intermolecular distances depend on the lattice dimensions and these in turn depend on the temperature, the energy profile calculated in this way is also temperature dependent. Campbell *et al.* based their calculations on the lattice dimensions reported by Edwards, Kington & Mason (1960). At LT they obtain an energy profile with a single minimum repeated every 72°, corresponding to an ordered arrangement of staggered molecules in the DOR arrangement. This energy profile is dominated by the contribution of non-bonded interactions, but with increasing temperature (larger intermolecular separation) the intramolecular contribution, which favours eclipsing, becomes relatively more important until, at RT, the profile shows distinct subsidiary minima for reorientation of the cyclopentadienyl ring through 36°. These results would indicate that the ordered crystal structure below the transition point has the DOR arrangement of staggered molecules; as the temperature is raised, there is a gradual onset of disorder as individual rings are reoriented by 36°. Campbell *et al.* also reported that a redetermination of the RT structure by X-ray analysis indicates a statistical 2:1 occupancy of the two ring orientations, in agreement with the earlier neutron-diffraction result.

Infrared spectroscopic evidence for crystalline ferrocene is compatible with the DOR structure at high temperatures (Winter, Curnette & Whitcomb, 1959), but when the crystals are cooled new absorption bands appear that are inconsistent with molecules on centrosymmetric sites (Hyams & Ron, 1973). Hyams & Ron suggested that the LT phase is ordered with molecules on non-centrosymmetric sites. From the absence of any sharp change in the intensity of the absorption bands at the transition temperature they proposed that the structure of the LT phase is preserved in domains in the HT phase, with a gradual decrease in domain size as the temperature is raised.

From oscillation and Weissenberg X-ray photographs Hyams & Herbstein (personal communication from Professor F. H. Herbstein, April, 1974) observed that in the LT phase the *b* and *c* axes are doubled and that the new cell is *A*-centred. Although the LT photographs showed no deviations from monoclinic symmetry and the reflections common to the two phases had similar intensities, Hyams & Herbstein concluded that the LT phase is actually triclinic. From precise measurements of the powder diffraction peaks in the range 15 to 295 K Calvarin & Bérar (1975) showed that below 163·9 K the crystal structure is indeed triclinic, but they did not observe any doubling of the cell axes.*

From all this conflicting evidence, a thorough reinvestigation of the structure of crystalline ferrocene seems overdue. In this paper we report results of new X-ray studies at RT and at 173 K. We also describe preliminary results of an X-ray investigation of the LT phase.

Experimental

All X-ray measurements were made on an Enraf–Nonius CAD-4 diffractometer (graphite-monochromatized Mo $K\alpha$ radiation) equipped with a LT device. Lattice dimensions measured over a range between 164 K and RT are in agreement with those reported by Calvarin & Bérar (1975). Values at RT (293 K) and at 173 K are:

	a	b	c	β
293 K	10·54 Å	7·61 Å	5·93 Å	121·03°
173 K	10·45	7·58	5·81	120·86.

Complete sets of intensity measurements were made at RT (sin θ/λ limit 0·66 Å^{-1}, 886 independent reflexions with $I \geq 3\sigma_I$) and at 173 K (sin θ/λ limit 0·68 Å^{-1}, 950 reflexions with $I \geq 3\sigma_I$). Intensities were converted to relative $|F|$ values in the usual way, but absorption corrections were not applied ($\mu \sim 1{\cdot}8$ mm^{-1}) in view of the difficulty of measuring the crystal shape accurately. In any case, the crystals used were small (about 3–4 × 10^{-1} mm in edge) and not particularly acicular or plate-like, so that absorption errors should not be serious.

The DOR coordinates† were used as the starting-point for least-squares refinement of the RT data (final $R = 0{\cdot}054$). The resulting coordinates were used in turn as starting-point for refinement of the 173 K data (final $R = 0{\cdot}050$). A modified weighting scheme (Dunitz & Seiler, 1973) with $r = 3{\cdot}5$ Å^2 (RT data) and $r = 3{\cdot}0$ Å^2 (173 K data) was employed for both analyses. Difference maps calculated with both data sets showed weak diffuse peaks near expected H positions. However, the observed positions were considered to be less reliable than calculated positions based on stereochemical criteria (C—H direction along bisector of CCC angle, C—H distance = 1·08 Å). Calculated H positions were therefore used in the final refinement stages. They are listed in Tables 1 and 2, with the

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* From a recent single-crystal study (Clec'h, Calvarin, Bérar & Kahn, 1978), all three axes are now reported to be doubled at 150 K.

† The negative signs associated with the *z* coordinates of C(1), C(2) and C(3) were erroneously omitted in the DOR publication.

Table 1. *Atomic positions and vibrational parameters* (*all* $\times 10^4$, *with e.s.d.'s in parentheses*) *from the X-ray analysis of ferrocene at* 293 K

H positions are calculated.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0	0	0	421 (4)	332 (4)	520 (4)	−66 (3)	261 (3)	−26 (3)
C(1)	228 (6)	2607 (5)	−300 (17)	837 (32)	317 (16)	1864 (85)	−80 (17)	889 (47)	−48 (27)
C(2)	413 (5)	1768 (7)	−2149 (9)	733 (24)	742 (27)	799 (31)	−182 (23)	411 (24)	117 (25)
C(3)	1579 (5)	659 (6)	−899 (11)	704 (26)	649 (23)	1145 (47)	−166 (22)	635 (32)	−124 (30)
C(4)	2170 (5)	697 (8)	1706 (12)	552 (22)	766 (30)	1012 (43)	−247 (21)	183 (26)	152 (34)
C(5)	1331 (10)	1956 (11)	2256 (13)	1936 (80)	1393 (60)	1065 (48)	−1356 (65)	1117 (57)	−817 (47)
H(1)	−602	3587	−687						
H(2)	−258	1957	−4251						
H(3)	1983	−156	−1888						
H(4)	3101	−70	3140						
H(5)	1496	2322	4148						

Table 2. *Atomic positions and vibrational parameters* (*all* $\times 10^4$, *with e.s.d.'s in parentheses*) *from the X-ray analysis of ferrocene at* 173 K

H positions are calculated.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0	0	0	247 (3)	189 (3)	277 (3)	−49 (2)	138 (2)	−19 (2)
C(1)	214 (6)	2630 (5)	−264 (17)	670 (30)	177 (13)	1659 (65)	−62 (16)	864 (41)	−75 (23)
C(2)	405 (4)	1780 (7)	−2180 (9)	449 (19)	549 (23)	472 (20)	−168 (17)	200 (16)	120 (17)
C(3)	1583 (5)	657 (6)	−931 (11)	479 (20)	415 (17)	815 (30)	−137 (16)	481 (22)	−125 (19)
C(4)	2190 (5)	712 (8)	1747 (12)	339 (18)	587 (27)	732 (31)	−206 (18)	5 (19)	224 (25)
C(5)	1349 (11)	1966 (11)	2310 (13)	1624 (72)	1085 (51)	771 (36)	−1157 (58)	934 (48)	−710 (39)
H(1)	−624	3604	−630						
H(2)	−273	1977	−4320						
H(3)	1979	−170	−1952						
H(4)	3136	−45	3208						
H(5)	1531	2331	4253						

positional and vibrational parameters obtained for the other atoms.*

Results

The atomic positions listed in Tables 1 and 2 lead to planar slightly irregular cyclopentadienyl rings. The C—C distances are 1·335–1·450 Å (average 1·389 Å) at RT, 1·346–1·441 Å (average 1·395 Å) at 173 K; the Fe—C distances are 2·009–2·054 Å (average 2·033 Å) at RT, 2·017–2·048 Å (average 2·033 Å) at 173 K. These results are in essential agreement with the 1956 DOR results and do not add anything to our knowledge of the crystal and molecular structure.

The vibrational parameters are more interesting. Figs. 1 and 2 show that the major axes of the vibrational ellipsoids of the C atoms are approximately tangential to the ring and remain nearly constant from RT to 173 K. At the lower temperature there is a noticeable decrease in mean-square amplitudes perpendicular to the ring plane (Fig. 1) and in the radial directions (Fig. 2). C(1), C(5), and C(4) have markedly anisotropic thermal ellipsoids at both temperatures, and it is clear that the observed shapes cannot be accounted for by disorder models that involve exclusively rotation of the cyclopentadienyl rings in their mean planes. This kind of disorder would lead to a pattern in which each ellipsoid is equally drawn out along the tangent to the cirumscribing circle, a pattern that retains the approximate fivefold symmetry of the cyclopentadienyl ring, in contrast to the markedly unsymmetrical pattern that is actually observed.

In particular, the shapes of the vibrational ellipsoids give no support to the disorder model involving occupancy of two alternative ring orientations (DOR and the one rotated by 36°) in 2:1 ratio, as proposed by Willis (1961) and by Campbell *et al.* (1976).* Such

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* A list of structure factors obtained at RT and 173 K has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34099 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* One argument that has been advanced in favour of the 2:1 model is the agreement between the measured entropy change $\Delta S = 5{\cdot}31\ \mathrm{J\ K^{-1}\ mol^{-1}} = R\ln 1{\cdot}89$ for the phase transition (Edwards, Kington & Mason, 1960) and the calculated configurational entropy $\Delta S = -R(\frac{2}{3}\ln\frac{2}{3} + \frac{1}{3}\ln\frac{1}{3}) = R\ln 1{\cdot}89$ for 2:1 statistical occupancy. The agreement is more apparent than real because the measured value is expressed per mole of ferrocene, whereas the calculated one is per mole of ring. When the two quantities are expressed in the same units the agreement is not so good.

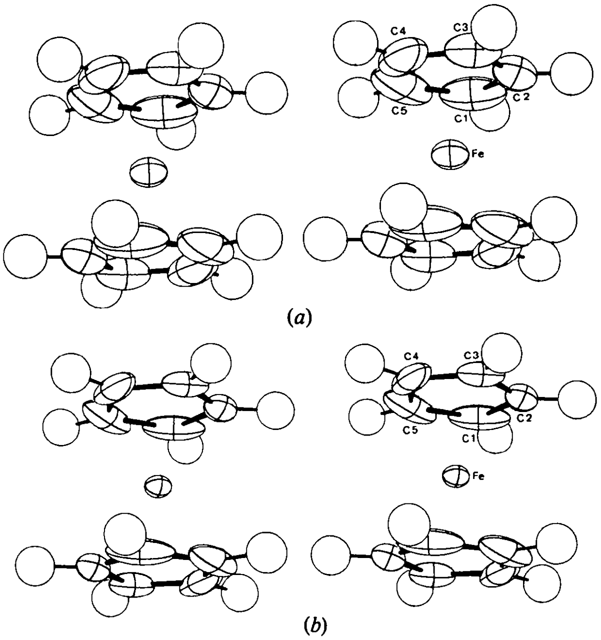

Fig. 1. Stereoscopic view of the ferrocene molecule in the crystal at (*a*) room temperature and (*b*) 173 K. Vibrational ellipsoids are shown at the 50% probability level (Johnson, 1965).

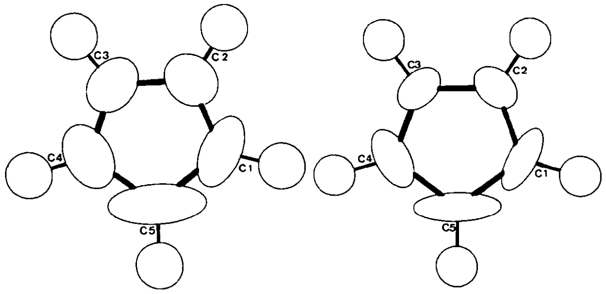

Fig. 2. Vibrational ellipsoids [50% probability level (Johnson, 1965)] of the C atoms in ferrocene at room temperature (left) and at 173 K (right), projected on the mean plane of a cyclopentadienyl ring.

a model may well lead to better agreement between observed and calculated *F* values than an ordered model, but so would countless other disorder models.

Some clues about the nature of the disorder present in the HT phase have been obtained from X-ray measurements made below the transition point.

Preliminary results of the LT analysis

At temperatures below 164 K the X-ray diffraction pattern of ferrocene contains additional reflexions with half-integral values of *hkl*. The additional reflexions occur only if all three indices are half-integral, indicating that the new unit cell with $\mathbf{A} = 2\mathbf{a}$, $\mathbf{B} = 2\mathbf{b}$, $\mathbf{C} = 2\mathbf{c}$ is *F*-centred.* Reflexion indices referred to this cell will be designated as *HKL*; the condition defining possible reflexions is then that *HKL* are either all odd or all even, the latter group of reflexions being common to both phases. The intensities of these common reflexions hardly change on passing from the HT to the LT phase; in particular, $H0L$ reflexions with $H = 4n + 2$, $L = 2n$ and $0K0$ reflexions with $K = 4n + 2$ (the reflexions that are systematically absent in the diffraction pattern of the HT phase) are generally very weak in the LT phase.

The LT space group cannot contain the glide planes and 2_1 screw axes of the HT phase because the corresponding symmetry operations are obviously incompatible with the doubling of the cell axes. Indeed, the only symmetry elements of the HT structure that can be retained in the LT space group are the inversion centres. Thus the LT structure must be triclinic. The X-ray diffraction patterns obtained from most crystal specimens that are cooled below the transition point show only very slight deviations from monoclinic symmetry; the triclinic crystals evidently tend to be formed as twinned intergrowths. Moreover, the deviations of α and γ from 90° are small and cannot be measured accurately because of the overlapping of *HKL* and $H\bar{K}L$ reflexions from the separate components of the twins. However, these angle deviations are detectable, and the values obtained for α and γ are compatible with those obtained by high-resolution powder diffractometry (Calvarin & Bérar, 1975) although not as accurate.

The detailed structure of the LT phase is still under investigation and will be reported later. Even without this information it is still possible to draw some general conclusions about the structure of the LT phase and, by inference, about the nature of the disorder in the HT phase. For a start we assume that the space group of the LT phase is $F\bar{1}$ ($P\bar{1}$ with allowance for the non-standard *F*-centred cell) so that the asymmetric unit consists of two independent molecules that may be eclipsed or staggered or anything between: the $F\bar{1}$ ($P\bar{1}$) assumption is not essential, it merely simplifies the subsequent argument. Now the similarity between the intensities of the common reflexions (those with *HKL* all even) indicates that the overall arrangement of Fe atoms and cyclopentadienyl rings must be very much the same in the two phases. On the other hand, the additional reflexions from the LT phase (those with *HKL* all odd) show that molecules that appear to be identical, *i.e.* related by a lattice translation, in the HT structure are distinctly different in the LT structure.

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* A few additional weak reflexions that appear to violate the systematic absences for *F*-centring have been observed from some crystal specimens. Nevertheless, the *F*-centred cell accounts for the overwhelming majority of the reflexions with non-integral values of *hkl*, and can be taken as being a close approximation to the actual structure.

This is depicted schematically in Fig. 3, where the ellipses represent projections of cyclopentadienyl rings in arbitrary orientations and the dots identify symmetry-related rings. (The Fe atoms in Fig. 3 need not be situated exactly at $\frac{1}{4}$,0,0, *etc.* and 0,$\frac{1}{4}$,0, *etc.* but they are not far from these idealized positions.)

The disappearance of reflexions with *HKL* odd without appreciable change in the intensities of *HKL*-even reflexions shows that the unit cell of the HT phase is obtained by superimposing molecules related by half a lattice translation in the LT structure. Moreover, the glide plane of the HT structure (and the weakness of $H0L$ reflexions with $H = 4n + 2$, $L = 2n$ in the LT structure) shows that the superposition of molecules (I) and (I′) must give almost the same result as the superposition of (II) and (II′). In fact, careful measurements on the HT phase at 173 K reveal small but significant intensities for some of the systematically absent $h0l$ reflexions – the glide-plane symmetry is only approximate, not exact. Small but significant intensities are also observed for a few reflexions with half-integral indices – the LT superstructure persists in the HT phase.

The relationships between the diffraction patterns of the LT and HT phases indicate that earlier views on the nature of the disorder in the HT phase must be revised. It is not necessary to assume that either the ordered LT structure or the disordered HT one has the DOR arrangement of staggered molecules. The onset of disorder must be attributed mainly to loss of the long-range order present in the LT phase, accompanied by, and possibly caused by, a gradual increase in the amplitude of libration of the cyclopentadienyl rings. This interpretation is also consistent with the results and conclusions reached by Hyams & Ron (1973) in their infrared spectroscopic study.

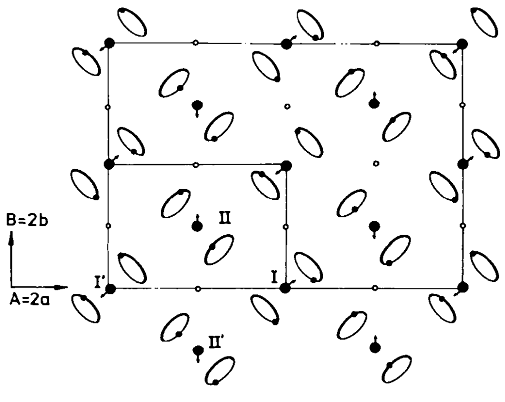

Fig. 3. Schematic arrangement of a layer of ferrocene molecules in the ordered LT phase. The ellipses represent projections of cyclopentadienyl rings in arbitrary orientations and the dots identify symmetry-related rings. An equivalent layer is related to the one shown by the transition $\frac{1}{2}$,0,$\frac{1}{2}$ (or 0,$\frac{1}{2}$,$\frac{1}{2}$) to produce an *F*-centred lattice.

Discussion

The evidence for the staggered antiprismatic arrangement of cyclopentadienyl rings in ferrocene is based primarily on space group symmetry arguments. Once the crystal structure is recognized to be disordered, conclusions drawn from the space group cease to be valid except in a statistical sense. Thus, the positional coordinates and vibrational parameters obtained for crystalline ferrocene at two temperatures above the transition point (Tables 1 and 2) do not necessarily describe the structure of an actual ferrocene molecule (with due allowance for vibration) at all.

In the disordered HT phase, the asymmetric unit of structure consists of a single cyclopentadienyl ring that may be regarded as an averaged superposition of the four symmetry-independent rings present in the unit cell of the ordered LT structure. However, the systematic absences indicate that the superposition of molecules (I) and (I′) (Fig. 3) must be almost indistinguishable from the superposition of (II) and (II′). This suggests that the superposition of only two half-molecules or rings will give a good approximation to the averaged structure.

Full-matrix refinement of the 173 K data in terms of a disordered model (space group $P2_1/a$, one half-weight Fe atom anisotropic plus ten half-weight C atoms all isotropic in the asymmetric unit) leads to isotropic B values in the range 2·0–3·3 Å^2 and to virtually the same level of agreement (R = 0·055) as that obtained in the conventional refinement with anisotropic temperature factors. The resulting atomic arrangement (Fig. 4) is clearly consistent with the vibrational-ellipsoid pattern obtained from the conventional refinement (Figs. 1 and 2) and is also very similar to the superposition pattern obtained in a recent neutron-diffraction study (Takusagawa & Koetzle, 1979). The two independent five-membered rings differ not only in their orientations but also in the positions of their centres. It is the combination of these two movements that produces more pronounced smearing for C(1), C(5) and C(4) than for the other two atoms.

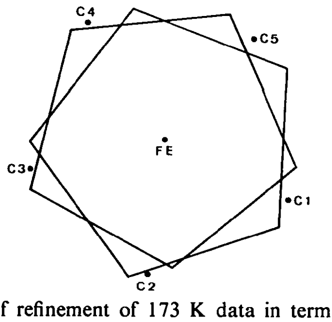

Fig. 4. Result of refinement of 173 K data in terms of ten half-weight C atoms with isotropic temperature factors. The positions obtained by anisotropic refinement of five single-weight C atoms are shown for comparison.

If we accept Fig. 4 as depicting the superposition of pairs of corresponding rings of molecules (I) and (I′) [or (II) and (II′), Fig. 3] then the relative orientation of the rings in a single representative ferrocene molecule is obtained by inverting one of the two rings through the centre of the figure. This produces a molecule that is neither exactly eclipsed nor staggered, although somewhat closer to the former. Our results for the LT phase show that the ferrocene molecules in this ordered structure have a similar conformation (Fig. 5) to the one deduced from refinement of the superposition model.

Further, the similarity between the vibrational-ellipsoid patterns obtained at RT and at 173 K (Fig. 2) suggests that the averaged molecule in the disordered RT structure can also be regarded in good approximation as a superposition of nearly eclipsed molecules. The increase in the vibrational amplitudes as the temperature is raised may be due to a combination of dynamic and static disorder; the possibility that an increasing fraction of the molecules have other ring arrangements (including the staggered one) can certainly not be excluded.

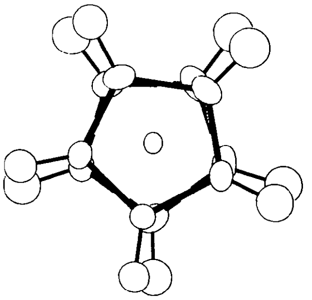

Fig. 5. Structure of a ferrocene molecule in the ordered LT phase [vibrational ellipsoids at 50% probability level (Johnson, 1965), from refinement of data from an untwinned crystal at 100 K]. The C–C distances are 1·419–1·431 Å (average 1·425 Å), the Fe–C distances are 2·038–2·052 Å (average 2·045 Å), and the rotation angle between the rings is 9°.

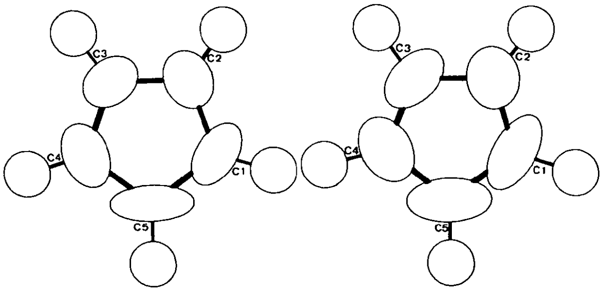

Fig. 6. Vibrational ellipsoids [50% probability level (Johnson, 1965)] of the C atoms in bis(cyclopentadienyl)cobalt (left) and bis(cyclopentadienyl)magnesium (right), both projected on the mean plane of a cyclopentadienyl ring [calculated from data provided by Bünder & Weiss (1975*a*,*b*)]. Compare with corresponding results in Fig. 2 for ferrocene.

However, there is no reason to believe that a major fraction of the molecules in crystalline RT ferrocene have the centrosymmetric staggered structure, and hence the earlier conclusions about the molecular symmetry of ferrocene have now to be revised.

The HT ferrocene structure seems to be able to accommodate itself to a remarkable variety of types of disorder. In isomorphous RT cobaltocene with Co–C = 2·10 Å the vibrational ellipsoids of the C atoms (Bünder & Weiss, 1975*a*) shown in Fig. 6 (left) are remarkably similar to those of RT ferrocene; the crystal structure must be disordered in a very similar manner to ferrocene. In the isomorphous Mg compound with Mg–C = 2·30 Å the RT vibrational ellipsoids (Bünder & Weiss, 1975*b*) shown in Fig. 6 (right) are somewhat larger than in ferrocene but they still show the same general pattern – large anisotropic ellipsoids for C(1), C(5) and C(4).* No phase transition has been reported for either of these compounds.

Vibrational parameters obtained in a RT analysis of nickelocene (Ni–C 2·17 Å) are also similar to those of RT ferrocene, but no doubling of the crystal axes has been detected down to 100 K (Seiler & Dunitz, unpublished). Nickelocene shows no first-order transition between 5 and 295 K (Ammeter, personal communication; Calvarin & Weigel, 1976) although heat-capacity measurements indicate that some sort of order–disorder transition occurs over the temperature range 170–240 K (Azokpota, Calvarin & Pommier, 1976). A crystal structure analysis at 100 K is under way.

The crystal structure of beryllocene has been described in terms of a unit cell with $a = 5{\cdot}893$, $b = 7{\cdot}683$, $c = 9{\cdot}343$ Å, $\beta = 87{\cdot}73°$, space group $P2_1/n$ (Wong, Lee, Lee, Chang & Liu, 1973), but the axis transformation $\mathbf{a}' = -\mathbf{a} + \mathbf{c}$, $\mathbf{c}' = \mathbf{a}$ leads to $a' = 10{\cdot}88$, $b' = 7{\cdot}68$, $c' = 5{\cdot}89$ Å, $\beta' = 120{\cdot}9°$, $P2_1/a'$, isomorphous with HT ferrocene. The structure is disordered at RT and at 153 K (Wong, Lee, Chao & Lee, 1972). At both temperatures the Be atoms do not sit on the statistical centres of symmetry but occupy two sites equally and oppositely displaced from these special positions, and the molecules show marked deviations from the C_{5v} symmetry observed in the gas phase (Haaland, 1968). It seems likely that the averaged structure corresponds not only to a superposition of Be positions but also to a disordered arrangement of rings. The actual structure of the individual molecules may then, as in ferrocene, be very different from the one suggested by the averaged structure.

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* The β_{ij} values cited by Bünder & Weiss (1975*a*,*b*) are obviously 10 times too small. In preparing Fig. 6 (left) we have also changed the value of β_{23} of C(5) from -7×10^{-4} to -27×10^{-3} since we suspect that the former value is in error. The H atom positions shown in Fig. 5 have been estimated from the published positions of the C atoms.

References

Azokpota, C., Calvarin, G. & Pommier, G. (1976). *J. Chem. Thermodyn.* **8**, 283–287.

Bohn, R. K. & Haaland, A. (1966). *J. Organomet. Chem.* **5**, 470–476.

Bünder, W. & Weiss, E. (1975*a*). *J. Organomet. Chem.* **92**, 65–68.

Bünder, W. & Weiss, E. (1975*b*). *J. Organomet. Chem.* **92**, 1–6.

Calvarin, G. & Bérar, J. F. (1975). *J. Appl. Cryst.* **8**, 380–385.

Calvarin, G. & Weigel, D. (1976). *J. Appl. Cryst.* **9**, 212–215.

Campbell, A. J., Fyfe, C. A., Harold-Smith, D. & Jeffrey, K. R. (1976). *Mol. Cryst. Liq. Cryst.* **36**, 1–23.

Clec'h, G., Calvarin, G., Bérar, J. F. & Kahn, R. (1978). *C. R. Acad. Sci. Sér. C*, **286**, 315–317.

Dunitz, J. D. & Orgel, L. E. (1953). *Nature (London)*, **171**, 121–122.

Dunitz, J. D., Orgel, L. E. & Rich, A. (1956). *Acta Cryst.* **9**, 373–375.

Dunitz, J. D. & Seiler, P. (1973). *Acta Cryst.* B**29**, 589–595.

Edwards, J. W., Kington, G. L. & Mason, R. (1960). *Trans. Faraday Soc.* **56**, 660–667.

Eiland, P. F. & Pepinsky, R. (1952). *J. Am. Chem. Soc.* **74**, 4971.

Fischer, E. O. & Pfab, W. (1952). *Z. Naturforsch. Teil B*, **7**, 377–379.

Haaland, A. (1968). *Acta Chem. Scand.* **22**, 3030–3032.

Haaland, A. & Nilsson, J. E. (1968). *Acta Chem. Scand.* **22**, 2653–2670.

Holm, C. H. & Ibers, J. A. (1959). *J. Chem. Phys.* **30**, 885–888.

Hyams, I. J. & Ron, A. (1973). *J. Chem. Phys.* **59**, 3027–3030.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Mulay, L. N. & Attalla, A. (1963). *J. Am. Chem. Soc.* **85**, 702–706.

Takusagawa, F. & Koetzle, T. F. (1979). *Acta Cryst.* B**35**, 1074–1081.

Willis, B. T. M. (1960). *Acta Cryst.* **13**, 1088.

Willis, B. T. M. (1961). AERE Report R3708, Harwell, Oxfordshire, England.

Winter, W. K., Curnette, B. & Whitcomb, G. E. (1959). *Spectrochim. Acta*, **12**, 1085–1102.

Wong, C., Lee, T. Y., Chao, K. J. & Lee, S. (1972). *Acta Cryst.* B**28**, 1662–1665.

Wong, C., Lee, T. Y., Lee, T. J., Chang, T. W. & Liu, C. S. (1973). *Inorg. Nucl. Chem. Lett.* **9**, 667–673.

Acta Cryst. (1979). B**35**, 1074–1081

A Neutron Diffraction Study of the Crystal Structure of Ferrocene*

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(*Received* 14 *October* 1978; *accepted* 21 *November* 1978)

Abstract

The structure of ferrocene has been refined with single-crystal neutron diffraction data measured at temperatures of 173 and 298 K [Fe(η^5-C_5H_5)$_2$, $C_{10}H_{10}Fe$, space group $P2_1/a$, $Z = 2$]. The positions of all H atoms have been varied in the refinements. The cyclopentadienyl ligands are found to be significantly non-planar, with the H atoms displaced toward the Fe atom, in agreement with the results of earlier electron diffraction studies [Bohn & Haaland (1966). *J. Organomet. Chem.* **5**, 470–476; Haaland & Nilsson (1968). *Acta Chem. Scand.* **22**, 2653–2670]. The crystal structure is disordered, as indicated by Willis's original neutron diffraction measurements [Willis (1960). *Acta Cryst.* **13**, 1088; (1961). AERE Report R3708, Harwell, Oxfordshire, England]. In the present work, refinements were carried out by three procedures: (*A*) conventional refinement with anisotropic thermal parameters introduced for all atoms, (*B*) extension of (*A*) to include third- and fourth-order thermal tensors for C and H atoms, and (*C*) refinement with the cyclopentadienyl ligands assumed to occupy two disordered positions. Based upon the results of these refinements and rigid-body-motion analyses of the thermal parameters, it appears that the disorder of the cyclopentadienyl rings results from the presence of molecules in different orientations randomly distributed throughout the crystal. A similar conclusion has been reached from X-ray diffraction data [Seiler & Dunitz (1979). *Acta Cryst.* B**35**, 1068–1074].

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* Research carried out at Brookhaven National Laboratory under contract with the US Department of Energy and supported by its Office of Basic Energy Sciences.

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