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BRIDGED FERROCENES

II *. THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,1′,2,2′,4,4′-TRIS(TRIMETHYLENE)FERROCENE

MANNY HILLMAN ** and ETSUKO FUJITA

Department of Energy and Environment, Brookhaven National Laboratory, Upton, N.Y. 11973 (U.S.A.)

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Summary

The crystal and molecular structure of 1,1′,2,2′,4,4′-tris(trimethylene)ferrocene has been determined by X-ray diffraction. This compound forms monoclinic needles of space group $C2/c$ with sixteen molecules in the unit cell, a 30.899(6), b 9.416(1), c 25.145(1) Å and β 127.31(1)°. The structure was solved from three-dimensional Patterson and Fourier syntheses and was refined by least squares. The structure consists of two crystallographically independent molecules showing similar geometries. The two cyclopentadienyl rings are eclipsed and the dihedral angle between the two rings, is 2.4°. The average iron to ring-carbon distance is 1.992 Å. The distance between the rings (3.15 Å) is significantly shorter than in ferrocene, and the rings appear to be slightly non-planar.

Introduction

The structural studies by X-ray diffraction on monobridged ferrocene derivatives with a two atom chain, such as 1,1′-tetramethylethyleneferrocene [1] and ferrocenophanethiazine-1,1′-dioxide [2] indicated that the bridge causes the two cyclopentadienyl rings to be tilted about 23° with respect to each other. In monobridged ferrocene derivatives with three carbon chains such as α-keto-1,1′-trimethyleneferrocene [3] and α-keto-γ-phenyl-1,1′-trimethylene-2′-methylferrocene [4] the two five-membered rings are tilted about 10°. A dibridged ferrocene derivative, 1,1′,3,3′-bis(trimethylene)ferrocene was found [5] to have a ring—ring tilt angle of 9° and an average iron to ring-carbon distance of 2.01 Å, signif-

* For part I see ref. 11.

** To whom requests for information should be sent.

icantly shorter than the value of 2.04—2.06 Å reported for most other ferrocene structures.

A correlation was shown [6—8] to occur between the tilt angle of the cyclopentadienyl rings and the NMR chemical shift due to the ring protons in mono- and poly-methylene bridged metallocene derivatives. Recently it was also suggested [9] that the trends in the quadrupole splitting and the isomer shifts in the Mössbauer spectra of the various trimethylene bridged ferrocene derivatives can be explained by trends in ring-tilting, non-planarity of the rings, and by the shortness of the Fe—ring distance. On this basis, the cyclopentadienyl rings of 1,1',2,2',4,4'-tris(trimethylene)ferrocene (abbreviated 124TTMF) were predicted to be parallel or slightly tilted, non-planar, and significantly closer than in ferrocene. In order to confirm these hypotheses and to determine other features, the X-ray analysis was carried out.

Experimental

124TTMF was prepared by the methods developed by Rinehart [10] et al. with only minor modification [11]. Yellow needles were obtained by recrystallization from hexane.

A crystal was mounted on a glass fiber, using epoxy cement, with the longest dimension (b^* axis) approximately parallel to the fiber axis. The precession photographs, using Zr-filtered Mo-K_α radiation (λ 0.7107 Å) indicated lattice symmetry $2/m$. The systematic absences, hkl ($h + k = 2n + 1$), $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$), were consistent with monoclinic space groups Cc and $C2/c$. Successful refinement of the structure in $C2/c$ verified the assumption of the centrosymmetric space group.

Unit cell parameters and the orientation matrix were determined on an Enraf—Nonius CAD-4 diffractometer equipped with a graphite monochromator using Cu-K_α radiation (λ 1.5405 Å). Twenty-five reflections whose θ values ranged from 36.7 to 59.4° were automatically centered and used in the least squares refinement of the lattice parameters and orientation matrix. Unit cell parameters obtained are shown in Table 1.

Intensity data were collected using θ—2θ scans with X-ray source and monochromator settings identical to those used for determination of the unit cell para-

TABLE 1

CRYSTAL DATA FOR 124TTMF

Molecular formula	$C_{19}H_{22}Fe$
Molecular weight	306.23
Crystal size	0.17 × 0.22 × 0.69 (mm)
Space Group	$C2/c$
a	30.899(6) Å
b	9.416(1) Å
c	25.145(1) Å
β	127.31(1)°
V	5818.9 Å^3
Measured density	1.37 g cm^{-3}
Calculated density	1.399 g cm^{-3}
Molecules per unit cell	16

meters. A variable scan rate of from 0.7 to 20° min^{-1} was used, and a total of 12 902 reflections in a hemisphere ($\pm h$, k, $\pm l$) was collected out to 2θ 140°. No significant fluctuations were observed in the intensities of three reflections (12,0,0; 0,$\bar{4}$,0; 0,0,10) monitored every hour of X-ray exposure time. Intensities were calculated from the peak scan count, CT, and background counts by the relationship:

$$I = CT - k(\text{bgd } 1 + \text{bgd } 2)$$

where k is the ratio of the total background to the peak scan time. The intensities were assigned standard deviations according to the formula:

$$\sigma_c(I) = [CT + k^2(\text{bgd } 1 + \text{bgd } 2)]^{1/2}$$

Lorentz and polarization corrections [12] were made in the usual way. The six principal faces of the crystal were identified as follows (distance in millimeters from the center of the crystal to the face is given in parentheses): {100} (0.083), {$\bar{1}$01} (0.110), (010) (0.346) and ($1\bar{1}\bar{1}$) (0.271). Absorption corrections were calculated [12] by the Gaussian grid method with a linear absorption coefficient for Cu-K_α of 81.9 cm^{-1}. The minimum and maximum corrections to F_0^2 were 2.725 and 14.556, respectively. After averaging symmetry-related observations, F_0^2 values were obtained for a total of 5520 unique reflections. 3934 reflections (m) were accepted as statistically above background on the basis that F_0^2 was greater than $3\sigma_c(F_0^2)$ and used for least-squares refinements.

Computations were performed using standard programs modified locally [12,13]. For structure factor calculations the scattering factors were taken from Doyle and Turner's tabulation [14] for all atoms. The scattering factors for iron were corrected for the real and imaginary anomalous dispersion components, using the dispersion factors tabulated by Cromer and Liberman [15]. The agreement factors are defined in the usual way as:

$$R = \sum ||F_0| - |F_c|| / \sum |F_0|$$

and

$$R_w = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2}$$

with

$$w^{-1} = [\sigma_c^2(F_0^2) + (0.06\ F_0^2)^2]/4F_0^2$$

In all least-square refinements, the quantity minimized was

$$\sum w(|F_0| - |F_c|)^2 \ .$$

Atomic coordinates for two iron atoms were deduced from a three-dimensional Patterson synthesis and refined to give the initial residual, $R = 0.386$. The remaining atoms were located and refined together with isotropic thermal parameters by full-matrix least squares. The positions were then iteratively refined with the anisotropic thermal parameters as a second block. A refinement of anisotropic thermal parameters for iron and isotropic thermal parameters for carbon

(Continued on p. 92)

TABLE 2

FINAL POSITIONAL AND THERMAL PARAMETERS[a,b]

Atom	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Unit A									
Fe	−0.11850(3)	0.21738(9)	0.02917(4)	0.00137(1)	0.00652(10)	0.00214(2)	0.00009(3)	0.00104(2)	0.00001(4)
C(1)	−0.1608(3)	0.3788(7)	−0.0308(3)	0.0019(1)	0.0107(10)	0.0032(2)	0.0013(3)	0.0011(1)	0.0013(4)
C(2)	−0.1579(3)	0.3851(7)	0.0284(3)	0.0019(1)	0.0092(9)	0.0038(2)	0.0012(3)	0.0018(1)	0.0007(3)
C(3)	−0.1817(2)	0.2563(8)	0.0310(4)	0.0015(1)	0.0139(10)	0.0044(2)	−0.0002(3)	0.0017(1)	−0.0018(4)
C(4)	−0.1963(2)	0.1694(8)	−0.0251(4)	0.0013(1)	0.0149(11)	0.0040(2)	−0.0005(3)	0.0011(1)	−0.0014(4)
C(5)	−0.1854(3)	0.2458(8)	−0.0645(3)	0.0016(1)	0.0150(11)	0.0028(2)	0.0007(3)	0.0007(1)	0.0005(4)
C(1′)	−0.0457(2)	0.2471(6)	0.0512(3)	0.0014(1)	0.0100(9)	0.0026(2)	−0.0001(2)	0.0012(1)	0.0001(3)
C(2′)	−0.0429(2)	0.2526(6)	0.1105(3)	0.0016(1)	0.0091(8)	0.0021(1)	0.0000(2)	0.0011(1)	0.0003(3)
C(3′)	−0.0623(2)	0.1198(6)	0.1163(3)	0.0020(1)	0.0070(7)	0.0025(2)	0.0005(2)	0.0012(1)	0.0006(3)
C(4′)	−0.0789(3)	0.0336(6)	0.0595(3)	0.0021(1)	0.0064(8)	0.0032(2)	0.0009(2)	0.0016(1)	0.0004(3)
C(5′)	−0.0668(2)	0.1109(7)	0.0209(3)	0.0017(1)	0.0093(8)	0.0028(2)	0.0011(2)	0.0013(1)	0.0002(3)
C(6)	−0.01340(4)	0.4831(9)	−0.0495(4)	0.0032(2)	0.0168(14)	0.0046(3)	0.0018(4)	0.0025(2)	0.0045(5)
C(7)	−0.0893(3)	0.4107(9)	−0.0501(4)	0.0031(2)	0.0188(14)	0.0041(3)	0.0013(4)	0.0025(2)	0.0035(5)
C(8)	−0.0372(3)	0.3688(8)	0.0195(4)	0.0025(1)	0.0140(11)	0.0036(2)	−0.0009(3)	0.0021(2)	0.0013(4)
C(9)	−0.1274(3)	0.4923(7)	0.0849(4)	0.0027(2)	0.0079(8)	0.0045(3)	0.0004(3)	0.0022(2)	−0.0013(4)
C(10)	−0.0780(3)	0.4274(8)	0.1532(3)	0.0028(2)	0.0112(10)	0.0032(2)	−0.0001(3)	0.0018(2)	−0.0019(4)
C(11)	−0.0298(3)	0.3804(7)	0.1541(3)	0.0022(1)	0.0106(9)	0.0027(2)	−0.0009(3)	0.0015(1)	−0.0022(3)
C(12)	−0.2111(3)	0.0087(9)	−0.0324(5)	0.0025(2)	0.0162(13)	0.0065(4)	−0.0031(4)	0.0026(2)	−0.0039(6)
C(13A)	−0.1636(10)	−0.0958(27)	−0.0161(12)	6.8(6)					
C(13B)	−0.1700(5)	−0.0819(14)	0.0230(6)	5.8(3)					
C(14)	−0.1116(4)	−0.1026(8)	0.0395(5)	0.0033(2)	0.0096(10)	0.0057(3)	−0.0007(4)	0.0027(2)	−0.0015(5)

Unit B

Fe	0.13250(3)	−0.00716(9)	0.23271(4)	0.00133(1)	0.00614(10)	0.00225(2)	−0.00001(3)	0.00116(1)	0.00016(4)
C(1)	0.0966(2)	−0.1606(7)	0.1645(3)	0.0019(1)	0.0086(8)	0.0034(2)	−0.0008(2)	0.0018(1)	−0.0017(3)
C(2)	0.1549(3)	−0.1636(7)	0.2007(3)	0.0022(1)	0.0080(8)	0.0043(2)	0.0002(3)	0.0024(2)	−0.0005(3)
C(3)	0.1721(3)	−0.0274(6)	0.1923(3)	0.0022(1)	0.0087(9)	0.0037(2)	−0.0003(3)	0.0022(1)	−0.0002(3)
C(4)	0.1246(3)	0.0607(7)	0.1530(3)	0.0024(1)	0.0111(9)	0.0032(2)	−0.0001(3)	0.0021(2)	0.0002(3)
C(5)	0.0782(3)	−0.0220(7)	0.1335(3)	0.0021(1)	0.0136(10)	0.0026(2)	−0.0002(3)	0.0016(2)	−0.0012(3)
C(1′)	0.1109(2)	−0.0558(7)	0.2906(3)	0.0019(1)	0.0102(8)	0.0026(2)	−0.0001(3)	0.0015(1)	0.0006(3)
C(2′)	0.1695(3)	−0.0554(8)	0.3278(3)	0.0020(1)	0.0163(11)	0.0022(2)	0.0009(3)	0.0011(1)	0.0015(4)
C(3′)	0.1855(3)	0.0829(8)	0.3231(3)	0.0022(1)	0.0155(11)	0.0025(2)	−0.0013(3)	0.0013(1)	−0.0014(4)
C(4′)	0.1369(3)	0.1677(7)	0.2799(3)	0.0025(1)	0.0090(9)	0.0031(2)	−0.0008(3)	0.0020(1)	−0.0013(3)
C(5′)	0.0911(2)	0.0828(6)	0.2618(3)	0.0020(1)	0.0079(8)	0.0027(2)	0.0000(2)	0.0018(1)	−0.0004(3)
C(6)	0.0617(3)	−0.2687(8)	0.1659(5)	0.0030(2)	0.0123(11)	0.0072(4)	−0.0031(4)	0.0036(2)	−0.0052(5)
C(7)	0.0355(3)	−0.2148(8)	0.2002(4)	0.0024(1)	0.0124(10)	0.0063(3)	−0.0024(3)	0.0032(2)	−0.0030(5)
C(8)	0.0751(3)	−0.1825(7)	0.2752(4)	0.0029(2)	0.0108(10)	0.0050(3)	−0.0010(3)	0.0029(2)	0.0008(4)
C(9)	0.1932(3)	−0.2760(8)	0.2485(5)	0.0026(2)	0.0110(11)	0.0065(4)	0.0025(4)	0.0028(2)	0.0025(5)
C(10)	0.2325(3)	−0.2237(11)	0.3209(5)	0.0026(2)	0.0263(19)	0.0061(4)	0.0046(5)	0.0027(2)	0.0066(7)
C(11)	0.2074(3)	−0.1843(10)	0.3580(4)	0.0028(2)	0.235(17)	0.0052(3)	0.0036(5)	0.0024(2)	0.0058(6)
C(12)	0.1232(4)	0.2185(8)	0.1425(4)	0.0041(2)	0.0099(10)	0.0054(3)	0.0017(4)	0.0037(2)	0.0033(5)
C(13A)	0.1058(10)	0.3079(28)	0.1801(12)	5.4(5)					
C(13B)	0.1562(4)	0.3049(13)	0.2071(6)	6.1(2)					
C(14)	0.1351(4)	0.3087(7)	0.2499(4)	0.0042(2)	0.0066(9)	0.0058(3)	−0.0002(3)	0.0038(3)	−0.0002(4)

[a] The form of the thermal ellipsoid expression is $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl]$. [b] Occupancy factors for C(13A) and C(13B) in Unit A are 0.36(1) and 0.61(1), respectively. The factors for C(13A) and C(13B) in Unit B are 0.29(1) and 0.71(1), respectively.

atoms converged with $R = 0.116$. Anisotropic thermal parameters were introduced for all carbon atoms and further refinement reduced R to 0.064. Examination of thermal ellipsoids for middle carbons (C(13) in Unit A and Unit B) of the 4,4'-trimethylene bridges gave strong indications of either static or dynamic disorder approximately normal to the bridges. A difference electron density map revealed two distinct maxima separated by 0.070 and 0.15 Å about the refined C(3) positions in Unit A and Unit B, respectively. Thus, further refinements included in each unit two partial atoms, C(13A) and C(13B) of Unit A, and C(13A) and C(13B) of Unit B with independent occupancies, α_{1-4}. Occupancy factors, 0.36(2) and 0.61(1) for C(13A) and C(13B) in Unit A, respectively, 0.29(1) and 0.71(1) for C(13A) and C(13B) in Unit B, respectively, were obtained. The introduction of individually refined occupancy factors for disordered atoms did not sifnificantly improve the R factor. The refinements converged to final values of $R = 0.063$ and $R_w = 0.087$. No attempt was made to locate hydrogen atoms in the analysis.

The number of variables (n) was 351, and the maximum shift was less than 0.1 standard deviation. The standard deviation of an observation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, was 1.39. The major feature on the final difference Fourier map was a peak of 0.32 e Å^{-3}; this compares to values of approximately 5 e Å^{-3} for typical carbon atoms in this structure. Final atomic parameters are listed in Table 2; a tabulation of the final observed and calculated structure factors was deposited with NAPS *.

Results and discussion

The asymmetric unit consists of two independent molecules, the corresponding bond distances and angles within the two crystallographically independent molecules showing only small differences. Figure 1 is a view of Unit A with the atom numbering scheme indicates. Interatomic distances and angles with their estimated standard deviation included in parentheses are collected in Tables 3 and 4.

The configuration of the cyclopentadienyl rings is eclipsed (shown in Fig. 2), and the two cyclopentadienyl rings are almost parallel; the average angle between the two least squares planes (2.3 and 2.5° for each unit) is 2.4°. The angle is much smaller than reported [1—5,16—27] for any other bridged ferrocenes except 1,1'-trithiaferrocene [23]. For comparison the angles of tilt for cyclopentadienyl rings, the average iron to ring distances, the average iron to ring-carbon distances and the average ring-carbon to ring-carbon distances for measured bridged ferrocenes are listed in Table 6. In the ferrocene derivatives with a two-atom bridge, the angles between the two least squares planes of the cyclopentadienyl rings are about 23°. Except in 1,1'-trithiaferrocene, the ring-ring angle is about 10° in ferrocene derivatives with one or two bridges of 3 atoms. In the trisulfide bridged

* The table of structure factors has been deposited as NAPS Document No. 03263 (24 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $5.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

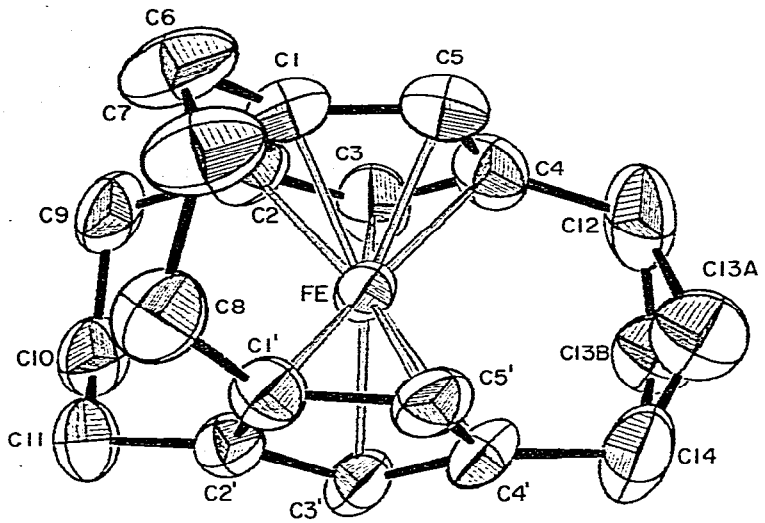

Fig. 1. A view of 1,1',2,2',4,4'-tris(trimethylene)ferrocene including disordered atoms, C(13A) and C(13B). (ORTEP diagram, 50% probability contours for thermal ellipsoids.)

structure, the long bond distances of 1.748 Å between sulfur and carbon and of 2.049 Å between sulfur and sulfur allow the rings to remain parallel.

Interesting features of the structure of 124TTMF are the non-planarity of the cyclopentadienyl rings and the short distance between the rings. The least squares planes of the cyclopentadienyl rings are given in Table 5. The root-mean-square deviation of the ring carbons from the least squares plane is 0.015 Å which is slightly larger than the errors associated with the atomic positions. The three bridged pairs of ring carbons are closer together than the two non-bridged

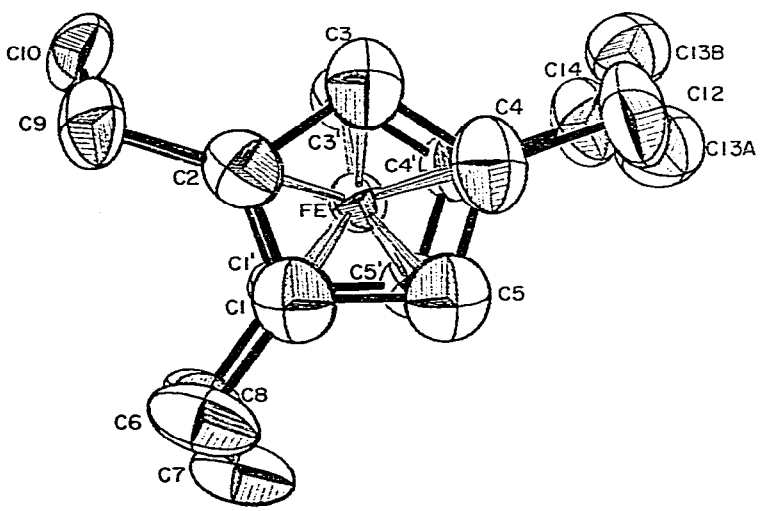

Fig. 2. The 1,1', 2,2', 4,4'-tris(trimethylene)ferrocene projected onto the cyclopentadienyl rings. (ORTEP diagram, 50% probability ellipsoids.)

TABLE 3

INTERATOMIC DISTANCES FOR 124TTMF

Atoms	Distances (Å)	
	Unit A	Unit B
Fe—C(1)	1.976(6)	1.989(6)
Fe—C(2)	1.986(6)	1.992(6)
Fe—C(3)	2.014(6)	2.016(6)
Fe—C(4)	1.968(6)	1.973(6)
Fe—C(5)	1.999(6)	1.997(6)
Fe—C(1′)	1.983(5)	1.989(5)
Fe—C(2′)	1.989(6)	1.978(6)
Fe—C(3′)	2.012(6)	2.014(6)
Fe—C(4′)	1.986(6)	1.985(6)
Fe—C(5′)	2.002(6)	2.006(5)
C(1)—C(2)	1.437(9)	1.442(8)
C(2)—C(3)	1.440(9)	1.452(8)
C(3)—C(4)	1.445(9)	1.434(9)
C(4)—C(5)	1.422(10)	1.433(9)
C(5)—C(1)	1.444(9)	1.448(9)
C(1′)—C(2′)	1.442(7)	1.451(8)
C(2′)—C(3′)	1.431(8)	1.423(10)
C(3′)—C(4′)	1.440(8)	1.448(9)
C(4′)—C(5′)	1.432(8)	1.438(8)
C(5′)—C(1′)	1.431(8)	1.437(8)
C(1)—C(6)	1.530(10)	1.499(9)
C(6)—C(7)	1.549(10)	1.583(9)
C(7)—C(8)	1.548(10)	1.532(10)
C(8)—C(1′)	1.507(8)	1.508(8)
C(2)—C(9)	1.518(9)	1.497(9)
C(9)—C(10)	1.573(10)	1.532(12)
C(10)—C(11)	1.549(9)	1.580(12)
C(11)—C(2′)	1.509(8)	1.530(10)
C(4)—C(12)	1.558(10)	1.505(9)
C(12)—C(13A)	1.599(26)	1.584(26)
C(12)—C(13B)	1.462(15)	1.529(13)
C(13A)—C(14)	1.349(24)	1.405(25)
C(13B)—C(14)	1.601(15)	1.558(12)
C(14)—C(4′)	1.518(10)	1.512(9)
C(13A)—C(13B)	1.123(24)	1.226(25)
C(1)—C(1′)	3.088(8)	3.088(8)
C(2)—C(2′)	3.089(9)	3.113(9)
C(3)—C(3′)	3.206(9)	3.226(9)
C(4)—C(4′)	3.158(9)	3.142(8)
C(5)—C(5′)	3.182(8)	3.161(8)

pairs of ring carbons in each unit. The cyclopentadienyl rings, therefore, appear to be slightly non-planar. The short distance between the rings is evident in two ways. The iron to ring distance of 1.573 Å and the average iron to ring-carbon distance of 1.992 Å are significantly shorter than the values in other ferrocene derivatives listed in Table 6.

The carbon—carbon bond distances in the cyclopentadienyl rings range from 1.422(10) to 1.452(8) Å. The carbon—carbon—carbon angles in the cyclopentadienyl rings range from 106.9(5) to 109.1(7)°. Apparently there are no particu-

TABLE 4

INTERATOMIC ANGLES FOR 124TTMF

Atoms	Angles (°)	
	Unit A	Unit B
C(1)—C(2)—C(3)	107.4(6)	108.5(6)
C(2)—C(3)—C(4)	107.4(6)	107.5(5)
C(3)—C(4)—C(5)	109.1(7)	108.3(6)
C(4)—C(5)—C(1)	107.1(6)	108.7(6)
C(5)—C(1)—C(2)	108.9(6)	106.9(5)
C(1')—C(2')—C(3')	107.9(5)	108.0(6)
C(2')—C(3')—C(4')	108.1(5)	108.2(6)
C(3')—C(4')—C(5')	107.7(5)	107.8(6)
C(4')—C(5')—C(1')	108.4(5)	108.0(5)
C(5')—C(1')—C(2')	107.8(5)	107.8(5)
C(2)—C(1)—C(6)	125.9(7)	127.7(7)
C(5)—C(1)—C(6)	124.6(7)	124.8(6)
C(1)—C(2)—C(9)	127.7(6)	126.8(6)
C(3)—C(2)—C(9)	124.1(6)	124.0(6)
C(3)—C(4)—C(12)	124.2(8)	127.0(6)
C(5)—C(4)—C(12)	125.8(7)	124.1(7)
C(2')—C(1')—C(8)	126.8(6)	127.0(6)
C(5')—C(1')—C(8)	124.7(6)	124.5(5)
C(1')—C(2')—C(11)	127.0(5)	126.7(7)
C(3')—C(2')—C(11)	124.6(5)	124.6(7)
C(3')—C(4')—C(14)	124.7(6)	124.5(6)
C(5')—C(4')—C(14)	126.9(6)	126.8(7)
C(1)—C(6)—C(7)	111.8(6)	114.1(5)
C(6)—C(7)—C(8)	115.1(6)	116.3(6)
C(1')—C(8)—C(7)	113.3(6)	112.9(5)
C(2)—C(9)—C(10)	113.8(5)	113.4(7)
C(9)—C(10)—C(11)	114.8(6)	117.2(7)
C(2')—C(11)—C(10)	112.8(5)	113.3(6)
C(4)—C(12)—C(13A)	114.2(10)	113.8(11)
C(4)—C(12)—C(13B)	115.6(8)	114.1(7)
C(12)—C(13A)—C(14)	128.8(18)	123.6(18)
C(12)—C(13B)—C(14)	120.6(10)	117.3(8)
C(4')—C(14)—C(13A)	116.0(12)	114.8(12)
C(4')—C(14)—C(13B)	113.8(7)	114.8(7)

larly short bonds or small angles in the cyclopentadienyl rings. These distances and angles are normal for ferrocene derivatives.

The conformation of the trimethylene bridges are shown in Fig. 2. The central methylene carbon atom of the 4,4'-bridge is disordered in two equivalent positions. The occupancy factors refined to the values of 0.36(2) and 0.61(1) for Unit A, 0.29(1) and 0.71(1) for Unit B rather than 0.5 as ordinarily expected. Although it is usually impossible to distinguish between static disorder and dynamic disorder by X-ray diffraction on crystals, a broad peak in the PMR spectrum of the compound at δ 1.8 ppm indicates that flipping exists [28]. Some of the carbon—carbon distances including the disordered atom appear unreasonable; this may be due to the difficulty of the refinement of atoms whose thermal ellipsoids are quite large. The average distance of the disordered carbon atoms to neighboring carbon atoms is 1.511 Å. The average distance of 1.512 Å between the carbon atom in the ring and the bridged carbon atom adjacent to it is shorter

TABLE 5

LEAST SQUARES PLANES[a,b] OF CYCLOPENTADIENYL RINGS
Equation $pX + qY + rZ = s$

Coefficient	Unit A		Unit B	
	I	II	I	II
p	—0.734	—0.753	—0.471	—0.498
q	0.421	0.380	0.332	0.302
r	—0.533	—0.536	0.817	0.813
s	5.132	1.984	1.952	5.066
Deviation of Atoms (Å)[c]				
C(1) or C(1′)	—0.001	0.006	0.009	0.001
C(2) or C(2′)	—0.011	0.006	0.005	—0.014
C(3) or C(3′)	0.020	—0.016	—0.017	0.021
C(4) or C(4′)	—0.021	0.019	0.023	—0.021
C(5) or C(5′)	0.014	—0.015	—0.019	0.012
Fe	—1.568	1.577	1.572	—1.574

[a] Direction cosines of the plane refer to the orthogonal axis system a, b, c^*. [b] All atoms except Fe weighted at unity. [c] In Unit A(I) and in Unit B(II), negative deviations are toward the iron atom. In the others, positive deviations are toward the iron atom.

than that of 1.544 Å between the middle carbon atom in the 1,1′- and 2,2′-bridges and one adjacent to it.

The molecular packing as viewed along the b axis is shown in Fig. 3. None of the intermolecular distances is significantly shorter than the sum of Van der Waals radii. The two intermolecular contacts less than 3.6 Å are the distance of 3.506(12) Å between C(3) (Unit A) at (x, y, z) and C(3) (Unit A) at $(-0.5, -x, 0.5 - y, -z)$ and the distance of 3.581(9) Å between C(5) (Unit A) at (x, y, z) and C(3′) (Unit B) at $(-0.5 + x, 0.5 - y, 0.5 + z)$.

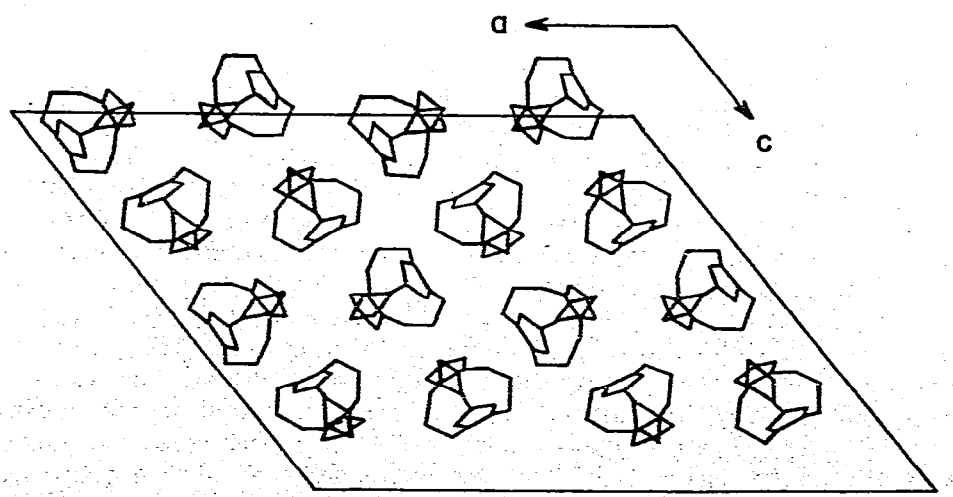

Fig. 3. Packing diagram of 1,1′,2,2′,4,4′-tris(trimethylene)ferrocene.

TABLE 6

BOND DISTANCES AND ANGLES OF BRIDGED FERROCENES

Compound[a]	Ring tilt	Distance (Å)			
		Fe—R	Avg(Fe—RC)	Avg(RC—RC)	Ref.
F	0°	1.66	2.04_5	1.40_3	16
BF	2.8°	1.66	2.03_5	1.40	17
F^+		1.70			18
One 2-atom bridge					
TMEF	23.2°	1.63_5	2.040	1.435	1
EADOF	23°	1.64	2.024	1.406	2
TQQF	23.7°	1.637	2.041	1.431	19
BPI	23.6°	1.640	2.039	1.423	20
One 3-atom bridge					
TMFO	8.8°	1.640	2.039	1.424	3
QMTMFO	10°	1.655	2.059	1.438	4
QHPTMF	10°	1.643	2.056	1.453	21
CPF	11.0°	1.645	2.046	1.423	22
TTF	2.85°	1.653	2.044	1.42	23
One 4-atom bridge					
BAI	7.33°	1.642	2.044		24
Two 3-atom bridges					
BTMF	9°		2.01		5
TKTMF	11.1°	1.616	2.023	1.431	25
BCPF	14.4°	1.615	2.025	1.436	26
Three 3-atom Bridges					
124TTMF	2.4°	1.573	1.992	1.436	this work
PKTMF	12.5°	1.60	2.012	1.435	27

[a] R Ring
RC Ring Carbon
F Ferrocene
BF Biferrocenyl
F^+ Ferricenium Tetrachlorobismuthate
TMEF 1,1′-Tetramethylethyleneferrocene
EADOF [2] Ferrocenophanethiazine-1,1′-Dioxide
TQQF 1,1′-(Tetraphenyl-*o*-phenylene)ferrocene
BPI Dipentalenyliron
TMFO α-Keto-1,1′-trimethyleneferrocene
QMTMFO α-Keto-γ-phenyl-1,1′-trimethylene-2′-methylferrocene
QHPTMF 1,1′-Trimethylene-2-(α-phenyl-α-hydroxypropyl)ferrocene
CPF 1,1′-(1″,3″-Cyclopentylene)ferrocene
TTF 1,1′-Trithiaferrocene
BAI Di-(π-azulene)iron
BTMF 1,1′,3,3′-Bis(trimethylene)ferrocene
TKTMF 1,1′,2,2′,3,4′,5′-Tetrakis(trimethylene)ferrocene
BCPF 1,1′,3,3′-Bis(1″,3″-Cyclopentylene)ferrocene
124TTMF 1,1′,2,2′,4,4′-Tris(trimethylene)ferrocene
PKTMF 1,1′,2,2′,3,3′,4,5,4′,5′-Pentakis(trimethylene)ferrocene

Conclusion

Bridging the cyclopentadienyl rings of ferrocene with one or two trimethylene groups introduces a strain that can be accommodated by ring tilting. A third non-adjacent bridge either must bring two cyclopentadienyl carbon atoms closer

together or the bridges must stretch. Apparently there are no abnormalities in any bond lengths or angles except those of the iron to ring-carbons. The non-bridged ring-carbon atoms remain further apart, but still closer than in ferrocene. The strain introduced by squeezing the iron atom is manifested in the failure [11] of the preparation of a tetrakis(trimethylene)ferrocene, a failure that resulted in a rearrangement to the less strained two-bridged [11,25] compound.

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13 Programs employed include Zalkin's FORDAP Fourier Summation program, the Busing—Martin—Levy ORFLS full matrix least square program, the Martin—Busing—Levy ORFFE function and error program, Johnson's ORTEP II plotting program and locally written programs; BOND, distances, angles and least-squares planes, F. Takusagawa; AVSORT, average and sort, G.J.B. Williams, et al.; PRJCTN, plotting, H.J. Bernstein, et al.
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