Journal of Organometallic Chemistry, 145 (1978) 213—223

CRYSTAL AND MOLECULAR STRUCTURES OF TWO POLYMETHYLFERROCENES: *sym*-OCTAMETHYLFERROCENE AND DECAMETHYLFERROCENE

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(Received September 1st, 1977)

Summary

X-ray structural analysis of *sym*-octamethylferrocene (I) and decamethylferrocene (II) was carried out. Sandwich conformations of I and II are staggered. The steric overcrowding of I is reflected in the deviation of methyl groups from the cyclopentadienyl plane away from the Fe atom and in a "gear mesh" of methyl groups within one ring. Shortened contacts between ligands in the molecule and between molecules in the crystal are absent. Intensive thermal motion precludes an accurate determination of the geometry of II at room temperature. X-ray analysis entirely confirms conclusions concerning the steric hindrance of vicinal methyl groups in *sym*-polymethylferrocenes drawn from results of an NMR study.

Introduction

Investigation of highly alkylated metallocenes has revealed several specific features connected with the "high space factor" within the molecule. The extensively used term "steric overcrowding" one associates with the notion of energetic unfavourability of usual sandwich conformations and the fact that C(Cp)—C(Alk) bond or bonds easily rupture to form less alkylated systems. However this is not always the case. For instance, the molecular ions of deca- and *sym*-octamethylferrocenes are highly stable [1,2]. Evidently, certain compensation effects take place that optimize the conformation and improve stability of the molecule.

The aim of the present work was to verify the conclusions made on the basis of an NMR study of polymethylferrocenes [3]. The NMR investigation revealed that, according to the number of adjacent methyl groups (1, 2 or 3), the ^{13}C and ^{1}H chemical shifts of a methyl group fall precisely into three subgroups, and that upfield shifts of vicinal methyl carbons with increase in the number of CH_3

groups in the molecule exceed by about an order of magnitude $\Delta\delta(C)$ those of the isolated methyl groups.

Interpretation of these findings was based on the hypothesis proposed by Grant et al. [4] about the redistribution of charge density in the vicinity of the nucleus of the spatially perturbed C(Me) atom (see also [5,6]). This hypothesis, however, does not account for all the effects observed and requires an additional assumption about effective shortening of C—H bonds of vicinal CH_3 groups to explain the difference between strong upfield shifts of $C(Me_{vic})$ signals and weak upfield $H(Me_{vic})$ shifts. To verify this assumption it is first of all necessary to confirm the steric hindrance in *sym*-octamethylferrocene (I) and decamethylferrocene (II) molecules and to determine their specific geometrical features.

Experimental

Crystals of I are monoclinic and of II orthorhombic. The X-ray study was carried out with an automatic Syntex $P2_1$ difractometer (Mo-K_α radiation (I) and Cu-K_α radiation (II), graphite monochromator). Crystal data are given in Table 1.

Molecules I and II are in a special position: I is in the center of symmetry, II on the two-fold axis.

Intensities of 3100 (I) and 840 (II) independent reflections were collected by the $\theta/2\theta$ scan technique to $2\theta = 63$(I) and $2\theta = 116°$ (II). Absorption was disregarded. 2611 (I) and 514 (II) reflections with $F^2 \geqslant 2\sigma$ were used for structure solution and refinement. Solution of both structures was carried out by the heavy atom method. In the structure of I all H atoms were located by the difference synthesis.

Least-squares refinement, full matrix anisotropic for Fe and C atoms of I and for Fe atoms of II, and isotropic for H atoms of I and C atoms of II, gave $R_I = 0.044$ ($R_w = 0.043$) and $R_{II} = 0.153$ ($R_w = 0.160$).

After refinement the scatter of C—H bond lengths was rather large (0.77—1.22 Å), and therefore coordinates of H atoms were corrected according to stereochemical considerations. The H(5) atom was placed on an extension of the bisectrix of C(4)C(5)C(1) angle and for methyl H atoms the following procedure was used. H atoms were placed along C—H vectors so that the length of these bonds were equal to 1.08 Å. Assuming that the coordinates of the first H atom

(continued on p. 217)

TABLE 1

CRYSTAL DATA FOR MOLECULES I AND II

	I	II
a (Å)	8.540(1)	11.885(2)
b (Å)	7.833(1)	15.221(2)
c (Å)	12.179(2)	10.000(1)
β (°)	106.98(1)	
V (Å^3)	779.1(1)	1809.0(1)
M	312.26	326.29
d_{meas} (g cm^{-3})		1.20
d_{calc} (g cm^{-3}	1.27	1.20
Z	2	4
Space group	$P2_1/n$	$C222_1$

TABLE 2

COORDINATES (X 10^4) AND PARAMETERS OF ANISOTROPIC TEMPERATURE FACTORS (X 10)[a] OF Fe AND C ATOMS IN MOLECULE I

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0	0	0	24.0(2)	20.0(2)	21.2(2)	−0.3(2)	5.5(1)	1.3(2)
C(1)	1653(3)	−1967(4)	206(2)	32(1)	27(1)	33(1)	6(1)	11(1)	4(1)
C(2)	2045(3)	−914(4)	1202(2)	29(1)	26(1)	29(1)	0(1)	2(1)	4(1)
C(3)	695(3)	−904(4)	1658(2)	38(1)	25(1)	22(1)	2(1)	6(1)	2(1)
C(4)	−566(3)	−1960(4)	944(2)	33(1)	28(1)	31(1)	−1(1)	11(1)	7(1)
C(5)	28(5)	−2616(3)	47(3)	42(1)	20(1)	35(1)	1(1)	8(1)	3(1)
C(6)	2711(6)	−2425(6)	−530(4)	56(2)	50(2)	52(2)	20(2)	30(2)	7(2)
C(7)	3648(4)	−14(7)	1711(4)	33(1)	49(2)	51(2)	−7(2)	−2(1)	3(2)
C(8)	603(6)	−13(7)	2724(3)	70(2)	47(2)	27(1)	8(2)	13(1)	−1(2)
C(9)	−2151(5)	−2386(7)	1166(4)	42(2)	56(2)	53(2)	−9(2)	16(2)	14(2)

[a] Temperature factor $T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$

TABLE 3

COORDINATES ($\times 10^3$) AND ISOTROPIC TEMPERATURE FACTORS ($\times$ 10) OF H ATOMS IN MOLECULE I

Atom	*x*	*y*	*z*	B_{iso} (Å^2)
H(5)	—63(4)	—342(4)	—66(3)	76(8)
	—63	—346	—63	
H(61)	342(6)	—161(6)	—58(4)	92(13)
	344	—141	—74	
H(62)	192(5)	—231(5)	—135(4)	116(14)
	192	292	—133	
H(63)	342(5)	—316(6)	—18(4)	79(11)
	354	—342	—9	
H(71)	457(6)	—70(7)	241(5)	116(12)
	454	—74	236	
H(72)	345(6)	76(7)	237(4)	113(13)
	340	115	211	
H(73)	406(5)	29(7)	121(4)	79(12)
	415	28	102	
H(81)	—68(4)	32(5)	268(3)	61(9)
	—61	23	278	
H(82)	137(8)	91(8)	282(5)	126(15)
	123	120	278	
H(83)	106(5)	—71(6)	332(4)	72(12)
	125	—79	346	
H(91)	—259(5)	—145(6)	181(4)	100(11)
	—259	—135	158	
H(92)	—182(5)	—348(6)	192(4)	95(10)
	—198	—350	171	
H(93)	—269(5)	—231(6)	38(4)	121(16)
	—306	—266	36	

TABLE 4

ATOMIC COORDINATES ($\times 10^3$) AND ISOTROPIC TEMPERATURE FACTORS ($\times$ 10) IN MOLECULE II

Atom	*x*	*y*	*z*	B_{iso} (Å^2)
Fe[a]	0	248(1)	1/4	
C(1)	38(4)	304(3)	75(4)	31(11)
C(2)	113(5)	345(4)	173(6)	91(16)
C(3)	167(2)	266(3)	206(3)	42(9)
C(4)	114(3)	177(2)	149(3)	9(6)
C(5)	30(4)	209(5)	51(5)	45(15)
C(6)	—34(4)	347(3)	—27(4)	34(11)
C(7)	176(3)	419(3)	205(4)	55(12)
C(8)	265(3)	229(3)	309(3)	62(11)
C(9)	134(3)	68(3)	173(4)	43(10)
C(10)	—34(4)	124(3)	13(6)	84(17)

[a] *Parameters of the anisotropic temperature ($\times$ 10) of Fe atom*

B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
42(3)	36(3)	53(3)	0	—5(4)	0

(then of the second and subsequently of the third) of each CH_3 group are correct and that C—H is 1.08 Å and HCH and CCH angles are each 109.5°, the coordinates of the second and third atoms (then of the first and third and, finally, of the first and second) were calculated. The averages between calculated coordinates and those obtained from difference synthesis were then taken. The procedure was repeated to convergence (2—3 iterations). These values are given in the second lines of Table 3 and are used in the calculation of interatomic distances.

Coordinates and temperature factors are given in Tables 2, 3 and 4. All computations were performed on an Eclipse S/200 mini-computer, using EXTL programs.

Unfortunately, due to intensive thermal motion that results in the small number of reflections, the accuracy of results in the case of II is rather low (cf. temperature factors of Fe atom in both structures, Tables 2 and 4). We are planning to repeat the study of this structure at lower temperatures, and meanwhile it is considered here only in general.

Geometry of the molecules

The geometry of I and II is shown in Figs. 1 and 2. In accordance with the special position of the molecules in the crystals (in the case of II axis 2 is practically parallel to the C(1)—C(5) bond of the Cp ring), Cp rings are parallel in both complexes and the sandwiches are staggered (Figs. 3 and 4).

Molecules of I and II are sterically crowded. Indeed, in their ideal models (planar parallel Cp rings, Me groups arranged on the extentions of Cp diagonals) the C· · ·C distances between adjacent methyls of the same ring are 3.19 Å and between the nearest methyls of different rings 3.31 Å for eclipsed and 3.71 Å for staggered conformations. Whereas the normal van der Waals C· · ·C distance between methyls freely rotating about C—C bonds is 4.2 Å [7], while for favour-

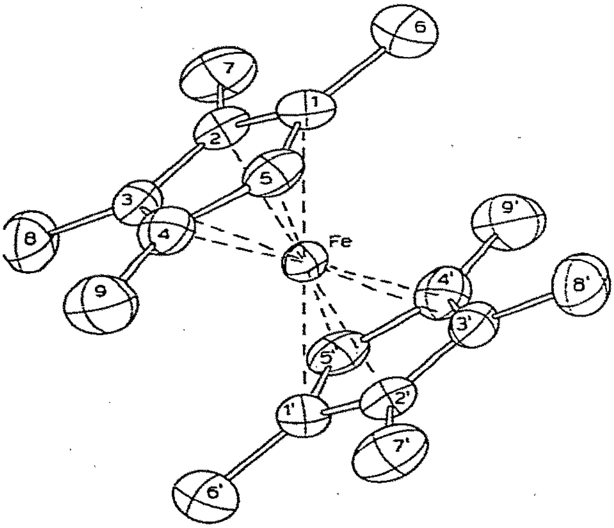

Fig. 1. Geometry of molecule I.

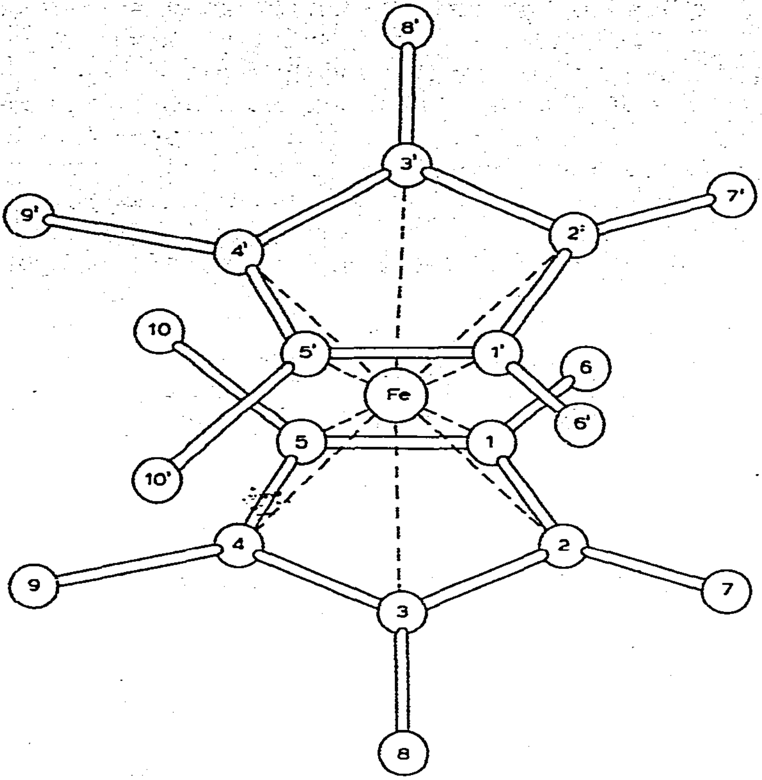

Fig. 2. Geometry of molecule II.

able mutual orientation (H atom of one methyl is located between a pair of H atoms of another CH_3 group) and for coordinated rotation in such an orientation ("engagement of gear wheels") this distance may be reduced to 3.57 Å [8]. Hence the staggered conformations of I and II, in which steric Me· · ·Me interactions between Cp rings are appreciably weakened. However, the Me· · ·Me distances within a Cp ring are independent of the conformation and remain shortened.

Bond lengths in I (Table 5) are in excellent agreement with results of electron diffraction study of ferrocene [9] and with the standard length of the C(sp^2)—C(sp^3) bond [10] (the latter values are given in brackets): Fe—C 2.054(3)

TABLE 5

BOND LENGTHS (*d* (Å)) IN MOLECULE I

Bond	*d*	Bond	*d*	Bond	*d*
Fe—C(1)	2.055(3)	C(1)—C(2)	1.425(4)	C(1)—C(6)	1.490(6)
Fe—C(2)	2.053(3)	C(2)—C(3)	1.418(4)	C(2)—C(7)	1.503(5)
Fe—C(3)	2.056(3)	C(3)—C(4)	1.433(4)	C(3)—C(8)	1.496(5)
Fe—C(4)	2.058(3)	C(4)—C(5)	1.427(5)	C(4)—C(9)	1.494(6)
Fe—C(5)	2.050(2)	C(5)—C(1)	1.437(5)	average	1.496(6)
average	2.054(3)	average	1.428(4)		

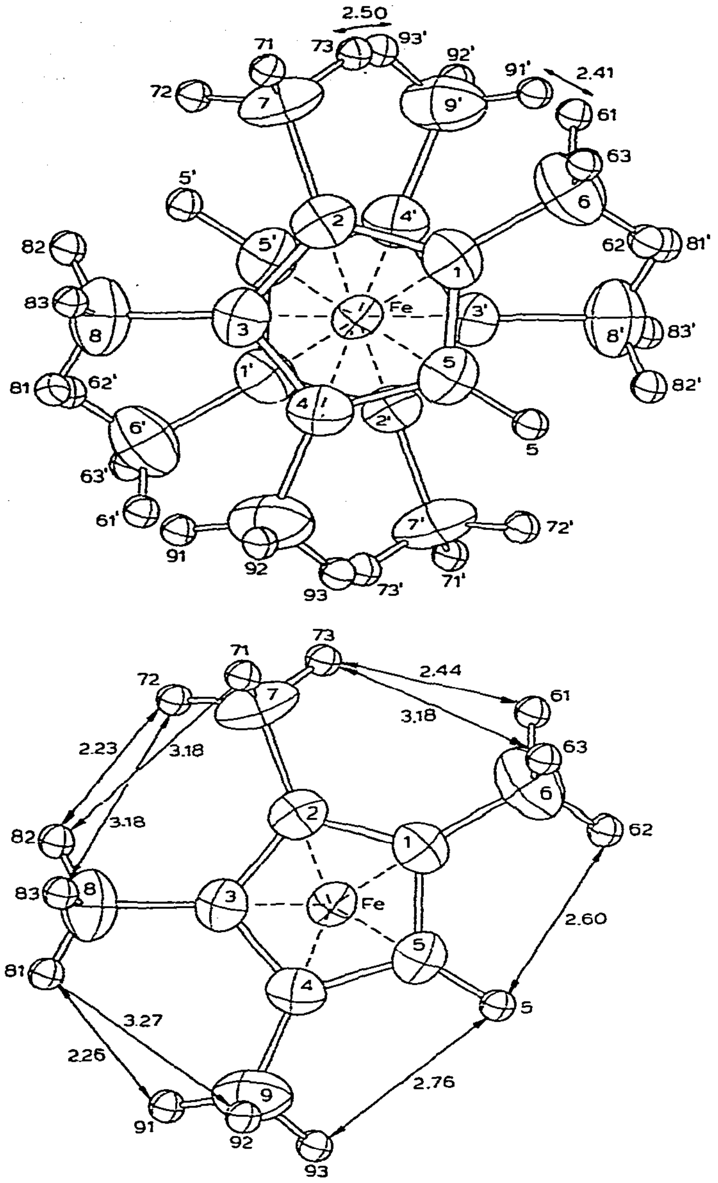

Fig. 3. Projection of molecule I on the plane of the Cp ring: (a) general view; (b) one Cp ring with short H· · ·H distances.

(2.058(2)), C(Cp)—C(Cp) 1.428(4) (1.431(3)), C(Cp)—C(Me) 1.496(6) (1.505(5)) Å. The average lengths in II have close values of 2.08(5), 1.48(4) and 1.55(9) Å, respectively. Bond angles in I (Table 6) have ideal values: CCC in Cp rings 108.0(3)°, exocyclic 126.0(3)°.

The equation of the mean-square plane passing through atoms of the Cp ring of I is

$$-0.2240x + 0.7926y - 0.5672z + 1.6568 = 0$$

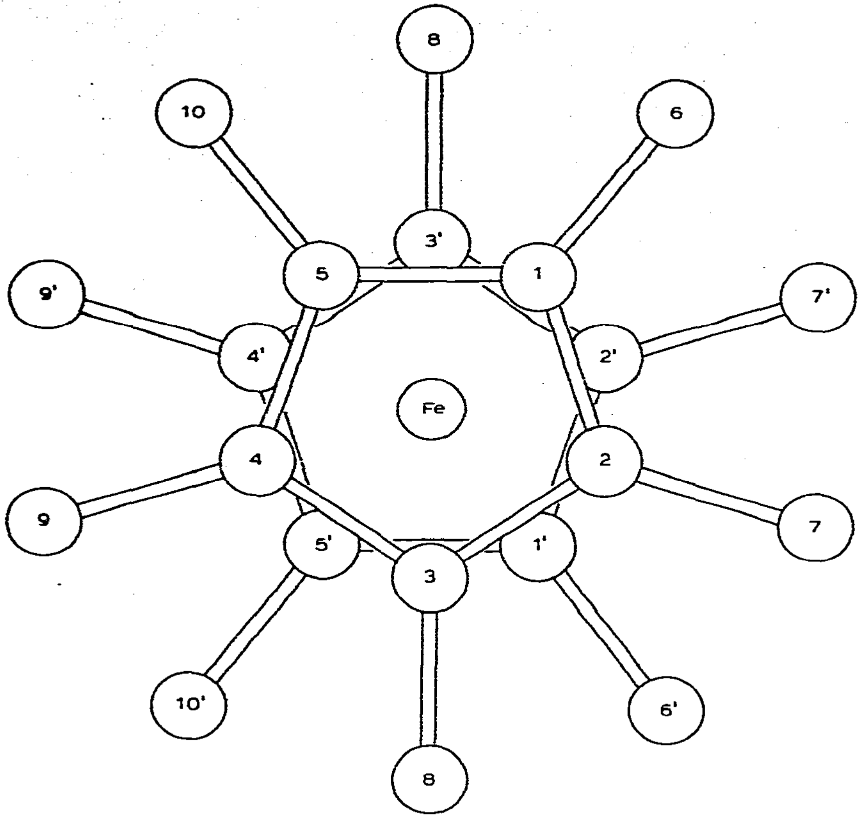

Fig. 4. Projection of molecule II on the plane of the Cp ring.

Deviations from the plane are as follows (Å): C(1), 0.000(3); C(2), 0.000(3); C(3) 0.000(3); C(4), 0.000(3); C(5), 0.000(3); Fe, 1.6568(8), C(6), −0.059(5); C(7), −0.043(5); C(8), −0.049(5); C(9), −0.090(5).

Thus, the Cp ring is strictly planar with methyl carbons 0.043—0.090 Å out of plane, inclined away from the Fe atom. The angles between the C(Cp)—C(Me) bonds and the Cp plane are C(1)—C(6) 3.4, C(2)—C(7) 2.4, C(3)—C(8) 2.7, and C(4)—C(9) 5.1°.

TABLE 6

BOND ANGLES (°) IN MOLECULE I

Angle		Angle	
C(1)C(2)C(3)	108.7(2)	C(6)C(1)C(5)	124.4(3)
C(2)C(3)C(4)	108.2(2)	C(6)C(1)C(2)	128.2(3)
C(3)C(4)C(5)	107.5(3)	C(7)C(2)C(1)	125.6(3)
C(4)C(5)C(1)	108.3(3)	C(7)C(2)C(3)	125.7(3)
C(5)C(1)C(2)	107.3(3)	C(8)C(3)C(2)	126.6(3)
Average	108.0(3)	C(8)C(3)C(4)	125.1(3)
		C(9)C(4)C(5)	127.0(3)
		C(9)C(4)C(3)	125.4(0)
		Average	126.0(3)

TABLE 7

SOME INTRAMOLECULAR C···C, C···H AND H···H DISTANCES, *d* (Å), IN MOLECULE I

Distance	*d*	Distance	*d*	Distance	*d*
C(6)···C(7)	3.22	C(6)···H(73)	2.86	H(71)···H(82)	3.38
C(7)···C(8)	3.19	C(7)···H(82)	2.90	H(72)···H(82)	2.23
C(8)···C(9)	3.16	C(8)···H(72)	2.85	H(72)···H(83)	3.18
C(6)···C(8)	3.79	C(8)···H(91)	2.87	H(81)···H(91)	2.26
C(6)···C(9)	3.85	C(9)···H(81)	2.88	H(81)···H(92)	3.27
C(7)···C(9)	3.85	H(5)···H(62)	2.60	H(61)···H(91)	2.41
C(6)···H(5)	2.93	H(5)···H(93)	2.76	H(61)···H(93)	3.25
C(9)···H(5)	2.98	H(61)···H(73)	2.44	H(73)···H(93)	2.50
		H(63)···H(73)	3.18	H(73)···H(91)	3.17

In the molecule of $C_5(CH_3)_5Fe(CO)_2SO_2CH_2{-}CH{=}CHC_6H_5$ [11], which also has a pentamethylcyclopentadienyl ligand, similar deviations of methyls from the Cp ring, away from the Fe atom are observed (deviations range from 0.025 to 0.191 Å). Among ferrocenes with a smaller number of substituents $(C_5H_4CH_3)_2FeI_3$ (with one substituent in each ring) [12] and $[C_5H_3(t\text{-}C_4H_9)_2]Fe$ (with two substituents in each ring in the 1,3 positions) [13] should be mentioned. In both molecules the atoms of substituents bonded to the Cp rings are in the Cp plane, but the presence of substituents distorts the parallelity of the rings (dihedral angles of 6.6 and 7°, respectively).

In the cation of bis(1,3-dimethylindenyl)iron (III) [14], which may also be considered as an octasubstituted ferrocene, the mutual orientation of the five-membered rings is closer to a staggered conformation ($\varphi = 21.7°$) and three of the four Me groups are also out of plane, inclined away from the Fe atom. However, a more detailed comparison of the geometry of I and III would not be correct, since indenyl ligands in III are nonplanar and deviations of C atoms of the bicyclic ligand from its mean plane are comparable with deviations of Me groups.

The short distances between nonbonded atoms of I are given in Table 7 (see also Figs. 1 and 3). As can be seen, the above-mentioned deviations of Me groups from Cp planes naturally do not affect the C···C distances between Me groups of the same ring, which are close (3.16—3.22 Å) to the ideal value of 3.19 Å. The latter value approachs the boundary of 3.17 Å between "normally shortened" and "strongly shortened" van der Waals C···C contacts [15]. On the contrary, C···C distances between methyls of different Cp rings are increased to 3.79—3.85 Å against the ideal value of 3.71 Å.

Mutual rotations of methyls about C(Cp)—C(Me) bonds are such that the shortest C···C distances between adjacent Me groups of the same Cp ring are 2.85—2.90 Å, i.e. even greater than the normal van der Waals distance of 2.82 Å [15]. The shortest H···H distances between adjacent methyls are 2.23—2.44 Å, whereas the "normal" value is 2.31 Å and the "normally shortened" distance 2.01 Å [15]*. At the same time for the most unfavourable orientation of adja-

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* The shortest H···H distance between Me groups of different Cp rings is slightly greater (2.41 and 2.50 Å).

cent methyls (two H atoms maximally close to each other the H· · ·H distance would have been reduced to 1.97 Å. Hence, Me groups are indeed in a "gear mesh", the distance between a "tooth" of one gear wheel and two "teeth" of another differing considerably; for instance, H(72)· · ·H(82) 2.23 and H(72)· · · H(83) 3.18 Å; H(81)· · ·H(91) 2.26 and H(81)· · ·H(92) 3.27 Å (see Table 7 and Fig. 3). Therefore, there are only two slightly shortened H· · ·H distances between adjacent Me groups in each Cp ring. The H(5) and H(5′) atoms of Cp rings do not have short intramolecular contacts.

Intermolecular contacts in crystals of I and II are usual.

As can be seen from Fig. 3, thermal vibrations of the Fe atom are isotropic, the Cp ring undergoes in-plane tilting vibrations with a small amplitude, while the amplitude of tangential vibrations of the Me groups is nearly twice as large.

Conclusion

The present X-ray study established that optimization of the geometry of polymethylferrocenes I and II is realized through minimal distortions of the ideal model. The planar parallel five-membered rings of the ferrocene system retain the possibility of unhindered free rotation in solution. All deviations from the ideal structure are associated with methyl groups within a ring. These facts once again emphasize the energetical favourability of the ferrocene system.

As for methyl groups, free rotation, independent of adjacent methyls in the same ring is inhibited. This undoubtedly enhances conformational barriers and is reflected in the redistribution of charge density about the C(Me) nucleus. On the other hand, the rate of rotation of the "system of methyl gear wheels" is sufficiently high to ensure that H(Me) signals of each CH_3 group are represented by singlets in the ^1H NMR spectrum. A priori one would expect deviations of C(7) and C(8) from the Cp plane to be the highest since they are the most sterically hindered. However, C(6) and C(9) exhibit maximal deviation and the unequal distances between "teeth" of adjacent methyl "gear wheels" ensure a minimal number of short H· · ·H contacts in the molecule (there are only two, 2.23 and 2.26 Å long, the normal distance being 2.31 Å).

Although not one of these rearrangements can remove the short C(Me)· · · C(Me) contacts, which are revealed in the strong upfield shifts of ^{13}C NMR signals, the general reduction of steric overcrowding is reflected in the possibility of the free rotation of rings and in the almost complete absence of H· · ·H contacts. The latter may presumably be associated with the observed trend of effective shortening of C(Me)—H bonds. In terms of NMR analysis such shortening means reduction of withdrawal of a C(Me)—H electron density towards an H nucleus and an increase of the δ(C(Me)) shielding constant not only as a result of redistribution of charge density about the C(Me) nucleus, but also due to its general increase.

It would be interesting to determine the variation of Fe—C(Cp), C(Cp)—C(Cp) and C(Cp)—C(Me) bond lengths in the $(Me_nC_5H_{5-n})_2M$ series with $n \to 5$ and for different M. We are planning to extend research in this direction to include compounds with M = Fe^{3+} and Co^{3+} and also to repeat the X-ray study of II at lower temperatures.

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