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XXXVI *. X-RAY CRYSTAL STRUCTURE OF [4][3][4](1,2,3)FERROCENOPHANE **

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Summary

The crystal and molecular structure of [4][3][4](1,2,3)ferrocenophane, a ferrocenophane bridged at three neighbouring positions, has been determined by X-ray diffraction. The compound crystallizes in the orthorhombic system, space group *Pcab* with unit cell dimensions a = 15.973(2), b = 17.007(2), c = 11.648(1) Å, and Z = 8. The two cyclopentadienyl rings are nearly eclipsed and the dihedral angle between the two rings is 10.4°. The bond lengths and angles in the cyclopentadienyl rings and methylene chains have been found in almost normal ranges in comparison with multibridged ferrocenophanes already reported.

Introduction

One of important studies in ferrocene chemistry is that of the influences of the numbers, lengths and positions of bridges on the molecular structures of multibridged ferrocenophanes, investigated by spectroscopies and X-ray crystal analysis. A number of ferrocenophane are already synthesized and selected ones have been analyzed by X-ray crystallography [3,4]. All of the tribridged

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[*] For part XXXV, see ref. 1.

[**] The nomenclature of ferrocenophanes described in this paper is according to the modified one presented by Vögtle and Neumann [2].

ferrocenophanes described by their X-ray diffractions are [3][3][3]ferrocenophanes bridged with only trimethylene chains and these were reported by Hillman et al. [4]. We have synthesized the tribridged [4][3][4](1,2,3)ferrocenophane (I) possessing a trimethylene bridge surrounded with two tetramethylene ones in the series of studies on the syntheses and structures of multibridged ferrocenophanes with tetramethylene bridges [5]. Compound I is interesting because of its molecular structure in comparison with those of the analogous ferrocenophanes. Furthermore, the structural study of I aids the discussion on the reason for the abnormal bond lengths and angles of tetrabridged [4][4][3]-[4](1,2,3,4)ferrocenophane previously reported by us [6], because the latter phane is an additionally bridged derivative of I with a tetramethylene chain. We wish to report the X-ray crystal analysis of I and a brief discussion on the comparison with other ferrocenophanes.

Experimental

Materials

The synthesis of [4][3][4](1,2,3)ferrocenophane (I) was described in a paper already published [5]. The yellow crystals used in the X-ray diffraction were grown from a hexane solution at room temperature.

Data collection

Systematic extinctions on Weissenberg photographs, using Ni-filtered Cu-K_α radiation, uniquely identified space group *Pcab*. A crystal with dimensions 0.45 × 0.40 × 0.20 mm was mounted with the b axis parallel to the ϕ axis of a Hilger & Watts Y290 four-circle diffractometer. The cell parameters and intensity data were obtained with Zr-filtered Mo-K_α radiation (λ = 0.7107 Å) at 21°C. The intensities of the 4082 unique reflections with $2\theta \leqslant 55°$ were collected by a 2θ—ω step scan (1 s count at each of 80 steps of 0.02° in 2θ, background count of 10 s at each end of the scan range), and 2352 reflections $[F_o \geqslant 3\sigma(F)]$ were used in the calculations. Three standard reflections, monitored every 50 measurements, showed no significant intensity variations throughout the data collection. Lorentz and polarization corrections were made but no absorption correction was applied. The density was measured by the flotation method in an aqueous solution of K_2HgI_4.

Crystal data: $C_{21}H_{26}Fe$, M_r = 334.28; orthorhombic, space group *Pcab*, a = 15.973(2), b = 17.007(2), c = 11.648(1) Å, V = 3164.2 Å^3; D_m = 1.40, D_x = 1.40 g cm^{-3}, Z = 8, μ(Mo-K_α) = 9.71 cm^{-1}, $F(000)$ = 1424.

Structure determination and refinement

The structure was solved by the heavy atom method. Atomic coordinates for the Fe atom was deduced from the Patterson map, and all the 21 carbon atoms were located in the Fourier map. The atomic coordinates and anisotropic thermal parameters of these atoms were refined by block-diagonal least-squares to give the residual, R = 0.086. The difference Fourier map revealed the remaining H atoms. The last full-matrix least-squares were carried out with the coordinates and the fixed isotropic thermal parameters B of 4.5 Å^2 for the hydrogens. The final R was reduced to 0.065. The atomic scattering factors were

TABLE 1

ATOMIC POSITIONAL PARAMETERS ($\times 10^4$ for non-H; $\times 10^3$ for H) WITH THEIR e.s.d.'s AND ISOTROPIC EQUIVALENT THERMAL PARAMETERS, B_{eq}. B_{eq} is defined as $B_{eq} = \frac{4}{3}\sum_i a_i^2\beta_{ii}$

Atom	x	y	z	B_{eq} (Å^2) [a]
Fe	1572(1)	2319(1)	193(1)	2.2
C(1)	820(4)	1677(4)	—865(5)	2.8
C(2)	347(3)	2073(3)	12(5)	2.8
C(3)	492(4)	2908(4)	—114(6)	3.2
C(4)	1065(4)	2996(4)	—1067(6)	3.5
C(5)	1257(4)	2253(5)	—1515(5)	3.5
C(1')	2350(4)	1542(4)	991(6)	3.0
C(2')	1738(3)	1856(3)	1765(5)	2.5
C(3')	1849(4)	2685(4)	1814(5)	2.9
C(4')	2516(4)	2882(4)	1042(6)	3.2
C(5')	2823(4)	2183(4)	553(6)	3.2
C(6)	830(5)	805(5)	—1153(7)	4.0
C(7)	1678(5)	378(5)	—1071(7)	4.4
C(8)	1968(5)	149(4)	120(7)	4.8
C(9)	2574(5)	684(5)	743(7)	4.1
C(10)	—150(4)	1696(4)	959(6)	3.5
C(11)	316(4)	1104(4)	1726(6)	3.6
C(12)	1057(5)	1416(4)	2408(6)	3.7
C(13)	128(5)	3571(4)	578(8)	4.1
C(14)	776(5)	4200(5)	940(8)	4.8
C(15)	1222(5)	4088(5)	2066(9)	4.7
C(16)	1348(5)	3250(4)	2542(6)	3.7
H(4)	123(5)	343(5)	—126(8)	
H(5)	159(5)	215(5)	—210(7)	
H(4')	268(5)	328(5)	93(8)	
H(5')	325(5)	212(5)	0(7)	
H(6a)	40(6)	58(5)	—68(8)	
H(6b)	63(6)	77(5)	—189(8)	
H(7a)	160(6)	—6(5)	—157(7)	
H(7b)	218(6)	67(5)	—126(8)	
H(8a)	151(6)	15(5)	75(8)	
H(8b)	219(5)	—36(5)	10(8)	
H(9a)	275(6)	49(5)	148(8)	
H(9b)	292(6)	69(5)	25(8)	
H(10a)	—36(5)	208(5)	153(8)	
H(10b)	—58(6)	153(5)	62(8)	
H(11a)	—12(5)	92(5)	226(8)	
H(11b)	54(6)	65(5)	135(8)	
H(12a)	95(5)	176(5)	297(8)	
H(12b)	136(5)	94(5)	283(8)	
H(13a)	—28(6)	383(5)	15(8)	
H(13b)	—12(5)	333(5)	135(8)	
H(14a)	121(6)	425(5)	41(8)	
H(14b)	50(5)	466(5)	92(8)	
H(15a)	173(6)	431(5)	207(8)	
H(15b)	95(6)	433(5)	265(8)	
H(16a)	169(5)	326(5)	331(8)	
H(16b)	83(6)	303(5)	273(8)	

[a] Isotopic B for hydrogen atoms is fixed, B = 4.5 Å^2.

taken from the International Tables for X-ray Crystallography [7]. The quantity minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1.0$ for all the F's. All the computations were carried out on HITAC 8800/8700 and HITAC M-200H computers at the Computer Centre of the University of Tokyo with the UNICS program system [8]. Final positional parameters are listed in Table 1.

Results and discussion

The molecular structure of I as an ORTEP drawing [9] and the atomic numbering are shown in Fig. 1. The drawing in Fig. 2 is a projection on the plane defined by the Fe atom and an intersection of the two cyclopentadienyl (Cp) least-squares planes. Selected bond lengths and angles are described in Tables 2 and 3, respectively.

The rotation of the two Cp rings through the Cp—Fe—Cp axis deviates only slightly from the eclipsed conformation, as shown in Fig. 2. The two tetramethylene chains bridging at the 1,1′- and 3,3′-positions take a half-chair and a boat forms, respectively. The conformational features of the Cp rings and the methylene chains are similar to that of [4][4][3][4](1,2,3,4)ferrocenophane [6] except for the flip direction of the 11-carbon of the trimethylene chain.

Each of the Cp rings shows a good planarity and the values of the atomic deviations from its own least-squares plane are less than 0.01 Å (Table 4). The α-carbon atoms (10- and 12-positions) of the trimethylene bridge deviate from the least-squares planes of the Cp rings in the same direction to the iron, while those of trimethylene ones in the opposite direction. The observation indicates that tri- and tetra-methylene chains are too short and too long, respectively, to connect two Cp rings of ferrocene without any deformation. The larger deviation of the 6- and 9-carbons in comparison with the 13- and 16-carbons is,

TABLE 2

BOND LENGTHS (in Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond	Length	Bond	Length
Fe—C(1)	2.038(6)	C(3′)—C(4′)	1.434(9)
Fe—C(2)	2.012(6)	C(4′)—C(5′)	1.406(9)
Fe—C(3)	2.027(6)	C(5′)—C(1′)	1.420(9)
Fe—C(4)	2.033(7)	C(1)—C(6)	1.521(10)
Fe—C(5)	2.055(7)	C(6)—C(7)	1.538(11)
Fe—C(1′)	2.039(6)	C(7)—C(8)	1.513(11)
Fe—C(2′)	2.011(6)	C(8)—C(9)	1.514(12)
Fe—C(3′)	2.037(6)	C(9)—C(1′)	1.530(10)
Fe—C(4′)	2.041(7)	C(2)—C(10)	1.503(9)
Fe—C(5′)	2.055(6)	C(10)—C(11)	1.538(10)
C(1)—C(2)	1.438(8)	C(11)—C(12)	1.521(10)
C(2)—C(3)	1.447(8)	C(12)—C(2′)	1.517(9)
C(3)—C(4)	1.447(9)	C(3)—C(13)	1.503(10)
C(4)—C(5)	1.403(10)	C(13)—C(14)	1.547(12)
C(5)—C(1)	1.421(9)	C(14)—C(15)	1.505(12)
C(1′)—C(2′)	1.434(8)	C(15)—C(16)	1.543(11)
C(2′)—C(3′)	1.423(8)	C(16)—C(3′)	1.510(9)

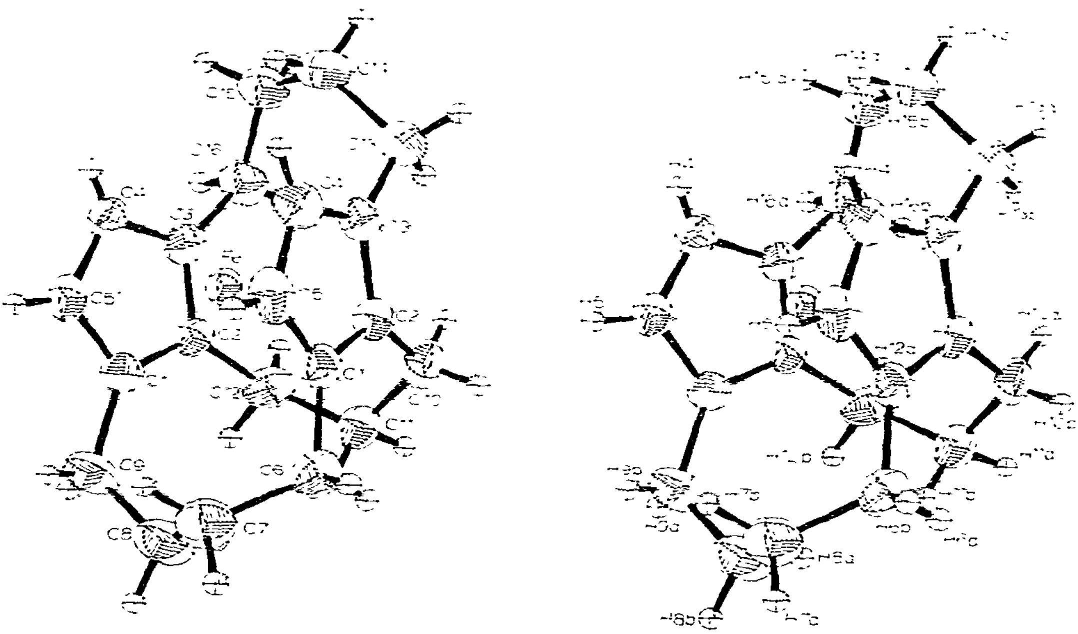

Fig. 1. ORTEP stereoview and atomic numbering of [4][3][4](1,2,3)ferrocenophane (I).

possibly, due to the difference of conformation between the two tetramethylene chains at the 1,1′- and 3,3′-positions. In fact, inspection of a Dreiding stereomodel shows that the distance between the two α-carbons in a half-chair conformation is significantly larger than that in a boat form, when the two Cp rings are nearly eclipsed. The large *exo* deviation of the α-carbon was also

TABLE 3

BOND ANGLES IN DEGREES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond	Angle	Bond	Angle
C(5)—C(1)—C(2)	108.3(5)	C(5′)—C(1′)—C(9)	122.7(6)
C(1)—C(2)—C(3)	107.7(5)	C(2′)—C(1′)—C(9)	129.3(6)
C(2)—C(3)—C(4)	106.3(5)	C(1′)—C(2′)—C(12)	128.0(5)
C(3)—C(4)—C(5)	109.3(6)	C(3′)—C(2′)—C(12)	123.9(5)
C(4)—C(5)—C(1)	108.4(6)	C(2′)—C(3′)—C(16)	126.0(5)
C(5′)—C(1′)—C(2′)	107.6(5)	C(4′)—C(3′)—C(16)	126.7(6)
C(1′)—C(2′)—C(3′)	108.0(5)	C(1)—C(6)—C(7)	117.1(6)
C(2′)—C(3′)—C(4′)	107.3(5)	C(6)—C(7)—C(8)	116.7(7)
C(3′)—C(4′)—C(5′)	108.4(6)	C(7)—C(8)—C(9)	118.7(7)
C(4′)—C(5′)—C(1′)	108.5(6)	C(8)—C(9)—C(1′)	121.0(7)
C(5)—C(1)—C(6)	123.3(6)	C(2)—C(10)—C(11)	116.7(6)
C(2)—C(1)—C(6)	128.3(6)	C(10)—C(11)—C(12)	116.8(6)
C(1)—C(2)—C(10)	126.8(5)	C(11)—C(12)—C(2′)	118.2(6)
C(3)—C(2)—C(10)	125.3(5)	C(3)—C(13)—C(14)	114.0(6)
C(2)—C(3)—C(13)	128.4(6)	C(13)—C(14)—C(15)	117.8(7)
C(4)—C(3)—C(13)	125.3(6)	C(14)—C(15)—C(16)	119.4(7)
		C(15)—C(16)—C(3′)	117.0(6)

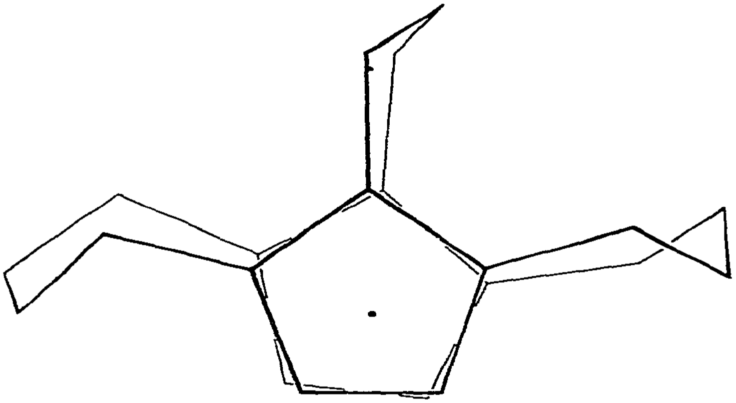

Fig. 2. Projection of the whole molecule on the plane defined by the Fe atom and an intersection of the two cyclopentadienyl least-squares planes.

found in [4][4][4][4](1,2,3,4)ferrocenophane trimer (0.15 Å in averaged value) [10] whose all tetramethylene bridges were in half-chair conformations. It is interesting that the α-carbons of tetramethylene chains in multibridged ferrocenophanes are displaced to the *exo* direction of the Cp plane in spite of the deviation toward the Fe atom of all H atoms in crystals of ferrocene [11].

The tilting (dihedral angle) of the two Cp rings in ferrocenophanes reflects the lengths of the methylene chains connecting the rings [3a—e]. The value (10.4°) of the angle in compound I is very similar to those of [3]ferrocenophane derivatives (10—11°) [3a,f], and smaller than that of a [3][3][3](1,2,3)-ferrocenophane possessing three trimethylene bridges at neighbouring positions (12.5°) [4b]. That is, the two tetramethylene bridges surrounding the tri-

TABLE 4

LEAST-SQUARES PLANES THROUGH THE CYCLOPENTADIENYL RINGS AND DEVIATIONS OF ATOMS (Å) FROM THE PLANES. X, Y and Z are coordinates referred to the a, b and c axes in Å

Atom	Deviation	Atom	Deviation
$-0.7770X + 0.0672Y - 0.6259Z + 0.1986 = 0$			
C(1)	0.003	C(6) [a]	0.101
C(2)	−0.004	C(10) [a]	−0.121
C(3)	0.004	C(13) [a]	0.027
C(4)	−0.003	H(4) [a]	−0.019
C(5)	0.000	H(5) [a]	−0.004
$-0.6510X + 0.0998Y - 0.7524Z + 3.047 = 0$			
C(1′)	−0.003	C(9) [a]	−0.165
C(2′)	0.008	C(12) [a]	0.078
C(3′)	−0.009	C(16) [a]	−0.030
C(4′)	0.007	H(4′) [a]	0.005
C(5′)	−0.002	H(5′) [a]	0.031

[a] Atoms not included in the calculation of the planes.

methylene one scarcely contribute to the tilting of the Cp rings. The distances of the Fe atom from the Cp ring carbons at the 2- and 2′-positions connected with the trimethylene bridge is obviously shorter than those at the others.

The structural characteristics of the ferrocenophane I are summarized as follows: (i) Almost all of the bond lengths and angles, and the tilting of Cp rings are in normal ranges in comparison with other ferrocenophanes [3,4,6,10, 12], (ii) the trimethylene bridge plays a major part in determining the conformation of the molecule, and (iii) the tetramethylene chains which are too long to connect the two Cp rings are adjusted to bridge without excessive strain by the *exo* deviation of the α-carbons from the Cp ring planes.

The result of the X-ray crystal analysis of I suggests that the presence of abnormal bond lengths and angles in [4][4][3][4](1,2,3,4)ferrocenophane [6] is caused by the bridging tetramethylene chain at the 1,1′-positions.

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