Crystal and Molecular Structure of [1.1.1]Ferrocenophane

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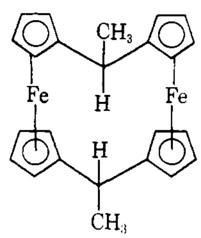
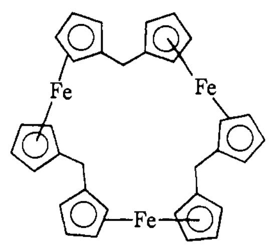
Abstract: The crystal and molecular structure of [1.1.1]ferrocenophane, $(C_5H_4CH_2C_5H_4)_3Fe_3$, has been determined in a three-dimensional X-ray crystallographic study. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with unit cell dimensions $a = 6.008$ (3), $b = 18.906$ (9), $c = 22.53$ (1) Å, $\beta = 108.52$ (1)°. The observed density of 1.63 (3) g/cm³ is in agreement with that calculated on the basis of four trimers per unit cell, $\rho_{calcd} = 1.62$ g/cm³. From 1139 independent observable reflections collected by diffractometer, the structure was solved and has been refined by least-squares techniques to a final value of the discrepancy index, R_1, 0f 0.030. The molecular geometry consists of three ferrocene units joined by methylene groups to form a single large ring. Each iron atom is sandwiched between two cyclopentadienyl rings of two different dicyclopentadienylmethane ligands. The resulting triangle of iron atoms is nearly equilateral, with an average Fe–Fe distance of 6.09 ± 0.09 Å. The bond distances and angles within the three individual ferrocene units are normal. Various idealized conformational structures for the molecule are presented and the actual geometry is shown to be a hybrid of these. Nonbonded hydrogen–hydrogen repulsions are concluded to be the predominant factor in determining the conformation of the lower members of the [1ⁿ]ferrocenophanes.

The formation of a series of cyclic, ferrocenic oligomers composed of alternating ligands and iron atoms results from the reaction of the dianion of dicyclopentadienylmethane with iron(II) chloride.[1] The detailed geometry of the resulting macrocyclic rings is of interest, since various conformational isomers of the methylene-linked ferrocene groups are possible. The molecular structure of a dimeric member of the series, 1,12-dimethyl[1.1]ferrocenophane (I), has been



I



II

previously determined in a single-crystal X-ray diffraction study.[2] The structure of trimeric [1.1.1]ferrocenophane (II) is described in the present report.

Collection and Reduction of X-Ray Data

The [1.1.1]ferrocenophane, $C_{33}H_{30}Fe_3$, was prepared as previously described.[1] Orange crystals suitable for X-ray structure analysis were obtained by recrystallization from carbon disulfide solution. A crystal was mounted along c^* on a goniometer head with a glass whisker and clear nail polish. Alignment was carried out on the precession camera using unfiltered Mo Kα radiation (λ 0.7107 Å). Systematic absences ($k \neq 2n$) along b^* (0k0) and in the h0l plane ($l \neq 2n$) indicated the probable space group to be $P2_1/c$.[3]

A second crystal, mounted along a^*, was aligned on a Picker four-circle automated X-ray diffractometer. The unit cell parameters were refined to convergence by means of a least-squares program in which the calculated values for χ, ϕ, and 2θ were fit to the observed angle settings of 21 independent, nonaxial reflections.[4] The results are $a = 6.008$ (3), $b = 18.906$ (9), $c = 22.53$ (1) Å, and $\beta = 108.52$ (1)° at room temperature (*ca.* 23 (2)°). The experimental density ($\rho = 1.63$ (3) g/cm³), measured pycnometrically in carbon tetrachloride, and the calculated volume ($V = 2427$ Å³) require four trimeric molecules per unit cell. The calculated density of 1.62 g/cm³ is in agreement with that observed.

Intensity data were collected on the Picker diffractometer using a crystal in the shape of a rod with an approximately heptagonal cross section, 0.14 × 0.18 mm. The length of the rod, 0.26 mm, corresponded to the mounting axis of the crystal, a^*. Data were obtained using Ni-filtered Cu K$\bar{\alpha}$ (λ 1.5418 Å) radiation at 23 ± 2°. Pulse-height analysis was used, increasing the peak-to-background ratio by a factor of 2.4. The symmetrically varying receiving aperture was set to a 3.0 × 3.0 mm opening. The scan range was 1.25 in 2θ plus the Kα_1 − Kα_2 difference, and the takeoff angle was 2.4°. Other experimental details were as reported previously.[5]

All of the independent reflections within the hkl, $hk\bar{l}$ quadrant of the sphere $\theta < 39°$ were measured in 3 days. Three independent standard reflections, well separated in reciprocal space, were measured with maximum intensity variations of ±1.6 to ±3.4%.

The raw data were corrected for background, use of attenuators, and Lorentz and polarization effects, but secondary extinction was not calculated because of the relatively low number of high-intensity reflections. The absorption correction ($\mu = 140$ cm⁻¹) was calculated by the program ACAC-3[4] on the basis of the exact crystal

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(1) T. J. Katz, N. Acton, and G. Martin, *J. Amer. Chem. Soc.*, **91**, 2804 (1969).

(2) J. S. McKechnie, B. Bersted, I. C. Paul, and W. E Watts, *J. Organometal. Chem.*, **8**, P29 (1967).

(3) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1962, p 99.

(4) Programs for the IBM 360-91 computer used in this work include local versions of MODE 1, the Brookhaven diffractometer setting program and cell constant and orientation refinement program; GSET, the Prewitt diffractometer setting program; ACAC-3, a revised version of the Prewitt absorption-correction and data-reduction program; XDATA, the Brookhaven Wilson plot and scaling program; the Zalkin Fourier program, FORDAP; the Busing–Martin–Levy structure-factor calculation and least-squares refinement program, ORFLS; and the Busing–Martin–Levy error-function program, ORFFE.

(5) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 6, 2223 (1967).

Table I. Final Positional and Thermal Parameters of the Atoms[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe_1	0.1745 (2)	0.2862 (1)	0.13013 (5)	20.9 (5)	1.46 (4)	1.04 (3)	−0.3 (1)	1.2 (1)	0.16 (3)
Fe_2	0.3375 (2)	0.4271 (1)	0.38325 (4)	21.7 (5)	1.19 (4)	0.97 (3)	−0.5 (1)	1.5 (1)	0.03 (3)
Fe_3	0.4294 (2)	0.1133 (1)	0.37838 (5)	20.4 (5)	1.25 (4)	1.20 (3)	0.0 (1)	1.5 (1)	0.01 (3)
C_1	0.073 (2)	0.3900 (3)	0.1219 (5)	24 (4)	0.9 (3)	2.0 (4)	0.4 (8)	4 (1)	−0.8 (2)
C_2	0.206 (2)	0.3750 (4)	0.0819 (4)	20 (4)	1.0 (3)	1.3 (3)	0.8 (8)	0 (1)	0.2 (3)
C_3	0.431 (2)	0.3500 (4)	0.1184 (5)	30 (6)	1.8 (3)	1.1 (3)	−1 (1)	4 (1)	0.5 (2)
C_4	0.438 (2)	0.3494 (3)	0.1827 (5)	8 (4)	1.2 (3)	2.0 (4)	−0.2 (8)	2.3 (9)	0.2 (2)
C_5	0.216 (2)	0.3752 (4)	0.1854 (4)	25 (5)	1.5 (3)	0.3 (3)	−2.0 (9)	0 (1)	0.1 (2)
C_6	0.128 (1)	0.3808 (4)	0.2407 (3)	30 (4)	1.5 (3)	0.3 (2)	−1.0 (9)	1.0 (8)	0.6 (2)
C_7	0.259 (2)	0.4366 (4)	0.2884 (3)	33 (6)	0.3 (3)	1.1 (2)	3 (1)	4 (1)	0.3 (2)
C_8	0.506 (2)	0.4436 (4)	0.3178 (4)	10 (5)	1.9 (4)	1.0 (2)	−1.4 (9)	0.7 (8)	−0.1 (3)
C_9	0.545 (2)	0.5017 (5)	0.3609 (4)	33 (5)	1.1 (3)	0.7 (2)	−3 (1)	1.5 (8)	−0.3 (3)
C_{10}	0.320 (2)	0.5311 (4)	0.3569 (4)	36 (5)	0.9 (3)	1.8 (3)	3 (1)	5 (1)	0.6 (3)
C_{11}	0.143 (2)	0.4911 (5)	0.3113 (4)	21 (4)	1.3 (3)	0.7 (2)	0 (1)	1 (1)	0.4 (2)
C_{12}	0.515 (2)	0.3827 (5)	0.4684 (4)	19 (4)	1.2 (3)	1.3 (3)	0 (1)	1.6 (9)	0.7 (3)
C_{13}	0.312 (2)	0.4204 (4)	0.4713 (4)	31 (4)	1.4 (3)	0.9 (3)	0 (1)	3 (1)	0.3 (2)
C_{14}	0.113 (2)	0.3903 (5)	0.4272 (4)	16 (4)	1.7 (3)	1.6 (3)	0 (1)	1 (1)	0.8 (2)
C_{15}	0.186 (2)	0.3331 (4)	0.3959 (4)	20 (5)	1.3 (3)	1.1 (2)	1.8 (9)	3.1 (9)	0.2 (2)
C_{16}	0.438 (2)	0.3279 (4)	0.4218 (4)	31 (6)	0.3 (3)	1.0 (3)	−1 (1)	2.3 (9)	0.1 (3)
C_{17}	0.597 (1)	0.2778 (4)	0.403 (4)	18 (3)	1.2 (3)	1.5 (2)	1.3 (9)	2.0 (8)	0.0 (3)
C_{18}	0.593 (2)	0.2027 (4)	0.4261 (3)	17 (4)	0.3 (3)	1.0 (2)	1 (1)	−0.5 (8)	0.1 (2)
C_{19}	0.762 (1)	0.1514 (6)	0.4220 (3)	26 (4)	1.0 (3)	1.0 (2)	0 (1)	−1.1 (7)	0.1 (2)
C_{20}	0.717 (2)	0.0875 (5)	0.4514 (4)	21 (4)	2.2 (5)	1.0 (2)	3 (1)	−0.8 (8)	−0.2 (3)
C_{21}	0.521 (2)	0.1004 (5)	0.4732 (3)	43 (5)	0.4 (4)	1.2 (2)	0 (1)	0.7 (9)	0.1 (2)
C_{22}	0.443 (1)	0.1710 (5)	0.4570 (3)	26 (4)	1.0 (4)	0.7 (2)	−3 (1)	1.7 (8)	−0.3 (2)
C_{23}	0.434 (2)	0.0626 (6)	0.2975 (4)	25 (4)	0.8 (3)	1.2 (3)	3 (1)	−2.2 (9)	−0.2 (2)
C_{24}	0.317 (2)	0.0212 (5)	0.3323 (4)	39 (5)	0.8 (3)	0.9 (2)	−2 (2)	0.3 (8)	−0.2 (3)
C_{25}	0.123 (2)	0.0604 (7)	0.3386 (4)	26 (5)	1.6 (4)	1.8 (3)	−1 (1)	1.2 (8)	−0.3 (3)
C_{26}	0.122 (2)	0.1258 (6)	0.3088 (5)	22 (6)	1.6 (6)	1.8 (3)	3 (1)	2 (1)	0.1 (3)
C_{27}	0.308 (2)	0.1270 (5)	0.2832 (3)	21 (4)	2.8 (5)	0.2 (2)	−4 (1)	−0.8 (8)	0.2 (3)
C_{28}	0.366 (2)	0.1895 (4)	0.2477 (4)	37 (4)	2.5 (3)	1.2 (3)	0 (1)	−1 (1)	0.4 (2)
C_{29}	0.204 (2)	0.1956 (4)	0.1798 (4)	29 (6)	0.9 (3)	1.1 (3)	−1.6 (9)	1 (1)	0.1 (2)
C_{30}	−0.035 (2)	0.2185 (4)	0.1580 (6)	18 (5)	1.0 (3)	2.4 (4)	−1.7 (9)	2 (1)	0.2 (2)
C_{31}	−0.108 (2)	0.2212 (4)	0.0911 (5)	24 (5)	1.9 (3)	1.0 (4)	−1 (1)	2 (1)	0.2 (2)
C_{32}	0.082 (2)	0.2000 (4)	0.0719 (4)	27 (4)	1.7 (3)	1.6 (3)	−0.3 (9)	3 (1)	−0.6 (2)
C_{33}	0.277 (2)	0.1842 (4)	0.1264 (6)	14 (4)	1.5 (3)	2.0 (3)	−0.6 (9)	1 (1)	−0.5 (2)
H_1	−0.09 (2)	0.410 (4)	0.111 (4)						
H_2	0.15 (2)	0.381 (4)	0.035 (5)						
H_3	0.58 (1)	0.332 (4)	0.099 (4)						
H_4	0.58 (2)	0.332 (4)	0.224 (4)						
H_{6a}	−0.05 (2)	0.393 (4)	0.226 (4)						
H_{6b}	0.14 (1)	0.331 (4)	0.267 (4)						
H_8	0.65 (2)	0.414 (4)	0.312 (4)						
H_9	0.73 (2)	0.522 (4)	0.391 (4)						
H_{10}	0.28 (2)	0.572 (4)	0.380 (4)						
H_{11}	−0.04 (2)	0.501 (4)	0.301 (4)						
H_{12}	0.69 (2)	0.395 (4)	0.490 (4)						
H_{13}	0.32 (2)	0.463 (4)	0.498 (4)						
H_{14}	−0.07 (2)	0.407 (4)	0.417 (4)						
H_{15}	0.10 (1)	0.297 (4)	0.352 (4)						
H_{17a}	0.54 (2)	0.277 (4)	0.359 (4)						
H_{17b}	0.77 (2)	0.291 (4)	0.422 (4)						
H_{19}	0.98 (2)	0.153 (7)	0.315 (4)						
H_{20}	0.80 (2)	0.044 (5)	0.451 (4)						
H_{21}	0.45 (2)	0.063 (5)	0.491 (4)						
H_{22}	0.31 (1)	0.203 (5)	0.462 (4)						
H_{23}	0.58 (1)	0.041 (4)	0.287 (3)						
H_{24}	0.37 (1)	−0.032 (5)	0.349 (4)						
H_{25}	0.00 (1)	0.031 (4)	0.362 (4)						
H_{26}	0.04 (2)	0.177 (5)	0.306 (4)						
H_{28a}	0.55 (2)	0.175 (4)	0.249 (4)						
H_{28b}	0.32 (1)	0.233 (4)	0.269 (4)						
H_{30}	−0.15 (2)	0.235 (4)	0.181 (4)						
H_{31}	−0.26 (2)	0.234 (4)	0.062 (4)						
H_{32}	0.12 (1)	0.200 (4)	0.026 (4)						
H_{33}	0.44 (2)	0.172 (4)	0.128 (4)						

[a] Atoms are labeled as indicated in Figure 1. Hydrogen atoms are labeled to correspond to the carbon atoms to which they are attached. Standard deviations, in parentheses, occur in the last significant figure for each parameter. [b] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Values reported are times 10^3. Hydrogen-atom isotropic thermal parameters were set equal to 3.0 and were not refined.

shape as a seven-faced rod described by nine boundary planes. Comparison of the intensity of the (200) reflection (χ = 90.0°) as a function of the angle ϕ (24 positions) gave agreement with the calculated intensities to within ±6%. The transmission factors ranged from 0.12 to 0.21. The data were placed on an approximately absolute scale through a modification of Wilson's method.[4] From the resulting values for $|F_o|$ and $|F_o|^2$, the structure was solved through the usual Patterson, Fourier, and least-squares refinement processes (see below). Scattering factor tables for the neutral atoms were obtained from the "International Tables for X-Ray Crystallography."[6] The calculated structure factors were appropriately[7] corrected for the effect of anomalous dispersion of the iron atoms. The hydrogen-atom scattering factors were those of Mason and Robertson.[8] Weights, $w = 4F^2/\sigma^2(F^2)$, where $\sigma(F^2)$ is the standard deviation of F^2 obtained from $\sigma(I)$ after absorption and Lp corrections, were applied. $\sigma(I)$ is the standard deviation of I, estimated[9] to be $\sigma(I) = [E + (T_E/2T_B)^2 \cdot (B_1 + B_2) + (\epsilon I)^2]^{1/2}$. In the above expression, E is total counts in the peak plus background observed for a scan time T_E, B_1, and B_2 are the background counts observed for time T_B at each extreme of the scan, and ϵ is the "ignorance factor,"[9c] set equal to 0.04, to prevent excessively high weight being given to the strong reflections. Of the 1383 reflections measured, those for which $I < 3\sigma(I)$ were excluded from the refinement (241 reflections). Although no systematic attempt was made to correct for secondary extinction, the (004), (032), and $(11\bar{2})$ reflections were excluded from the final refinement cycles since they appeared to be significantly affected by secondary extinction. Subsequent calculations and refinement were carried out on the remaining 1139 reflections.

Determination of the Structure

Using the corrected data, a Patterson map was computed[4] and solved for the positions of two iron atoms (x, y, z in the general position of the space group $P2_1/c$). The coordinates of the iron atoms were then refined along with the overall scale factor in a least-squares calculation and the results were used to determine a set of phased structure factors for a difference Fourier synthesis. The first difference map readily revealed the third iron atom and four carbon atoms. A second map yielded coordinates of additional carbon atoms. Reiteration of the refinement-difference map procedure gave positions for the remaining carbon atoms. Refinement of the positional parameters and isotropic temperature factors for the 3 iron and 33 carbon atoms converged at values of 0.064 and 0.080 for the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w \cdot (|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, respectively. At this stage, a difference Fourier map showed only a small apparent anisotropic thermal motion for most of the atoms; a search for hydrogen atoms, all but six of which are positionally constrained by bonding to ring carbons, readily revealed the coordinates of all 30 hydrogen atoms of the asymmetric unit. Refinement was continued in which anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were assigned to all iron and carbon atoms. After several cycles of anisotropic refinement[10] of iron and carbon in the absence of hydrogen atoms the value for R_1 was reduced to 0.051 and that of R_2 to 0.064. The addition of all hydrogen atoms to the model and refinement of their positional parameters only (isotropic thermal B's were fixed at 3.0) further reduced the values for R_1 and R_2 which converged at 0.030 and 0.036, respectively. Application of the Hamilton R-factor significance test[11] indicated the location and refinement of the hydrogen atoms to be significant at the 99.5% confidence level. A final difference Fourier map had no region of electron density greater than 0.3 electron/Å^3, or about 0.08 times the peak height of a typical carbon atom.

The atomic positional and thermal parameters, with their standard deviations as derived from the inverse matrix of the last least-squares refinement cycle, are given in Table I.[12] The root-mean-square amplitudes of vibration derived from the atomic anisotropic thermal parameters are summarized in Table II. A drawing of the structure showing the atom-labeling

Table II. Root-Mean-Square Amplitudes of Vibration (Å)[a,b]

Atom	Minimum	Intermediate	Maximum
Fe_1	0.147 (2)	0.169 (2)	0.189 (2)
Fe_2	0.142 (3)	0.151 (3)	0.192 (2)
Fe_3	0.150 (2)	0.167 (2)	0.185 (2)
C_1	0.07 (5)	0.18 (2)	0.24 (2)
C_2	0.12 (3)	0.16 (2)	0.22 (2)
C_3	0.11 (4)	0.18 (2)	0.24 (2)
C_4	0.10 (4)	0.15 (2)	0.22 (2)
C_5	0.08 (5)	0.15 (2)	0.23 (2)
C_6	0.04 (7)	0.18 (1)	0.23 (1)
C_7	0.04 (7)	0.11 (2)	0.25 (2)
C_8	0.12 (3)	0.16 (2)	0.19 (2)
C_9	0.11 (4)	0.14 (2)	0.25 (2)
C_{10}	0.11 (2)	0.15 (2)	0.26 (2)
C_{11}	0.11 (2)	0.16 (2)	0.20 (2)
C_{12}	0.10 (2)	0.18 (2)	0.20 (2)
C_{13}	0.11 (2)	0.16 (2)	0.23 (2)
C_{14}	0.12 (2)	0.16 (2)	0.23 (2)
C_{15}	0.11 (3)	0.14 (2)	0.21 (2)
C_{16}	0.07 (4)	0.15 (2)	0.23 (2)
C_{17}	0.12 (2)	0.18 (2)	0.19 (2)
C_{18}	0.06 (6)	0.14 (2)	0.21 (2)
C_{19}	0.13 (2)	0.14 (2)	0.25 (1)
C_{20}	0.13 (2)	0.16 (2)	0.26 (2)
C_{21}	0.08 (5)	0.16 (2)	0.28 (2)
C_{22}	0.09 (3)	0.13 (2)	0.23 (1)
C_{23}	0.08 (5)	0.13 (2)	0.28 (2)
C_{24}	0.11 (2)	0.15 (2)	0.27 (2)
C_{25}	0.16 (2)	0.20 (2)	0.23 (2)
C_{26}	0.13 (3)	0.21 (1)	0.22 (2)
C_{27}	0.06 (4)	0.15 (2)	0.27 (2)
C_{28}	0.15 (2)	0.22 (1)	0.27 (1)
C_{29}	0.12 (2)	0.16 (2)	0.23 (2)
C_{30}	0.11 (2)	0.19 (2)	0.23 (2)
C_{31}	0.16 (4)	0.19 (2)	0.25 (2)
C_{32}	0.14 (2)	0.20 (2)	0.22 (2)
C_{33}	0.14 (2)	0.17 (2)	0.23 (2)

[a] Taken along the principal axes of the thermal ellipsoids. The orientation of these axes may be worked out from the data of Table I and the unit cell parameters. [b] See footnote a, Table I.

(6) See ref 3, Vol. III, 1962, p 201 ff.
(7) See ref 3, Vol. III, 1962, p 213 ff.
(8) R. Mason and G. Robertson in "Advances in Structure Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience, New York, N. Y., 1966, p 57.
(9) (a) G. M. Brown and H. A. Levy, *J. Phys. (Paris)*, **25**, 497 (1964); (b) R. D. Ellison and H. A. Levy, *Acta Crystallogr.*, **19**, 260 (1965); (c) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).
(10) Because of dimension limitations of the least-squares refinement program used, it was necessary to carry out the anisotropic refinement of the asymmetric unit in sections. Initial refinement of the heavy atoms was performed with "random" groupings of carbon atoms; in the final stages, the molecule was divided into three "ferrocene groups," each refined with its adjacent methylene groups.
(11) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
(12) A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Reprint Office, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

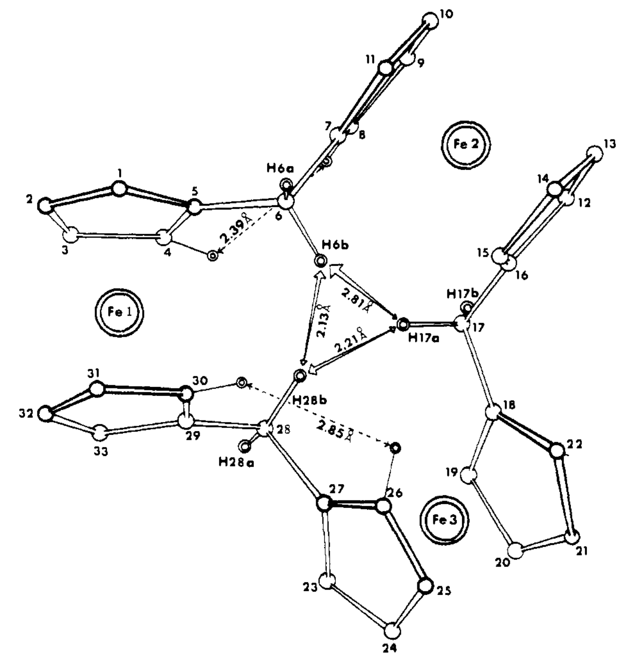

Figure 1. The molecular structure of [1.1.1]ferrocenophane as viewed along the cell axis a. Ring hydrogen atoms, numbered according to their carbons, are shown only for cases of significant intramolecular interactions.

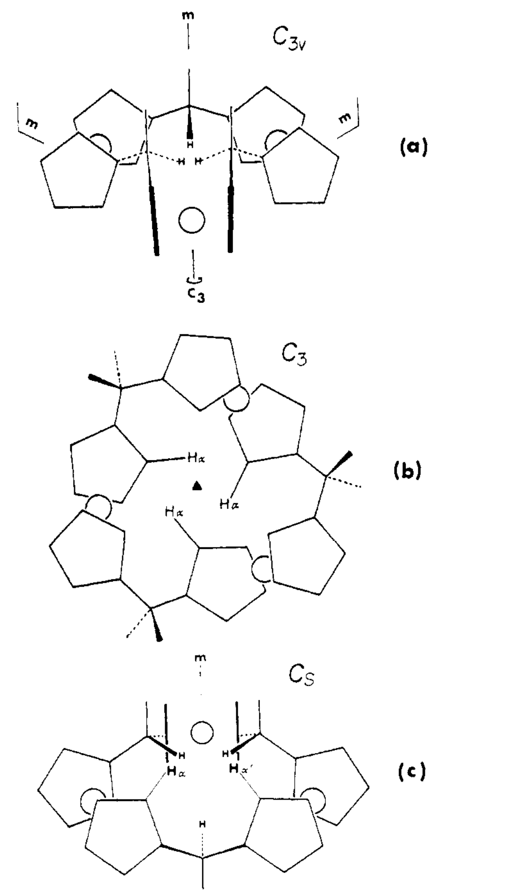

Figure 2. Possible idealized trimer conformations and their point group symmetry. Mirror planes are indicated as m. Strongly interacting hydrogen atoms are shown.

scheme appears in Figure 1. Intramolecular bond distances and interbond angles are listed in Table III.

General Description of the Structure. The molecular structure of [1.1.1]ferrocenophane (II) consists of three iron atoms approximating the vertices of an equilateral triangle of which three dicyclopentadienylmethane ligands form the sides (Figure 1). The average iron–iron distance is 6.09 ± 0.09 Å (Table IV) and the mean iron–ring distance is 1.65 ± 0.01 Å. The plane formed by the three iron atoms makes an angle of 24.6° with the principal axis of ferrocene 1 (containing Fe_1), 17.6° with ferrocene 2, and 28.2° with ferrocene 3. Further details are presented in Table IV.

Figure 2 depicts three possible idealized conformations of the trimer which have point group symmetry higher than C_1. A fourth conformation, having D_{3h} symmetry, is not shown because it requires severe bond strain at the three methylene carbon atoms as well as extremely unfavorable nonbonded hydrogen-atom interactions. The structure having C_{3v} symmetry may be referred to as the "crown" conformation, by analogy to the nomenclature adopted for 1,4,7-cyclononatriene[13] and related molecules.[14] The closest nonbonded hydrogen atom contacts in the crown conformer occur at the center of the molecule, among three methylene protons (Figure 2a). This steric interaction may be relieved by symmetrically moving the methylene carbon atoms away from the C_3 axis, which results in the loss of the three vertical mirror planes to produce the C_3 conformation shown in Figure 2b. The nonbonded repulsion interaction among three of the α ring hydrogen atoms effectively provides a limit to further separation of methylene groups by symmetric distortion of the crown conformer. A conformation having idealized C_s symmetry is shown in Figure 2c. Here some lessening of the central methylene hydrogen atom contact has been achieved, but the H_α–$H_{\alpha'}$ intraligand nonbonded repulsions are quite severe, with the H_α–$H_{\alpha'}$ contact distances being less than 2 Å.

The actual conformation found in the present investigation for [1.1.1]ferrocenophane may be achieved from a geometry somewhat between those in Figures 2a and 2b by inverting the conformation of one of the three methylene groups, as in going from the C_{3v} to the C_s idealized symmetry. The resultant structure (Figure 1) is similar to that of Figure 2c, in which the approximate mirror plane passes through C_6 and Fe_3, perpendicular to the plane of the iron-atom triangle, but is sufficiently distorted to have only C_1 molecular symmetry.[15] Although in the absence of extensive calculations it is of course difficult to determine whether such a conformation represents a repulsive potential energy minimum, studies with molecular-framework models confirm that interproton contacts in the observed structure are less severe than in the three idealized conformations depicted in Figure 2.

A summary of closest hydrogen–hydrogen contacts appears in Table IV. An interesting feature of the central portion of the molecule is the short distance between the methylene hydrogen atoms 6b, 17a, and 28b (Figure 1). Two of the values, 2.1 ± 0.1 Å between H_{6b} and H_{28b}, and 2.2 ± 0.1 Å. between H_{17a} and H_{28b}, are

(13) See P. Radlick and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 344 (1963); K. G. Untch and R. J. Kurland, *ibid.*, **85**, 346 (1963).

(14) A. S. Lindsey, *J. Chem. Soc.*, 1685 (1965); R. C. Cookson, B. Halton, and I. D. R. Stevens, *ibid.*, *B*, 767 (1968).

(15) Display of the molecule on the cathode-ray screen of the ADAGE computer greatly facilitated the search for noncrystallographic symmetry elements. We thank Mr. Joel Sussman for assistance.

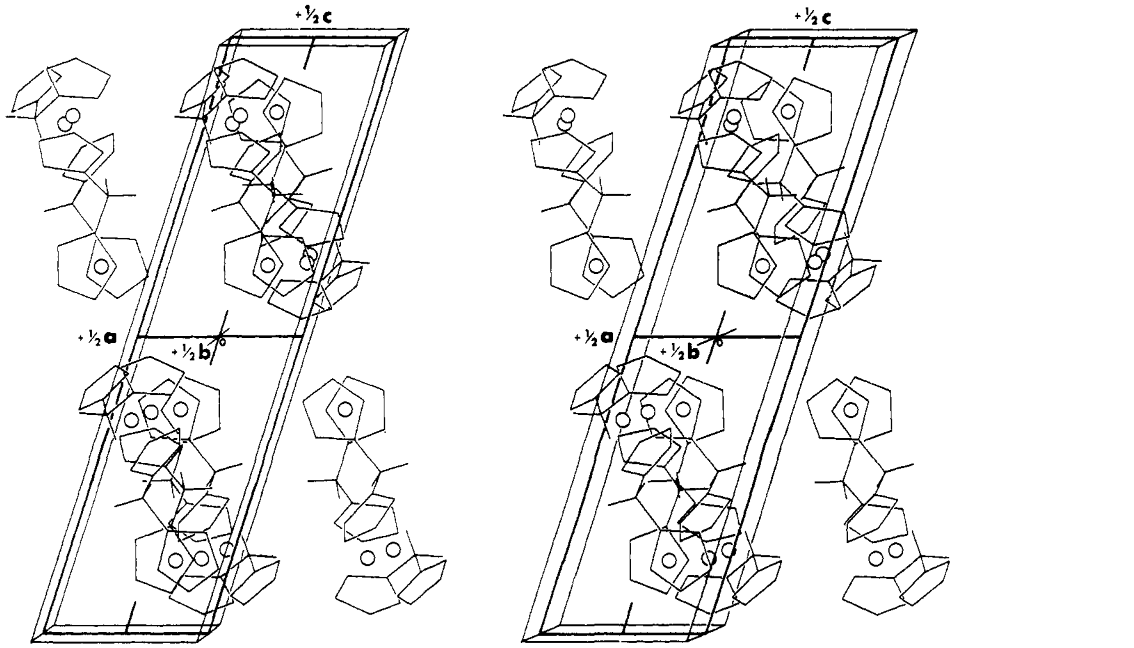

Figure 3. Stereoscopic view of the crystal packing. Molecules shown outside the unit cell are those in the x, y, z and x̄, ȳ, z̄ equivatent positions translated by $+a$ and $-a$, respectively.

Table III. Selected Geometric Features of Dicyclopentadienylmethane Ligands[a]

	Bond distances, Å Minimum	Maximum	Mean (σ mean)
C–C			
Ring A[b]	1.41 (1)	1.44 (1)	1.43 (1)
Ring B	1.40 (1)	1.43 (1)	1.42 (1)
Ring C	1.42 (1)	1.44 (1)	1.43 (1)
Ring D	1.41 (1)	1.45 (1)	1.43 (1)
Ring E	1.42 (1)	1.44 (1)	1.43 (1)
Ring F	1.41 (1)	1.44 (1)	1.42 (1)
Aliphatic	1.497 (7)	1.54 (1)	1.52 (1)
C–H			
Ring A	1.01 (8)	1.15 (9)	1.07 (7)
Ring B	0.98 (9)	1.12 (8)	1.02 (7)
Ring C	1.01 (8)	1.16 (9)	1.09 (6)
Ring D	0.99 (8)	1.17 (9)	1.08 (8)
Ring E[c]	0.95 (9)	1.05 (8)	0.99 (4)
Ring F	1.09 (9)	1.14 (9)	1.11 (2)
Aliphatic	0.94 (8)	1.13 (8)	1.05 (7)
C–Fe			
Ring A	2.033 (7)	2.060 (7)	2.04 (1)
Ring B	2.024 (7)	2.055 (7)	2.04 (1)
Ring C	2.045 (7)	2.062 (7)	2.053 (8)
Ring D	2.036 (8)	2.075 (7)	2.05 (1)
Ring E	2.030 (7)	2.076 (7)	2.05 (2)
Ring F	2.021 (8)	2.065 (8)	2.04 (2)
	Bond angles, deg Minimum	Maximum	Mean (σ mean)[d]
C–C–C			
Ring A	107.0 (7)	109.0 (8)	108.0 (7)
Ring B	107.5 (8)	108.6 (8)	108.0 (4)
Ring C	107.5 (7)	108.7 (7)	108.0 (5)
Ring D	107.2 (7)	109.2 (8)	108.0 (8)
Ring E	107.4 (7)	108.4 (6)	108.0 (4)
Ring F	106.1 (8)	109.2 (8)	108 (1)
C–CH_2–C	113.1 (6)	114.5 (6)	113.8 (6)

[a] *Cf.* footnote *a*, Table I. [b] Ring labeling is as follows: A, C_1–C_5, B, C_{29}–C_{33}; C, C_7–C_{11}; D, C_{12}–C_{16}; E, C_{18}–C_{22}; F, C_{23}–C_{27}. [c] Positional parameters of H_{19}, possibly spurious, and are not included in this calculation. [d] The mean value of 108° is required by geometry in planar five-membered rings.

somewhat less than the 2.4-Å value[16] commonly quoted for the van der Waals distance between two nonbonded hydrogen atoms. By comparison, the closest interaction between two α ring protons is 2.4 ± 0.1 Å between H_4 and H_8, both of which are in the same dicyclopentadienylmethane ligand. The observation[1] that carbon disulfide solutions of II exhibit a singlet in the proton nmr spectrum for all methylene protons suggests that in solution the molecule may be fluxional,

Table IV. Summary of Major Nonbonded Intramolecular Interactions[a]

A. Distance between Iron Atoms, Å	
Fe_1–Fe_2	6.085 (2)
Fe_2–Fe_3	5.963 (3)
Fe_1–Fe_3	6.235 (2)
Av Fe–Fe	6.09 ± 0.09
B. Distance between Selected Hydrogen Atoms, Å	
H_{6b}–H_{28b}	2.1 (1)
H_{6b}–H_{17a}	2.8 (1)
H_{17a}–H_{28b}	2.2 (1)
H_4–H_8	2.4 (1)
H_{26}–H_{30}	2.9 (1)
H_{15}–H_{22}	3.0 (1)
C. Ring Splaying in Ferrocene Groups;[b] ϕ, Deg[c]	
Ferrocene 1	3.9 (4)
Ferrocene 2	2.6 (5)
Ferrocene 3	4.6 (4)
D. Angle between Ferrocene Major Axis[d] and Plane of Iron Atoms, Deg	
Ferrocene 1	25 (1)
Ferrocene 2	18 (1)
Ferrocene 3	28 (1)

[a] *Cf.* footnote *a*, Table I. [b] Ferrocenes are numbered according to their iron atoms. [c] ϕ is the tilt angle. *Cf.* ref 17. [d] Major axis of a ferrocene is the average normal to the two rings of the group.

(16) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

with rapid intramolecular conformational equilibria averaging the magnetic environments of all six methylenic hydrogen atoms.

The geometry of the three individual ferrocene moieties is normal[17] (Tables III and IV), with ϕ (dihedral angle between the two five-membered rings) values ranging from 2.6 to 4.6°. The relative rotational orientation angles, ω,[17] are 19° for ferrocene 1, 11.5° for ferrocene 2, and 24.5° for ferrocene 3; the analogous angles measured between the CH_2 substitutents of the rings are 53, 61.5, and 24.5°, respectively.

Previous studies of polyferrocene units by X-ray diffraction methods have been reported.[2,18] In the only other [1^n]ferrocenophane to be structurally characterized, 1,12-dimethyl[1.1]ferrocenophane,[2] the molecule was found to be twisted by 31° from the idealized conformation (I) in order to relieve hydrogen-hydrogen interactions of the type H_α–$H_{\alpha'}$. The resultant proton–proton contact distance between nearest α hydrogen atoms of the same ligand was increased to 2.0 Å. A point not emphasized by the authors is that the analogous distance between α protons on *different* ligands must also be close to 2.0 Å, and that a greater degree of twist would thus diminish the intraligand interactions only at the expense of increasing interligand repulsions. It therefore appears that the minimization of intramolecular nonbonded hydrogen contacts is the most important factor controlling the molecular conformation of the [1^n]ferrocenophanes, at least for small values of n.

Intermolecular Geometry and Crystal Packing. The packing of four trimeric molecules in the unit cell is illustrated in Figure 3. It is evident from the figure that the crystal lattice is composed of "layers" of relatively flat ferrocenophanes stacked approximately along a. The crystals were observed to be readily cleaved perpendicular to this direction, which appears to be a macroscopic consequence of the layered packing of the molecules in the lattice.

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(17) See, for example, M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 716 (1969), Table VIII.
(18) M. R. Churchill and J. Wormald, *ibid.*, **8**, 1970 (1969), and references cited therein.

Enthalpies of Formation of Globular Molecules. I. Adamantane and Hexamethylenetetramine[1]

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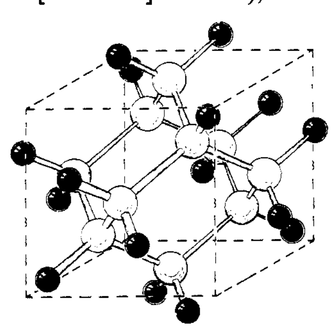
Abstract: Enthalpies of combustion at 298.15°K have been measured for crystalline adamantane (tricyclo-[3.3.1.1^{3,7}]decane) and hexamethylenetetramine (1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane). The derived enthalpies of formation for the two compounds in the crystalline state, $\Delta H_f°$(c), at 298.15°K are -47.14 ± 0.19 and $+29.65 \pm 0.18$ kcal/mol, respectively. Use of adjuvant data for both compounds permits evaluation of corresponding enthalpy values, $\Delta H_f°$(g), at 298.15°K for the gaseous compounds as -32.96 ± 0.19 and 47.6 ± 0.7 kcal/mol. The strain energies of both compounds are discussed.

Few "globular"[3] molecules approach geometrical or force-fields phericity to the extent of adamantane ($C_{10}H_{16}$, tricyclo[3.3.1.1^{3,7}] decane), which is the simplest saturated polycyclic hydrocarbon possessing the cage-like skeleton characteristic of the crystalline lattice of diamond. This substance undergoes an apparently first-order transition at 208.62°K[4] from a body-centered tetragonal lattice to a face-centered cubic array.[5] The nature of the transition, with its accompanying entropy increment of 3.87 cal/(mol °K), has been further delineated by additional analysis of crystallographic data[6,7] and by nuclear magnetic resonance[8,9] as involving rotational reorientation of the molecules. Moreover, higher temperature thermal data[10] through



Adamantane [$C_{10}H_{16}$]

(1) Supported in part by the Division of Research of the United States Atomic Energy Commission.
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