

X-Ray Studies on Constrained Ferrocene Derivatives. Part I. Crystal Structure of 1,12-Dimethyl[1,1]Ferrocenophane (1,1'' : 1',1'''-Diethylidenediferrocene)

By James S. McKechnie, Carol A. Maier, Bruce Bersted, and Iain C. Paul,* W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801

The crystal and molecular structure of the title compound has been determined by X-ray diffraction methods. Crystals are monoclinic with $a = 18.14(3)$, $b = 6.10(2)$, $c = 18.67(3)$ Å, $\beta = 119^\circ 40'(10')$, space group $P2_1/c$, and $Z = 4$; each molecule has C_2 crystallographic symmetry. The structure was refined to R 0.083 on 1765 non-zero structure amplitudes collected photographically. The molecules exist in the eclipsed-form with an *exo*-methyl configuration. The cyclopentadienyl rings bonded to one iron atom are twisted with respect to each other by 21.5 and 23.9° in the two independent molecules, while the angle of tilt between such rings is slight (2 – 3°). There are dihedral angles of $30^\circ 10'$ and $31^\circ 28'$ between cyclopentadienyl rings in the same ligand in the two molecules. There is considerable geometric evidence that the molecular conformation is dictated by intramolecular $H \cdots H$ contacts, both within ligands and between ligands. The $Fe \cdots Fe$ distances are $4.620(2)$ and $4.595(2)$ Å.

CRYSTALLOGRAPHIC measurements have revealed that the two cyclopentadienyl rings in ferrocene and ferrocene derivatives can take up many different relative orientations. These orientations can be described by an angle of twist, defined as the mean of the angles of projection made by a carbon in one ring to the nearest carbon in the second ring, viewed down the line joining the centres of mass of the two rings (*i.e.* the angle α in Figure 1), and an angle of tilt, which is the angle be-

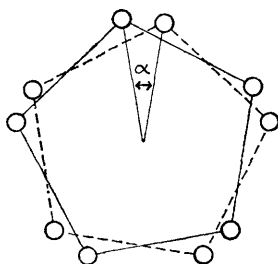


FIGURE 1 The angle of twist (α) between two cyclopentadienyl rings in a ferrocene unit

tween the normals to the best planes through the two rings. While the cyclopentadienyl rings are staggered by 36° in crystalline ferrocene,¹ very small angles of twist are reported for 1,1'-diacetylferrocene² and ferrocene-1,1'-dicarboxylic acid.³ Large angles of tilt have been found in molecules such as 1,1'-tetramethylethylenferrocene,⁴ in α -oxo-1,1'-trimethylenferrocene,⁵ and in 1,1',3,3'-bis(trimethylene)ferrocene,⁶ where the cyclopentadienyl rings are bridged by two- or three-carbon chains. Some molecules with two 'ferrocene units' have been studied crystallographically. These include biferrocenyl (I),^{7,8} and biferrocenyl ketone

(II),⁹ where angles of twist of 16 – 17° and 5° , respectively, have been found but with very small angles of tilt, and bis(fulvaleneiron) (III),¹⁰ and bis(*asym*-indacenyliron) (IV),¹¹ where the angles of twist are constrained to values close to zero.

The synthesis of 1,12-dimethyl[1,1]ferrocenophane (V) † has been reported.¹² The 1H n.m.r. spectrum of (V) was interpreted in terms of an *exo*-methyl configuration, and, on the basis of non-bonded interactions between methine hydrogens, the *gauche* geometry (VI) was preferred to the eclipsed form (VII).¹² We have carried out a single-crystal X-ray analysis on (V) in order to check these assignments and to provide structural information on an example of a [1,1]-ferrocenophane molecule. A preliminary account of this work has been published.¹³ The chemistry of ferrocenophanes has recently been reviewed.¹⁴

EXPERIMENTAL

A sample of (V) was recrystallized from light petroleum (b.p. 60 – $80^\circ C$) as orange prisms elongated along the b axis, in which direction the cross-section is rhomboidal, with the corners of the crystal along the major diagonal often truncated. The lengths of the major and minor diagonals were 0.22 and 0.12 mm. The two well-developed faces parallel to b were identified as (001) and (100).

Crystal Data.— $C_{24}H_{24}Fe_2$, $M = 424.2$. Monoclinic, $a = 18.14(3)$, $b = 6.10(2)$, $c = 18.67(3)$ Å, $\beta = 119^\circ 40'(10')$, $U = 1795 \times 10^{-24}$ cm³, $D_m = 1.51$, $Z = 4$, $D_c = 1.57$. Space group $P2_1/c$ or Pc from systematic absences: $h0l$, when $l = 2n + 1$. Cell data were obtained from precession photographs (Mo- K_α , $\lambda = 0.7107$ Å).

Data were obtained by the equi-inclination Weissenberg method, by use of Co- K_α radiation ($\lambda = 1.790$ Å). In-

⁸ Z. L. Kaluski, Y. T. Struchkov, and R. L. Avoyan, *Zhur. strukt. Khim.*, 1964, **5**, 743; *J. Struct. Chem. (USSR)*, 1964, **5**, 683.

⁹ J. Trotter and A. C. MacDonald, *Acta Cryst.*, 1966, **21**, 359.

¹⁰ M. R. Churchill and J. Wormald, *Inorg. Chem.*, 1969, **8**, 1970.

¹¹ R. Gitany, I. C. Paul, N. Acton, and T. J. Katz, *Tetrahedron Letters*, 1970, 2723.

¹² W. E. Watts, *J. Amer. Chem. Soc.*, 1966, **88**, 855; T. H. Barr, H. L. Lentzer, and W. E. Watts, *Tetrahedron*, 1969, **25**, 6001.

¹³ J. S. McKechnie, B. Bersted, I. C. Paul, and W. E. Watts, *J. Organometallic Chem.*, 1967, **8**, P. 29.

¹⁴ W. E. Watts, *Organometallic Chem. Rev.*, 1967, **2**, 231.

† 1,1'' : 1',1'''-diethylidenediferrocene.

¹ J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Cryst.*, 1956, **9**, 373.

² G. J. Palenik, *Inorg. Chem.*, 1970, **9**, 2424.

³ G. J. Palenik, *Inorg. Chem.*, 1969, **8**, 2744.

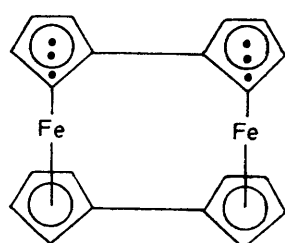
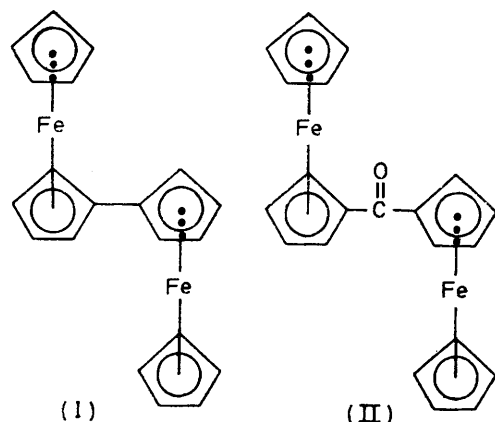
⁴ M. Burke Laing and K. N. Trueblood, *Acta Cryst.*, 1965, **19**, 373.

⁵ N. D. Jones, R. E. Marsh, and J. H. Richards, *Acta Cryst.*, 1965, **19**, 330.

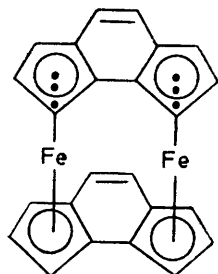
⁶ I. C. Paul, *Chem. Comm.*, 1966, 377.

⁷ A. C. MacDonald and J. Trotter, *Acta Cryst.*, 1964, **17**, 872.

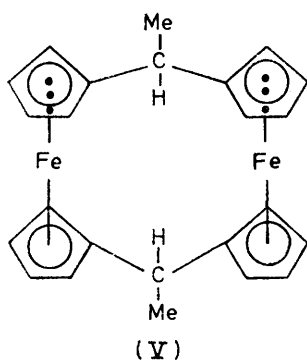
tensities were estimated visually by comparison with a calibrated strip. The levels $h0-4l$ were measured, giving a total of 1765 independent non-zero intensities. The data were corrected for Lorentz and polarization factors, and



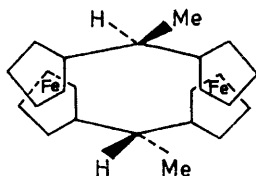
(III)



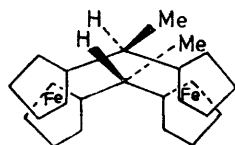
(IV)



(V)



(VI)



(VII)

spot-shape variation, but not for absorption [$\mu(\text{Co-K}\alpha) = 29.4 \text{ cm}^{-1}$]. The separate layers of data were initially placed on the same relative scale by correlation of exposure times.

Structure Analysis.—An initial assumption that the space group was $P2_1/c$ did not provide an explanation for the large number of peaks on the $P(u, 0, w)$ section of the Patterson map, nor did it account satisfactorily for the

single large peak in a general position on the $P(u, \frac{1}{2}, w)$ section. A careful re-examination of the precession photographs led us to consider the space group to be either $P2/c$ or Pc . The latter space group would require two crystallographically independent ferrocenophane molecules and four independent iron atoms in the asymmetric unit. We could find no evidence to support such an arrangement, while many of the larger peaks could be explained if

TABLE I

Final positional parameters, in fractions of the unit cell edge with standard deviations in parentheses

	x	y	z
Fe(1)	0.11332(10)	0.0494(3)	0.88295(9)
C(1)	0.0760(6)	0.258(2)	0.7117(5)
C(2)	0.1239(5)	0.099(2)	0.7801(5)
C(3)	0.1992(5)	0.164(2)	0.8536(5)
C(4)	0.2330(6)	-0.022(2)	0.9061(6)
C(5)	0.1766(7)	-0.196(2)	0.8648(6)
C(6)	0.1116(6)	-0.123(2)	0.7898(6)
C(7)	0.0143(6)	-0.038(2)	0.9017(5)
C(8)	0.0918(7)	-0.034(3)	0.9773(5)
C(9)	0.1261(7)	0.182(3)	0.9879(6)
C(10)	0.0689(7)	0.306(2)	0.9184(7)
C(11)	0.0023(6)	0.174(1)	0.8652(5)
C(23)	0.1358(6)	0.356(2)	0.6825(6)
Fe(1')	0.59819(9)	0.2378(3)	0.20627(9)
C(1')	0.4111(5)	0.446(2)	0.1406(5)
C(2')	0.4811(5)	0.357(2)	0.1279(4)
C(3')	0.5451(6)	0.501(2)	0.1303(5)
C(4')	0.5948(7)	0.376(2)	0.1060(7)
C(5')	0.5608(7)	0.177(3)	0.0858(6)
C(6')	0.4905(6)	0.156(2)	0.0998(5)
C(7')	0.6112(6)	0.064(2)	0.3043(5)
C(8')	0.6689(6)	-0.014(2)	0.2796(5)
C(9')	0.7213(5)	0.162(2)	0.2842(5)
C(10')	0.6967(5)	0.345(2)	0.3130(5)
C(11')	0.6285(4)	0.284(2)	0.3258(5)
C(23')	0.3416(6)	0.540(2)	0.0574(5)
H(1)	0.051(5)	0.42(2)	0.733(5)
H(3)	0.223(6)	0.30(2)	0.859(6)
H(4)	0.285(6)	-0.05(2)	0.966(6)
H(5)	0.187(6)	-0.30(2)	0.902(6)
H(6)	0.074(6)	-0.23(2)	0.774(6)
H(7)	-0.016(6)	-0.17(2)	0.878(6)
H(8)	0.131(5)	-0.14(2)	1.031(6)
H(9)	0.165(6)	0.24(2)	1.040(6)
H(10)	0.087(6)	0.43(2)	0.912(6)
H(23a)	0.181(6)	0.45(2)	0.729(6)
H(23b)	0.105(3)	0.46(2)	0.625(6)
H(23c)	0.153(6)	0.20(2)	0.662(6)
H(1')	0.421(6)	0.60(2)	0.158(6)
H(3')	0.520(6)	0.68(2)	0.125(5)
H(4')	0.654(6)	0.41(2)	0.111(5)
H(5')	0.576(7)	0.06(2)	0.084(7)
H(6')	0.449(6)	0.03(2)	0.078(6)
H(7')	0.564(6)	-0.02(2)	0.296(6)
H(8')	0.677(6)	-0.12(2)	0.258(6)
H(9')	0.761(6)	0.13(2)	0.262(6)
H(10')	0.719(6)	0.48(2)	0.311(6)
H(23a')	0.316(6)	0.39(2)	0.020(6)
H(23b')	0.306(6)	0.62(2)	0.073(6)
H(23c')	0.356(5)	0.67(2)	0.029(6)

$P2/c$ were the true space group. A detailed study of the Patterson map indicated that we were dealing, not with one independent ferrocenophane molecule, but with two independent ferrocenophane 'half-molecules,' each ferrocenophane molecule having C_2 crystallographic symmetry.

The positions of the two independent iron atoms were obtained by the identification of the $\text{Fe} \cdots \text{Fe}$ vectors in the Patterson map. An electron-density map, based on the signs of the contribution of the iron atoms to the calculated structure factors, allowed the positions of all the carbon atoms to be determined. Inclusion of all the iron

TABLE 2
Final thermal parameters with standard deviations in parentheses *

	b_{11} ($\times 10^4$)	b_{22} ($\times 10^3$)	b_{33} ($\times 10^4$)	b_{12} ($\times 10^3$)	b_{13} ($\times 10^4$)	b_{23} ($\times 10^3$)
Fe(1)	29(1)	20(1)	18(1)	1(1)	22(1)	0(1)
C(1)	36(4)	4(4)	22(3)	-3(3)	37(6)	-1(2)
C(2)	23(3)	8(4)	22(3)	2(2)	26(6)	1(2)
C(3)	28(4)	10(4)	36(4)	-3(2)	33(7)	-1(2)
C(4)	36(4)	30(5)	33(4)	5(2)	34(8)	2(2)
C(5)	47(5)	17(5)	35(4)	8(3)	41(8)	7(2)
C(6)	34(4)	3(4)	35(4)	2(2)	44(7)	2(2)
C(7)	47(5)	15(4)	28(4)	1(2)	49(7)	2(2)
C(8)	55(6)	54(7)	16(4)	9(3)	30(8)	7(3)
C(9)	46(5)	57(7)	19(4)	-1(3)	6(8)	-11(3)
C(10)	46(5)	30(5)	42(5)	-9(3)	57(9)	-15(3)
C(11)	33(4)	5(4)	22(3)	-1(2)	30(6)	-5(2)
C(23)	40(4)	17(4)	38(4)	-2(2)	49(8)	6(2)
Fe(1')	27(1)	16(1)	15(1)	0(1)	22(1)	-1.8(3)
C(1')	32(4)	-6(3)	21(3)	1(2)	25(6)	3(1)
C(2')	27(4)	12(3)	13(2)	0(2)	19(5)	2(2)
C(3')	36(4)	26(2)	22(3)	2(2)	30(7)	6(2)
C(4')	47(5)	32(5)	40(5)	-2(3)	61(9)	1(3)
C(5')	40(5)	44(8)	29(4)	5(3)	38(8)	-5(3)
C(6')	36(4)	21(4)	18(3)	-1(2)	30(6)	-5(2)
C(7')	35(4)	3(4)	32(4)	1(2)	36(7)	0(2)
C(8')	36(4)	6(4)	32(4)	5(2)	27(7)	-2(2)
C(9')	33(4)	15(4)	25(3)	1(2)	28(6)	-1(2)
C(10')	24(4)	16(4)	21(3)	-1(2)	22(6)	1(2)
C(11')	23(3)	1(4)	19(3)	0(3)	11(5)	2(2)
C(23')	44(5)	23(5)	23(4)	4(2)	33(7)	8(2)

* All hydrogen atoms were given a B_0 of 4.0 \AA^2 . Thermal parameters are expressed as $\exp -[b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl]$.

and carbon atoms in a structure-factor calculation, gave R 0.27. A cycle of full-matrix least-squares refinement on

on all the atoms other than hydrogen gave R 0.15. The weighting scheme had $\sqrt{w} = |F_o|/26.9$, when $|F_o| < 26.9$, $\sqrt{w} = 26.9/|F_o|$, when $|F_o| \geq 26.9$, and the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. Before further refinement, the scale factors of the individual hkl layers of data were adjusted so that $k_n \Sigma |F_o| = \Sigma |F_c|$ for each layer. Refinement of positional and anisotropic thermal parameters for the two iron atoms, and positional and isotropic thermal parameters for the carbon atoms gave R 0.11. The positions of the twenty-four hydrogen atoms were obtained from a three-dimensional difference-Fourier map. Least-squares refinement of the positional parameters of the hydrogen atoms as well as the positional and anisotropic thermal parameters for the non-hydrogen atoms gave a final R of 0.083 on the 1765 observed data. The final weighted factor R' was 0.092 $\{R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}\}$. In the final least-squares refinement, the isotropic thermal parameters for the hydrogen atoms were held constant at 4 \AA^2 . In the refinements involving the hydrogen atoms it was necessary to refine each 'molecule' separately owing to computer storage limitations.

The final values for the positional and thermal parameters are given in Tables 1 and 2. The final values of the observed and calculated structure factors are listed in Supplementary Publication No. SUP 20492 (3 pp., 1 microfiche).^{*} The scattering factors for iron(II) and carbon were taken from ref. 15 with a correction for the real component of anomalous dispersion for iron from ref. 16; the scattering curve for hydrogen was taken from ref. 17.

The anisotropic temperature factor for C(1') is not positive definite.[†] This is probably due to the presence

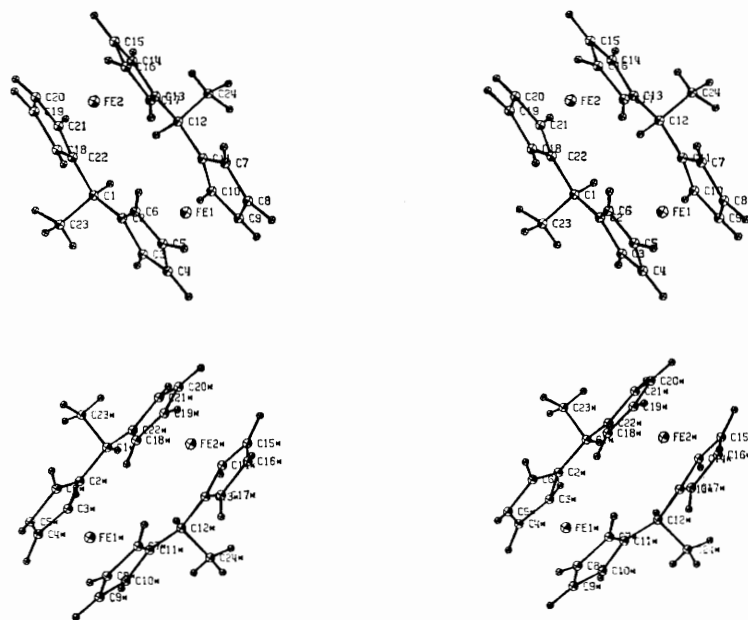


FIGURE 2 Stereoscopic views of the two molecules of (V); (a) molecule (1), (b) molecule (2)

the positional and isotropic temperature parameters of the iron atoms, followed by two cycles of similar refinement

* See note about Supplementary Publications in Notice to Authors No. 7, in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

† A refinement with the temperature factor for C(1') isotropic gave a B_0 value of 1.7 \AA^2 and resulted in values of R and R' of 0.084 and 0.093. No significant changes in molecular dimensions occurred.

in the data of some systematic errors which are, however, unlikely to cause serious errors in the positional parameters.

¹⁵ 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 201-212.

¹⁶ R. W. James, in 'The Optical Principles of the Diffraction of X-Rays,' Bell, London, 1962, pp. 135-192, 608-610.

¹⁷ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

RESULTS AND DISCUSSION

The results of the analysis confirm the *exo*-methyl configuration as suggested by Watts,¹² but show that the molecules exist in the eclipsed rather than the expected *gauche* form. The two crystallographically independent 'half molecules' crystallize with C_2 symmetry and stereoscopic pictures of the two molecules [hereafter referred to as molecule (1), unprimed, and molecule (2), primed] are shown in Figure 2. There is a very similar geometrical arrangement in the two independent molecules. Figure 3 shows the atom numbering used

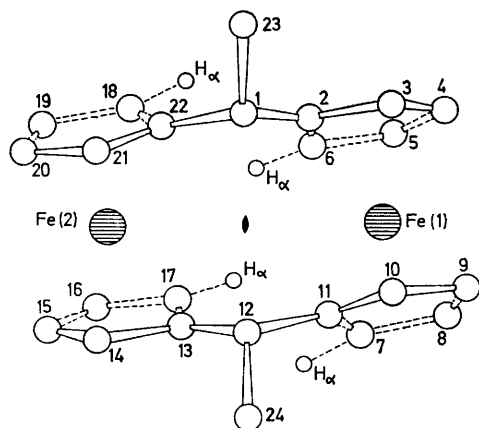


FIGURE 3 A single molecule of (V) viewed along the b axis and showing the α -protons which determine the molecular conformation

TABLE 3

Bond lengths (\AA) with standard deviations in parentheses *

	Molecule (1)	Molecule (2)
Fe...C(2)	2.046(9)	2.025(11)
Fe...C(3)	2.015(9)	2.039(12)
Fe...C(4)	2.040(13)	2.027(13)
Fe...C(5)	2.014(12)	2.036(14)
Fe...C(6)	2.019(11)	2.042(13)
Fe...C(7)	2.062(11)	2.024(11)
Fe...C(8)	2.048(11)	2.036(12)
Fe...C(9)	2.022(13)	2.025(13)
Fe...C(10)	2.014(12)	2.018(12)
Fe...C(11)	2.020(11)	2.037(10)
C(1)-C(2)	1.493(13)	1.504(13)
C(1)-C(23)	1.554(15)	1.545(15)
C(1)-C(22)	1.526(14)	1.528(13)
C(2)-C(3)	1.432(13)	1.437(14)
C(2)-C(6)	1.399(15)	1.377(14)
C(3)-C(4)	1.427(16)	1.413(17)
C(4)-C(5)	1.407(17)	1.330(22)
C(5)-C(6)	1.384(16)	1.428(17)
C(7)-C(8)	1.416(16)	1.420(15)
C(7)-C(11)	1.426(14)	1.390(14)
C(8)-C(9)	1.424(23)	1.407(15)
C(9)-C(10)	1.414(19)	1.407(15)
C(10)-C(11)	1.380(16)	1.423(13)

* C-H distances are 0.77—1.23(10) \AA .

in the analysis. Bond distances (uncorrected for thermal librations) and angles in the two molecules are given in Tables 3 and 4. The estimated standard deviations for Fe-C bonds are 0.009—0.014, for C-C bonds 0.013—0.023 \AA , and for the C-C-C angles 0.6—1.2°. The dimensions found in the molecules are in fairly close

agreement. The mean C-C bond distance in the four crystallographically independent cyclopentadienyl rings is 1.407 ± 0.025 \AA , while the mean internal C-C-C angle in a ring is $108.0 \pm 1.3^\circ$. The mean bond length agrees well with that found in ferrocene (1.40 \AA),¹ but is slightly shorter than those found in ferrocene

TABLE 4

Bond angles (deg.) * with standard deviations in parentheses

	Molecule (1)	Molecule (2)
C(2)-C(1)-C(22)	117.5(8)	115.8(9)
C(2)-C(1)-C(23)	109.7(9)	108.0(7)
C(22)-C(1)-C(23)	106.6(6)	109.7(9)
C(1)-C(2)-C(3)	121.0(8)	120.4(7)
C(1)-C(2)-C(6)	132.6(6)	131.0(7)
C(3)-C(2)-C(6)	106.3(6)	107.7(7)
C(2)-C(3)-C(4)	108.7(9)	107.2(7)
C(3)-C(4)-C(5)	105.9(8)	107.5(8)
C(4)-C(5)-C(6)	109.7(1.2)	111.2(1.2)
C(2)-C(6)-C(5)	109.4(1.0)	106.2(7)
C(8)-C(7)-C(11)	107.5(7)	108.8(9)
C(7)-C(8)-C(9)	107.8(9)	107.8(7)
C(8)-C(9)-C(10)	107.1(8)	107.5(6)
C(9)-C(10)-C(11)	109.4(1.2)	108.7(8)
C(7)-C(11)-C(10)	108.2(8)	107.2(6)
C(7)-C(11)-C(12)	127.3(8)	131.2(6)
C(10)-C(11)-C(12)	123.8(9)	121.6(8)

* External C-C-H angles are 107—145°, σ 5—8°.

TABLE 5

Details of some best planes in the structure ^a

	Molecule (1)	Molecule (2)
C(1)	0.045	0.190
C(2)	0.007	-0.007
C(3)	-0.010	0.014
C(4)	0.009	-0.022
C(5)	-0.001	0.014
C(6)	-0.006	0.001
C(7)	-0.009	0.008
C(8)	0.006	-0.007
C(9)	0.005	0.004
C(10)	-0.011	0.001
C(11)	0.009	-0.004
C(12)	-0.149	-0.047
C(13)	0.436	-0.086
C(22)	0.097	-0.432
C(23)	1.282	1.709
C(24)	-1.673	-1.277
Fe(1)	-1.634	-1.650
χ^2	2.3	8.8
P^b	>0.10	>0.10
		~ 0.025
		~ 0.5

^a Distances involving atoms included in the plane calculation are italicized. ^b The probability (P) that the distances of the atoms from the best plane form a normal distribution.

derivatives where bridging groups link the two rings (1.42 and 1.44 \AA) of a single 'ferrocene-unit'.^{4,5} Librational motion will cause an apparent shortening of the C-C bonds and the magnitude of this effect will be greatest in ferrocene where there is less intramolecular constraint (there is considerable evidence to indicate that the barrier to rotation in gaseous ferrocene is very low¹⁸).

The details of some best planes in the structure are given in Table 5, while Table 6 lists some important

¹⁸ E. A. Seibold and L. E. Sutton, *J. Chem. Phys.*, 1955, **23**, 1967; R. K. Bohn and A. Haaland, *J. Organometallic Chem.*, 1966, **5**, 470; A. Haaland and J. E. Nilsson, *Chem. Comm.*, 1968, 88; *Acta Chem. Scand.*, 1968, **22**, 2653; A. Haaland, *ibid.*, 1969, **23**, 1836.

intramolecular contacts. Within the accuracy of the analysis, the five atoms in each of the five-membered

TABLE 6
Important intramolecular contacts (Å) in the two molecules

	Molecule (1)	Molecule (2)
C(6) ··· C(7)	3·374(15)	3·377(14)
C(5) ··· C(8)	3·310(17)	3·358(17)
C(4) ··· C(9)	3·250(18)	3·239(16)
C(3) ··· C(10)	3·258(16)	3·288(14)
C(2) ··· C(11)	3·328(14)	3·350(12)
H(6) ··· H(17)	2·37(16)	
H(7) ··· H(17)	2·53(16)	
H(7') ··· (H18')	2·08(15)	
H(7') ··· H(17')	2·51(15)	
H(1) ··· H(12)	2·23(14)	3·20(15)

rings are coplanar. The iron atoms lie from 1·634' to 1·650 Å from these planes. In both molecules, there is a

the closest C(ring) ··· C(ring) contacts in a 'ferrocene-unit' are between C(3) and C(10) and between C(4) and C(9) in both molecules; the longest distance is between C(6) and C(7).

There are also large dihedral angles between the two cyclopentadienyl rings of the same organic ligand. In molecule (1), this angle is 30° 10', while in molecule (2) it is 31° 28'. There is an angle of 30° 47' between the two rings attached to the carbonyl group in biferrrocenyl ketone.⁹ Such large angles are probably dictated by interactions between the α -protons (Figure 3) on the cyclopentadienyl rings [*e.g.*, H(6) ··· H(18)].

The cyclopentadienyl rings in each of the two crystallographically independent 'ferrocene units' are also twisted or rotated with respect to each other; in molecule (1) the mean C-(centre of mass of ring 1)-(centre of mass of ring 2)-C projection angle is 21·5° while that in molecule (2) is 23·9°. Churchill and Wormald¹⁹ have compiled a Table showing the angles

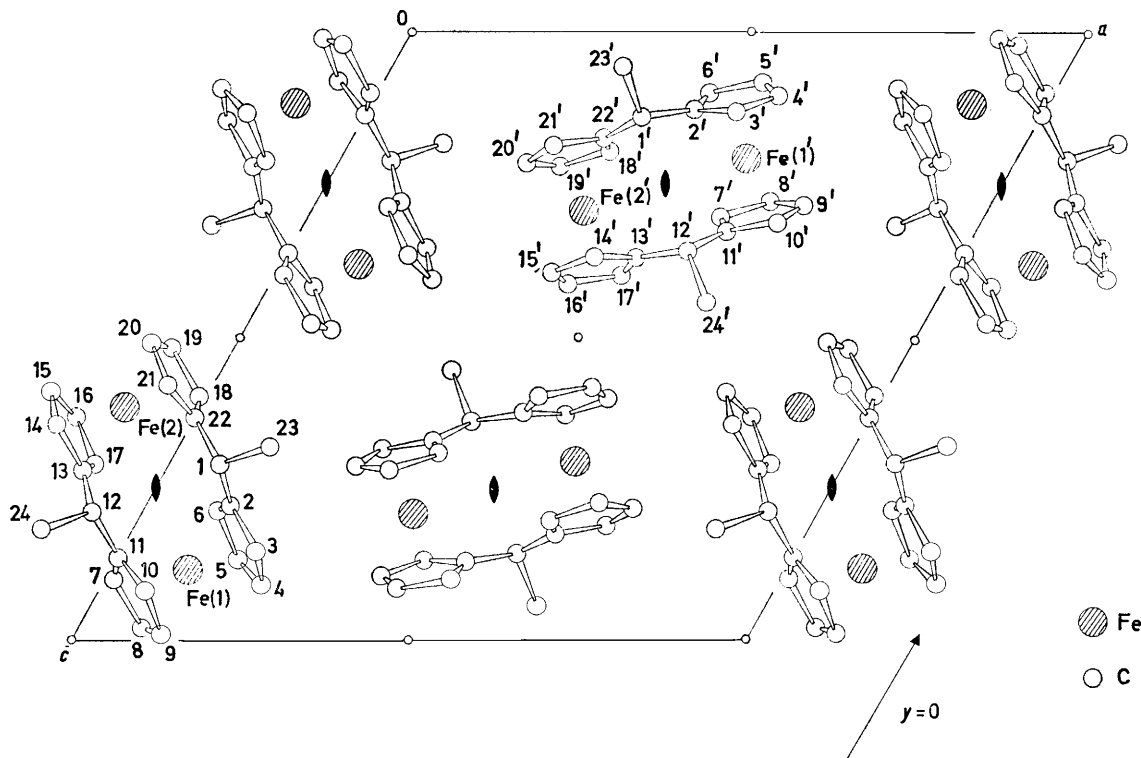


FIGURE 4 The packing of molecules in the unit cell

significant difference in the displacement of C(1) from the planes of the two cyclopentadienyl rings to which it is attached. In the molecule (1), C(1) deviates by 0·045 Å from the best plane through the atoms C(2)–C(6), whereas it lies –0·149 Å from the plane through the atoms C(18)–C(22) [symmetry-related to C(7)–C(11)]; in molecule (2), the corresponding deviations are 0·190 and –0·047 Å. The angle of tilt between the two cyclopentadienyl rings in the molecule (1) is 3° 9', while that in molecule (2) is 2° 58'. The nature of the tilt can be appreciated from Table 6, which shows that

of tilt and twist in all the ferrocene derivatives. The angles of twist in the 1,12-dimethyl[1,1]ferrocenophane molecules are somewhat unusual in that they lie almost mid-way between the fully eclipsed and fully staggered positions.

The conformation of the molecules is probably determined by intramolecular H ··· H interactions. In the analysis of a [1,1,1]ferrocenophane, it was said²⁰

¹⁹ M. R. Churchill and J. Wormald, *Inorg. Chem.*, 1969, **8**, 716.

²⁰ S. J. Lippard and G. Martin, *J. Amer. Chem. Soc.*, 1970, **92**, 7291.

that the conformation in the [1,1]ferrocenophane will be determined as much by interactions between α -protons on different ligands [*i.e.*, H(6) \cdots H(17) and H(7') \cdots H(18') see Figure 2] as between α -protons on the same ligand [*i.e.*, H(6) \cdots H(18), H(7) \cdots H(17), H(6') \cdots H(18'), and H(7') \cdots H(17'), see Figure 2]. These six H \cdots H distances are effectively equal, 2.08–2.51(16) Å, within the rather large standard deviations involving such distances, thus tending to confirm the ideas of ref. 20. The very low reliability of the hydrogen positions, however, renders a detailed discussion of these distances meaningless. The C–C–C bond angles [117.5(8) and 115.8(9)°] at the carbon atom bearing the methyl group are substantially greater than tetrahedral, while the C–C–C bond angles external to the cyclopentadienyl rings are significantly unequal (mean 130.5°, as against 121.7°). These differences from normal values are probably a consequence of steric overcrowding between the cyclopentadienyl rings in the same ligand.

The ^1H n.m.r. spectrum of (V) shows that one of the four protons on a cyclopentadienyl ring is deshielded with respect to the other three. Our results would strongly imply that this must be the proton α to the exocyclic C–C bond and on the side of the bond removed from the methyl group [*i.e.*, H(6) or its equivalent]. The deshielding may result from the unusual steric overcrowding experienced by this proton or be a consequence of its proximity to two cyclopentadienyl rings.¹²

The Fe(1) \cdots Fe(2) distances in the two molecules are 4.595(2) and 4.620(2) Å. These are much longer than the distances reported in bis(*asym*-indacenyliron) [3.887(1) Å],¹¹ and in bis(fulvaleneiron) [3.984(4) Å],¹⁰ but are shorter than the distances (5.12–5.97 Å) found in molecules^{7,9,21} where the iron atoms are *trans* to the linked cyclopentadienyl rings. Intermolecular contacts <3.8 Å are given in Table 7 with the molecular packing

TABLE 7

Intermolecular contacts <3.8 Å			
C(18) \cdots C(8) ^I	3.65	C(21') \cdots C(23) ^{II}	3.51
C(5') \cdots C(16') ^I	3.58	C(15) \cdots C(24') ^{III}	3.67
C(5') \cdots C(17') ^I	3.72	C(16) \cdots C(24') ^{III}	3.72
C(16') \cdots C(4) ^I	3.79	C(20) \cdots C(9') ^{IV}	3.76
C(4') \cdots C(24') ^{II}	3.79	C(20) \cdots C(10') ^{IV}	3.65
C(20') \cdots C(23) ^{II}	3.76		

Roman numerals refer to molecules in the following equivalent positions:

I $x, -y, -\frac{1}{2} + z$	II $x, 1 - y, -\frac{1}{2} + z$
III $-1 + x, -1 + y, z$	IV $-1 + x, y, z$

shown in Figure 4. There are no unusually short distances.

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²¹ F. Hanic, J. Ševčík, and E. L. McGandy, *Chem. zvesti.*, 1970, **24**, 81.