sextet A and doublet T states have different Fe-S bond lengths. The time-averaged structure observed in the diffraction experiment would be a superposition of two molecular geometries for a complex with intermediate magnetic moment.

The room-temperature magnetic moment of tris(*N,N*-diethyldithiocarbamato)iron is 4.2 BM and such a disorder might, therefore, be detectable in the present room-temperature study.

Average U_{ii} values for the Fe, S, and C atoms are summarized in Table X. Though the sulfur atoms have the largest U_{ii} values at room temperature of the three atom types listed, the ratio of $(U_{ii})_{279°}/(U_{ii})_{79°}$ is not anomalous and smaller than the ratio of the temperatures.

It may be shown that the superposition of two gaussian distributions of equal occupancy at distance $2x_0$ gives a (nongaussian) distribution with root-mean-square displacement, *i.e.*

$$(U_{ij})_{\text{new}} = (U_{ij})_{\text{old}} + x_0^2$$

This expression can be easily extended to the case of nonequal occupancy. But since the room-temperature magnetic moment of 4.2 BM is not too different from the average of the pure high-spin and low-spin values (5.9 and 2.2 BM neglecting spin-orbit coupling), we may use the expression as given above.

It follows that with x_0 = 0.05 Å the apparent increase in the corresponding thermal motion parameter would be 0.0025 Å^2, or only 5% of the observed value of U_{ij}. Clearly, no conclusion can be drawn from the present temperature factors as to the nature of the magnetic transition.

Difference maps obtained after refinement was completed did not show any evidence of the existence of disorder. It is possible that such disorder would be observable in the difference maps of a sample in which the relative populations of the two states differ considerably. The resulting distribution would be asymmetric and, therefore, less well approximated by a harmonic vibration. Further information may also be obtained by accurate studies of a complex with intermediate magnetic moment at liquid nitrogen temperature.

Table X. Average U_{ii} Values at 279 and 79°K (Å^2)

	279°K	79°K	Ratio col 2/ col 3
Fe	0.0399	0.0133	3.0
S	0.0500	0.0179	2.8
C (of SCS group)	0.0407	0.0176	2.3

Acknowledgment. We wish to thank Dr. R. J. Kurland for helpful discussions on the nature of the magnetic transition. We are indebted to the referee for the inclusion of $Fe(S_2CS(t\text{-}Bu)_2)_3$ in Table VII and Figure 2. Support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. $Fe(S_2CNEt_2)_3$, 13963-59-2.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2269.

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680

Crystallographic Elucidation of the Molecular Geometry of Bis(pentalenyl)iron, Including the Location and Refinement of Hydrogen Atoms

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Received January 29, 1973

Bis(pentalenyl)iron, $(C_8H_6)_2Fe$, crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (D_2^4; No. 19) with a = 13.809 (3), b = 10.828 (2), c = 7.339 (2) Å and Z = 4. Observed and calculated densities are 1.582 (10) and 1.574 g cm^{-3}, respectively. A single-crystal X-ray structural analysis of this species has been completed. Diffraction data to 2θ = 55° (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been located, the final discrepancy indices being R_F = 6.65% and R_{wF} = 3.74% for 1475 independent reflections. The completed analysis shows the molecule to be [4,5,6,7,8,4′,5′,6′,7′,8′-*decahapto*-1,1′-dihydro-1,1′-bipentalenyl] iron, *i.e.*, a highly substituted ferrocene derivative with a bridge of only two carbon atoms between the two five-membered π-cyclopentadienyl systems. The molecule has C_2 symmetry within the limits of experimental error. The "ferrocene" moiety is distorted such that iron-carbon distances are in the range 1.985 (5)-2.077 (5) Å in ring A and 1.974 (4)-2.088 (5) Å in ring B. The angle CpA-Fe-CpB (where CpA and CpB are the centroids of the two delocalized five-membered rings) is 161.7 (3)°, and the interplanar angle is 23.6°.

Introduction

Although highly substituted pentalenes, such as dibenzopentalene(1) and hexaphenylpentalene,(2) have been prepared, and evidence has been presented for the existence of 1-methylpentalene (albeit, at −196°),(3) the parent hydrocarbon, pentalene (I), has successfully eluded synthesis.(4) (We may note

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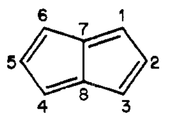
(1) C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).

(2) E. LeGoff, *J. Amer. Chem. Soc.*, 84, 3975 (1962).

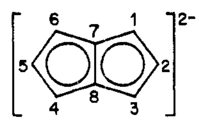
(3) R. Bloch, R. A. Marty, and P. de Mayo, *J. Amer. Chem. Soc.*, 93, 3071 (1971).

(4) (a) See, *inter alia*, E. D. Bergmann in "Non-benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience, New York, N. Y., 1959; (b) G. M. Badger in "Aromatic Character and Aromaticity," Cambridge University Press, New York, N. Y., 1969.



I

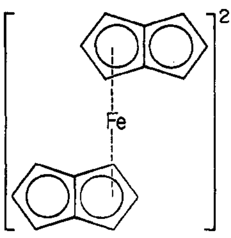
that pentalene is an eight π-electron system and is expected to be nonaromatic.[5]) However, the pentalenyl dianion, II, an



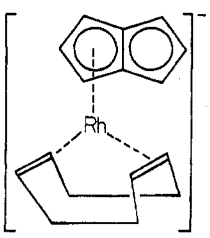
II

aromatic ten π-electron system, has been synthesized and may conveniently be isolated in the form of its stable dilithium salt.[6]

The relationship of the pentalenyl dianion to the cyclopentadienyl anion is similar to that between naphthalene and benzene; the formation of transition metal complexes of the pentalenyl dianion is therefore not surprising. Katz and coworkers some years ago reported such species as the dipentalenyliron dianion[7] III, the pentalenylcycloocta-1,5-dienerhodium anion[8] IV, and various hydropentadienyl species.[7,8]

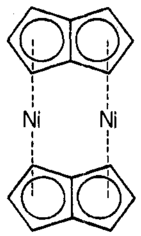


III



IV

More recently bis(pentalenylnickel)[9] (V) and a series of



V

"sandwich complexes" of iron and cobalt with pentalene[10] have been synthesized. Among these latter complexes was bis(pentalenyl)iron, for which no *unambiguous* structure could be assigned. We now report the results of a single-crystal X-ray diffraction study of bis(pentalenyl)iron.

Experimental Procedure and Correction of Data

Orange-red crystals of bis(pentalenyl)iron were supplied by Professor T. J. Katz of Columbia University. A survey of Weissenberg and precession photographs (with accompanying oscillation and cone-axis photographs) indicated D_{2h} (*mmm*) Laue symmetry, yielded approximate cell dimensions, and revealed the systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$, consistent only with the nonpolar noncentrosymmetric orthorhombic space group $P2_12_12_1$ (D_2^4; No. 19).[11]

The crystal selected for data collection was placed in a thin-walled glass capillary and was persuaded to adhere to the side by means of a small quantity of silicone oil. The crystal was a rather irregular elongated plate with approximate dimensions 0.45 × 0.14 × 0.06 mm (relative to a, b, and c, respectively). The crystal was accurately centered on a Picker FACS-1 diffractometer, being orientated such that a^* was coincident with the instrumental ϕ axis.

Unit cell dimensions and their estimated standard deviations were determined from a least-squares fit of the 2θ, ω, and χ values of the resolved Mo Kα_1 (λ = 0.70926 Å) peaks of 12 high angle (2θ = 30–48°) reflections measured under "high resolution" conditions[12] at 26°. The resulting values are a = 13.8093 (27), b = 10.8277 (23), and c = 7.3391 (15) Å. The unit cell volume is 1097.4 Å^3, yielding a calculated density of 1.574 g cm^{-3} for M = 260.01 and Z = 4. [The experimental density is 1.582 (10) g cm^{-3} by neutral buoyancy in aqueous barium iodide.]

Intensity data were collected[12] using niobium-filtered molybdenum radiation by executing a coupled θ–2θ (crystal-counter) scan from 0.65° in 2θ below the Mo Kα_1 peak to 0.65° in 2θ above the Mo Kα_2 peak. Peaks were scanned at a rate of 1.0 deg min^{-1}, thereby accumulating C counts in t_C seconds. Stationary-crystal, stationary-counter background counts, each of 20-sec duration, were recorded at the high and low 2θ limits of the scan, yielding $B2$ and $B1$ counts (respectively) for a total background counting time of t_B = 40 sec. Copper foil attenuators whose transmission factors for Mo Kα radiation were accurately known (and which reduced the diffracted beam by successive factors of ~3.0–3.5) were inserted as necessary to keep the counting rate below ~8500 counts sec^{-1}, thereby avoiding any significant coincidence losses. The take-off angle was 3.0° and the scintillation counter was positioned ~33 cm from the crystal with an aperture of 6 × 6 mm.

Prior to the collection of intensity data, the strong axial 400 reflection was measured by a θ–2θ scan at χ = 90° and a 10° intervals from ϕ = 0° to ϕ = 350°. The maximum variation from the mean intensity was ~3%, indicating that an absorption correction was not necessary (μ = 13.7 cm^{-1}).

A unique set of data in the range 0° < 2θ ≤ 55° was measured. This included 1475 Laue-independent reflections and 21 systematically absent reflections (each of which was found to confirm the extinction conditions for space group $P2_12_12_1$). Three strong check reflections (400, 020, 201) were measured after each batch of 48 reflections in order to monitor any possible crystal decomposition, etc. No such problems were encountered. (The check reflections had root-mean-square deviations in intensity of 0.60, 1.01, and 0.85%, respectively.)

The integrated intensity, I, and its estimated standard deviation, $\sigma(I)$, were calculated *via* the equations below.

$$I = q[(C + 4.5) - (t_C/t_B)(B1 + B2 + 9.0)]$$

$$\sigma(I) = q[(C + 4.5) + (t_C/t_B)^2(B1 + B2 + 9.0) + 24.75 + q^{-2}p^2I^2]^{1/2}$$

The symbol q represents the correction for attenuator used, the "ignorance factor" (p) was set equal to 0.04, and numerical terms arise from the statistics involved in the truncation of the last digit of C, $B1$, and $B2$ which occurs on the punched-tape output from the FACS-1 system.

Any negative I was reset to zero. Table I provides a summary of the strength of the data set. As can easily be seen, approximately 30% of the data has ([$I/\sigma(I)$]) ≤ 3.0. (This is, of course, simply the result of using a small crystal for data collection; however, no better crystal could be obtained.) All data were retained, none being rejected on the basis of being "not significantly above background." [Retaining the weak data, *i.e.*, those with $I \leq 3\sigma(I)$, leads to a higher value for the discrepancy index R_F (*vide infra*), but

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(5) See, *inter alia*, ref 4a, Chapters I and IV; H. C. Longuet-Higgins in "Theoretical Organic Chemistry; Kekule Symposium," Butterworths, London, 1959; M. J. S. Dewar, *Chem. Soc. Spec. Publ.*, No. 21, 177 (1967); N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 3072 (1971), and references cited therein.

(6) T. J. Katz and M. Rosenberger, *J. Amer. Chem. Soc.*, **84**, 865 (1962); T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).

(7) T. J. Katz and M. Rosenberger, *J. Amer. Chem. Soc.*, **85**, 2030 (1963).

(8) T. J. Katz and J. J. Mrowca, *J. Amer. Chem. Soc.*, **89**, 1105 (1967).

(9) T. J. Katz and N. Acton, *J. Amer. Chem. Soc.*, **94**, 3281 (1972).

(10) T. J. Katz, N. Acton, and J. McGinnis, *J. Amer. Chem. Soc.*, **94**, 6205 (1972).

(11) "International Tables for X-Ray Crystallography," Vol. 1, 2nd ed, Kynoch Press, Birmingham, England, 1965, p 105.

(12) A detailed account of the experimental procedure has appeared previously: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 12, 525 (1973).

Table I. Summary of "Significance" of Data Collected

$I/\sigma(I)$	n_i[a]	Σn_i[a]	$I/\sigma(I)$	n_i[a]	Σn_i[a]
≤0.0	91	91	≤6.0	152	706
≤1.0	117	208	≤10.0	208	914
≤2.0	136	344	≤20.0	358	1272
≤3.0	103	447	≤25.0	203	1475
≤4.0	107	554			

[a] n_i is the number of reflections within a given range of $I/\sigma(I)$; Σn_i is the cumulative number of reflections up to a certain maximum value of $I/\sigma(I)$. With an "ignorance factor" of 0.04, no reflection can have $I/\sigma(I) > 25.0$.

has the advantage of maintaining a relatively high ratio of observations to parameters and thence results, *inter alia*, in decreased estimated standard deviations on atomic parameters.[13]]

Unscaled structure factor amplitudes, F, and their standard deviations, $\sigma(F)$, were calculated from the expressions

$$F = (I/Lp)^{1/2}$$

$$\sigma(F) = (\sigma(I)/Lp)^{1/2} \text{ for } \sigma(I) \geqslant I$$

and

$$\sigma(F) = [F^2 - [F^2 - (\sigma(I)/Lp)]^{1/2}] \text{ for } \sigma(I) < I$$

The Lorentz-polarization correction, Lp, is given by $(1 + \cos^2 2\theta)/(2 \sin 2\theta)$.

Solution and Refinement of the Structure

During the subsequent structural analysis the following programs were used on the IBM 370/155 computer at the University of Illinois at Chicago Circle: FORDAP (Fourier synthesis, by A. Zalkin), SFIX (a modified version of C. T. Prewitt's SFLS5, for structure factor calculations and full-matrix least-squares refinement), STAN1 (distances, angles, and their estimated standard deviations, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral iron and carbon were taken from the compilation of Cromer and Waber[14] and were corrected for both the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[15] The contributions of neutral hydrogen atoms were calculated using the scattering curve of Mason and Robertson.[16]

The residual $\Sigma w(|F_o| - |F_c|)^2$ was minimized during least-squares refinement processes. Here, $w(hkl) = [\sigma(F_{hkl})]^{-2}$. Discrepancy indices used below are defined as follows

$$R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and

$$R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

The position of the iron atom was determined from a Patterson synthesis; a subsequent three-dimensional Fourier synthesis led to the unambiguous location of all 16 carbon atoms. Refinement of positional and isotropic thermal parameters converged smoothly to values of $R_F = 11.1\%$ and $R_{wF} = 8.8\%$. The use of anisotropic thermal parameters for all nonhydrogen atoms led to convergence with $R_F = 8.7\%$ and $R_{wF} = 6.1\%$. At this stage a difference-Fourier synthesis revealed the 12 hydrogen atoms in the molecule. Further refinement, with hydrogen atoms in calculated positions (with C–H = 0.95 Å, the appropriate trigonal or tetrahedral stereochemistry at carbon, and thermal parameters of $B = 5.0$ Å^2), converged with $R_F = 7.9\%$ and $R_{wF} = 5.3\%$.

The significance of the decrease in R_{wF} on inclusion of the hydrogen atoms prompted us to attempt the refinement of their parameters. Refinement of all positional parameters, anisotropic thermal parameters for iron and carbon atoms, isotropic thermal parameters for hydrogen atoms, and an overall scale factor led quickly and smoothly to convergence $[(\Delta/\sigma)_{\max} < 0.08]$ with $R_F = 7.22\%$ and $R_{wF} = 4.38\%$. At this point all atomic coordinates (x,y,z) were transformed to $(-x, -y, -z)$ and refinement was continued. Three cycles of least-squares refinement led to convergence ($\Delta/\sigma < 0.05$) at the reduced discrepancy indices $R_F = 6.55\%$ and $R_{wF} = 3.74\%$. Clearly, the absolute configuration of the molecule was that defined by the reversed coordinates. We may note here that positional and thermal parameters of all hydrogen atoms are sensible [*viz.*, d(C–H) = 0.86–1.05 Å, and B(H) = 3.0–7.3 Å^2].

Table II. Final Positional and Isotropic Thermal Parameters[a] for Bis(pentalenyl)iron, with Esd's[b]

Atom	x	y	z	B, Å^2
Fe	0.112763 (47)	0.202171 (57)	0.099688 (86)	2.563
C(1A)	0.20985 (37)	0.42149 (44)	−0.04035 (65)	3.48
C(2A)	0.12195 (50)	0.50431 (43)	−0.03621 (75)	4.22
C(3A)	0.06071 (37)	0.47647 (46)	0.09619 (91)	4.14
C(4A)	0.07948 (39)	0.28884 (53)	0.34424 (62)	3.91
C(5A)	0.16122 (41)	0.21209 (57)	0.36516 (61)	4.15
C(6A)	0.23393 (39)	0.24913 (46)	0.23700 (67)	3.56
C(7A)	0.19571 (34)	0.34985 (44)	0.13640 (59)	2.91
C(8A)	0.10237 (38)	0.37620 (43)	0.20712 (62)	3.42
C(1B)	0.20578 (40)	0.32919 (45)	−0.20472 (67)	3.77
C(2B)	0.29443 (45)	0.24806 (57)	−0.21083 (82)	4.56
C(3B)	0.27689 (42)	0.13257 (56)	−0.15931 (73)	4.53
C(4B)	0.10376 (46)	0.03646 (46)	−0.04482 (65)	3.95
C(5B)	0.01280 (40)	0.09962 (51)	−0.04580 (65)	3.96
C(6B)	0.02696 (35)	0.22042 (51)	−0.12071 (72)	3.80
C(7B)	0.12739 (37)	0.23124 (41)	−0.16446 (56)	2.89
C(8B)	0.17320 (37)	0.11854 (45)	−0.12363 (67)	3.33
H(1A)	0.2769 (34)	0.4647 (45)	−0.0385 (64)	4.8 (10)
H(2A)	0.1170 (42)	0.5602 (48)	−0.1181 (69)	5.7 (12)
H(3A)	0.0013 (29)	0.5135 (38)	0.1148 (66)	3.9 (9)
H(4A)	0.0219 (36)	0.2817 (48)	0.4150 (73)	5.6 (11)
H(5A)	0.1674 (43)	0.1469 (50)	0.4522 (77)	6.6 (14)
H(6A)	0.2982 (36)	0.2077 (49)	0.2258 (66)	5.0 (11)
H(1B)	0.1991 (30)	0.3676 (39)	−0.3253 (54)	3.0 (8)
H(2B)	0.3544 (38)	0.2824 (49)	−0.2202 (73)	6.1 (13)
H(3B)	0.3298 (39)	0.0695 (54)	−0.1152 (90)	7.3 (14)
H(4B)	0.1163 (40)	−0.0430 (46)	0.0016 (65)	5.5 (11)
H(5B)	−0.0521 (33)	0.0589 (43)	−0.0055 (64)	4.5 (10)
H(6B)	−0.0184 (35)	0.2850 (51)	−0.1275 (78)	6.4 (13)

[a] For nonhydrogen atoms the "equivalent isotropic thermal parameters" are listed. These correspond to the average of the mean square displacements along the three principal axes of the atomic vibration ellipsoid. [b] Esd's (estimated standard deviations), shown in parentheses, are right adjusted to the last digit of the preceding number. They are derived from the inverse of the final least-squares matrix.

Data were inspected for evidence of extinction and for indications that a β-filter correction[12] might be necessary; no evidence for such systematic effects was found. The standard deviation in an observation of unit weight, defined by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 0.86; this function was not markedly dependent on sin θ or $|F_o|$, thereby indicating a correctly chosen weighting scheme. The number of reflections (m) was 1475 and the number of parameters refined (n) was 202; the m:n ratio was 7.3:1.

The correctness of the refined structure was confirmed by a final difference-Fourier synthesis on which the highest feature was a peak of height 0.59 e Å^{-3}. A table of observed and calculated structure factor amplitudes is available.[17] Final fractional atomic coordinates and their estimated standard deviations, along with isotropic thermal parameters, are listed in Table II; anisotropic thermal parameters for nonhydrogen atoms are collected in Table III.

Discussion of the Molecular Structure

Interatomic distances and their estimated standard deviations (esd's) are collected in Table IV; bond angles, with esd's, are shown in Table V. Figure 1 shows the molecular stereochemistry, the scheme used for labeling all atoms, and the 50% probability envelopes of the atomic thermal vibration ellipsoids (or, in the case of hydrogen atoms, spheres). The carbon atom skeleton of the molecule is shown more clearly in Figure 2.

The present bis(pentalenyl)iron crystal consists of one opti-

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(13) These effects are well known. An excellent recent documentation is J. A. McGinnety, *J. Amer. Chem. Soc.*, **94**, 8406 (1972); see particularly Refinement of the Structure on p 8407.

(14) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(15) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(16) R. Mason and G. B. Robertson, *Advan. Struct. Res. Diffr. Methods*, **2**, 57 (1966).

(17) See paragraph at end of paper regarding supplementary material.

Table III. Anisotropic Thermal Parameters[a] for Bis(pentalenyl)iron

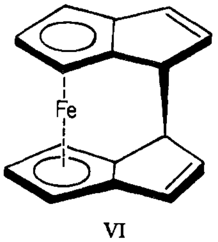
Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle$[b]
Fe	2.90 (3)	2.61 (3)	2.18 (2)	−0.41 (3)	−0.07 (3)	−0.21 (3)	0.160, 0.177, 0.201
C(1A)	3.83 (24)	3.06 (20)	3.55 (22)	−0.68 (21)	0.01 (20)	−0.08 (21)	0.18, 0.21, 0.23
C(2A)	5.60 (31)	2.48 (20)	4.58 (28)	−0.26 (27)	0.06 (29)	0.01 (22)	0.18, 0.24, 0.27
C(3A)	3.68 (23)	3.42 (22)	5.33 (27)	0.47 (21)	−0.48 (29)	−0.89 (27)	0.19, 0.21, 0.27
C(4A)	4.70 (24)	4.34 (24)	2.71 (19)	−0.72 (28)	0.99 (18)	−1.10 (21)	0.16, 0.22, 0.27
C(5A)	5.46 (29)	4.35 (27)	2.65 (22)	−0.22 (27)	−0.64 (20)	0.12 (24)	0.18, 0.23, 0.27
C(6A)	3.52 (24)	3.84 (23)	3.33 (24)	−0.07 (21)	−1.37 (20)	−0.69 (21)	0.15, 0.22, 0.25
C(7A)	2.77 (21)	3.01 (20)	2.96 (23)	−0.57 (18)	−0.52 (19)	−0.88 (19)	0.14, 0.20, 0.22
C(8A)	4.16 (26)	3.16 (21)	2.94 (19)	0.09 (21)	0.07 (22)	−1.00 (20)	0.16, 0.23, 0.23
C(1B)	4.58 (28)	3.98 (27)	2.74 (20)	−1.00 (21)	0.99 (21)	0.28 (21)	0.16, 0.22, 0.26
C(2B)	3.58 (27)	5.49 (32)	4.62 (27)	−0.41 (24)	1.46 (24)	−1.17 (27)	0.18, 0.24, 0.29
C(3B)	4.68 (32)	4.76 (31)	4.14 (28)	0.64 (28)	1.29 (24)	−0.49 (24)	0.19, 0.25, 0.27
C(4B)	5.88 (31)	2.82 (20)	3.14 (22)	−1.01 (25)	−0.27 (25)	−0.36 (17)	0.18, 0.21, 0.28
C(5B)	4.46 (28)	4.29 (26)	3.13 (23)	−1.75 (23)	−0.55 (21)	−0.38 (20)	0.17, 0.21, 0.28
C(6B)	3.34 (20)	4.66 (30)	3.40 (22)	−0.66 (22)	−0.92 (21)	0.07 (25)	0.17, 0.22, 0.25
C(7B)	3.74 (25)	2.89 (21)	2.02 (18)	−0.58 (21)	−0.26 (19)	−0.22 (15)	0.15, 0.19, 0.23
C(8B)	4.35 (23)	2.93 (21)	2.70 (21)	−0.22 (20)	0.54 (22)	−0.92 (20)	0.15, 0.21, 0.24

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameters and have units of Å^2. They enter the expression for the structure factor in the form: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see figures.

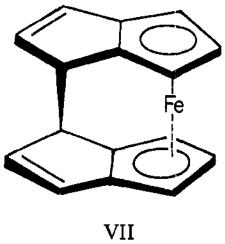
Table IV. Interatomic Distances (Å) with Esd's for Bis(pentalenyl)iron[a,b]

Atoms	Distance	Atoms	Distance
(A) Distances from Iron Atom			
Fe–C(4A)	2.077 (5)	Fe–C(4B)	2.088 (5)
Fe–C(5A)	2.063 (5)	Fe–C(5B)	2.069 (5)
Fe–C(6A)	2.018 (5)	Fe–C(6B)	2.015 (5)
Fe–C(7A)	1.985 (5)	Fe–C(7B)	1.974 (4)
Fe–C(8A)	2.048 (5)	Fe–C(8B)	2.050 (5)
Fe–CpA[b]	1.642 (5)	Fe–CpB	1.640 (5)
Fe· · ·C(1A)	2.914 (5)	Fe· · ·C(1B)	2.921 (5)
Fe· · ·C(2A)	3.423 (5)	Fe· · ·C(2B)	3.426 (6)
Fe· · ·C(3A)	3.056 (5)	Fe· · ·C(3B)	3.053 (6)
(B) Carbon–Carbon Distances within π-Cyclopentadienyl Systems			
C(4A)–C(5A)	1.411 (8)	C(4B)–C(5B)	1.430 (8)
C(5A)–C(6A)	1.433 (8)	C(5B)–C(6B)	1.432 (8)
C(6A)–C(7A)	1.419 (7)	C(6B)–C(7B)	1.428 (7)
C(7A)–C(8A)	1.419 (7)	C(7B)–C(8B)	1.407 (7)
C(8A)–C(4A)	1.417 (7)	C(8B)–C(4B)	1.430 (8)
(C) Other Carbon–Carbon Bond Distances			
C(7A)–C(1A)	1.524 (7)	C(7B)–C(1B)	1.544 (7)
C(1A)–C(2A)	1.510 (8)	C(1B)–C(2B)	1.508 (8)
C(2A)–C(3A)	1.323 (8)	C(2B)–C(3B)	1.329 (9)
C(3A)–C(8A)	1.474 (8)	C(3B)–C(8B)	1.464 (8)
C(1A)–C(1B)	1.568 (7)		
(D) Selected Interannular Distances			
C(7A)· · ·C(7B)	2.723 (6)		
C(6A)· · ·C(8B)	3.116 (7)	C(8A)· · ·C(6B)	3.117 (7)
C(5A)· · ·C(4B)	3.647 (7)	C(4A)· · ·C(5B)	3.639 (7)
C(7A)· · ·C(8B)	3.164 (7)	C(8A)· · ·C(7B)	3.165 (6)
C(6A)· · ·C(4B)	3.579 (7)	C(4A)· · ·C(6B)	3.566 (7)
C(5A)· · ·C(5B)	3.845 (7)		
C(1A)· · ·C(7B)	2.524 (7)	C(7A)· · ·C(1B)	2.517 (7)
(E) Carbon–Hydrogen Distances			
C(1A)–H(1A)	1.04 (5)	C(1B)–H(1B)	0.98 (4)
C(2A)–H(2A)	0.86 (5)	C(2B)–H(2B)	0.91 (5)
C(3A)–H(3A)	0.92 (4)	C(3B)–H(3B)	1.05 (6)
C(4A)–H(4A)	0.95 (5)	C(4B)–H(4B)	0.94 (5)
C(5A)–H(5A)	0.96 (6)	C(5B)–H(5B)	1.04 (5)
C(6A)–H(6A)	1.00 (5)	C(6B)–H(6B)	0.94 (5)

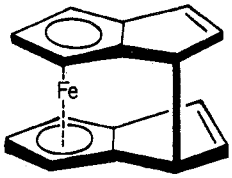
[a] Esd's were calculated by considering each element of the full positional correlation matrix whose magnitude was greater than 0.1. The calculation was performed using the FORTRAN IV program STAN1 by B. G. DeBoer. [b] Bond lengths are not corrected for the effects of thermal motion.



VI

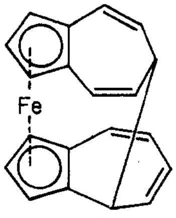


VII



VIII

cal hand of (4,5,6,7,8,4′,5′,6′,7′,8′-*decahapto*-1,1′-dihydro-1,1′-bipentalenyl)iron; the molecule has C_2 symmetry within the limits of experimental error (see Table VIA) and the absolute configuration corresponds to that shown in VI. It should be emphasized that with space group $P2_12_12_1$ the absolute configuration obtained is that of the particular crystal selected from the bulk sample. Any chosen crystal has a 50% chance of having molecules with the absolute configuration of VI and a 50% chance of containing molecules of the other enantiomer, VII. The alternative achiral structure, VIII, having C_s symmetry, is presumably not favored because it would be of higher energy with more pronounced interannular carbon···carbon repulsions.



IX

The two pentalene ligands in bis(pentalenyl)iron thus dimerize *via* 1-endo, 1′-endo carbon-carbon bond formation. This situation is strongly reminiscent of bis(azulene)iron (IX) which Churchill and Wormald[18] have shown to contain two azulene frameworks linked *via* 4-endo, 6′-endo carbon-carbon bond formation. However, it should be emphasized that bis-

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(18) M. R. Churchill and J. Wormald, *Inorg. Chem.*, 8, 716 (1969).

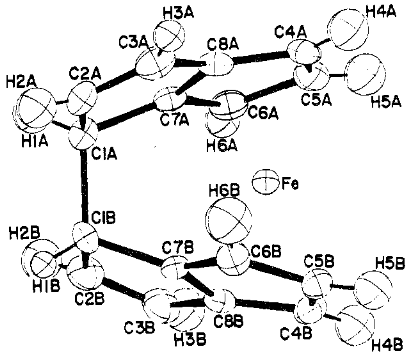

Figure 1. The molecular stereochemistry and labeling of all atoms, including hydrogens, in the bis(pentalenyl)iron molecule (ORTEP diagram, 50% probability contours for atomic vibration ellipsoids).

Table V. Interatomic Angles (deg) for Bis(pentalenyl)iron

Atoms	Angle	Atoms	Angle
(A) Angles around Iron Atom			
C(7A)–Fe–C(6A)	41.5 (2)	C(7B)–Fe–C(6B)	42.0 (2)
C(6A)–Fe–C(5A)	41.1 (2)	C(6B)–Fe–C(5B)	41.0 (2)
C(5A)–Fe–C(4A)	39.8 (2)	C(5B)–Fe–C(4B)	40.3 (2)
C(4A)–Fe–C(8A)	40.2 (2)	C(4B)–Fe–C(8B)	40.4 (2)
C(8A)–Fe–C(7A)	41.2 (2)	C(8B)–Fe–C(7B)	40.9 (2)
C(7A)–Fe–C(7B)	86.9 (2)		
C(6A)–Fe–C(8B)	100.0 (2)	C(8A)–Fe–C(6B)	100.2 (2)
C(5A)–Fe–C(4B)	122.9 (2)	C(4A)–Fe–C(5B)	122.8 (2)
CpA· · ·Fe· · ·CpB	161.7 (3)		
(B) Angles within π-Cyclopentadienyl Systems			
C(8A)–C(4A)–C(5A)	107.0 (5)	C(8B)–C(4B)–C(5B)	106.8 (4)
C(4A)–C(5A)–C(6A)	108.9 (5)	C(4B)–C(5B)–C(6B)	108.6 (5)
C(5A)–C(6A)–C(7A)	107.2 (5)	C(5B)–C(6B)–C(7B)	107.1 (4)
C(6A)–C(7A)–C(8A)	107.6 (4)	C(6B)–C(7B)–C(8B)	108.5 (4)
C(7A)–C(8A)–C(4A)	109.2 (5)	C(7B)–C(8B)–C(4B)	108.9 (5)
(C) Angles Involving Bridged Five-Membered Rings			
C(7A)–C(1A)–C(2A)	100.5 (4)	C(7B)–C(1B)–C(2B)	100.1 (4)
C(1A)–C(2A)–C(3A)	113.2 (5)	C(1B)–C(2B)–C(3B)	113.1 (5)
C(2A)–C(3A)–C(8A)	108.9 (5)	C(2B)–C(3B)–C(8B)	109.1 (5)
C(3A)–C(8A)–C(7A)	107.5 (4)	C(3B)–C(8B)–C(7B)	108.2 (4)
C(8A)–C(7A)–C(1A)	109.0 (4)	C(8B)–C(7B)–C(1B)	108.7 (4)
C(2A)–C(1A)–C(1B)	111.4 (4)	C(2B)–C(1B)–C(1A)	111.4 (4)
C(7A)–C(1A)–C(1B)	109.0 (4)	C(7B)–C(1B)–C(1A)	108.4 (4)
C(1A)–C(7A)–C(6A)	141.9 (5)	C(1B)–C(7B)–C(6B)	141.3 (5)
C(3A)–C(8A)–C(4A)	142.9 (5)	C(3B)–C(8B)–C(4B)	142.5 (5)
(D) Angles Involving Hydrogen Atoms			
H(1A)–C(1A)–C(2A)	117 (3)	H(1B)–C(1B)–C(2B)	107 (2)
H(1A)–C(1A)–C(7A)	109 (3)	H(1B)–C(1B)–C(7B)	113 (2)
H(1A)–C(1A)–C(1B)	109 (3)	H(1B)–C(1B)–C(1A)	115 (3)
H(2A)–C(2A)–C(1A)	118 (4)	H(2B)–C(2B)–C(1B)	120 (3)
H(2A)–C(2A)–C(3A)	129 (4)	H(2B)–C(2B)–C(3B)	125 (4)
H(3A)–C(3A)–C(2A)	125 (3)	H(3B)–C(3B)–C(2B)	125 (3)
H(3A)–C(3A)–C(8A)	126 (3)	H(3B)–C(3B)–C(8B)	124 (3)
H(4A)–C(4A)–C(8A)	129 (3)	H(4B)–C(4B)–C(8B)	126 (3)
H(4A)–C(4A)–C(5A)	124 (3)	H(4B)–C(4B)–C(5B)	127 (3)
H(5A)–C(5A)–C(4A)	125 (4)	H(5B)–C(5B)–C(4B)	124 (3)
H(5A)–C(5A)–C(6A)	126 (4)	H(5B)–C(5B)–C(6B)	128 (3)
H(6A)–C(6A)–C(5A)	123 (3)	H(6B)–C(6B)–C(5B)	128 (3)
H(6A)–C(6A)–C(7A)	129 (3)	H(6B)–C(6B)–C(7B)	125 (3)

(pentalenyl)iron contains only a two-carbon-atom bridge between the π-cyclopentadienyl rings of its ferrocene system, whereas the bis(azulene)iron molecule has a four-carbon-atom bridge.

The bridge of only two carbon atoms causes severe distortions in the ferrocene portion of the present molecule but molecular C_2 symmetry is retained. The two five-membered delocalized rings are not parallel (unlike ferrocene[19]) but are tilted relative to one another. This tilt may be defined in two (nonequivalent) ways: (i) as the dihedral angle between the two planar five-membered rings, giving a value of 23.6° (see Table VI); (ii) as the angle CpA–Fe–CpB, which has a value of 161.7 (3)°. [Here, CpA is the centroid of the system C(4A)–C(5A)–C(6A)–C(7A)–C(8A) and CpB is the centroid of the ring defined by C(4B)–C(5B)–C(6B)–C(7B)–C(8B).]

To our knowledge the only other ferrocene derivative which has been shown to have a comparable deviation from planarity

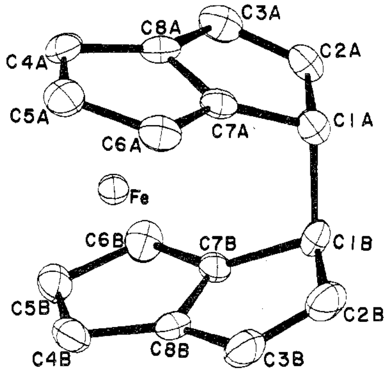

Figure 2. The carbon atom skeleton of bis(pentalenyl)iron (ORTEP diagram, 50% probability ellipsoids).

Table VI[a]

(A) Distances (Å) of Atoms from the Line Passing through Fe and the Midpoint of the C(1A)–C(1B) Bond, Indicating the Molecular C_2 Symmetry

Atom	Distance	Atom	Distance	Δ[b]
C(1A)	0.784	C(1B)	0.784	0.000
C(2A)	1.938	C(2B)	1.936	0.002
C(3A)	2.565	C(3B)	2.563	0.002
C(4A)	1.979	C(4B)	1.988	0.009
C(5A)	1.923	C(5B)	1.922	0.001
C(6A)	1.946	C(6B)	1.947	0.001
C(7A)	1.361	C(7B)	1.362	0.001
C(8A)	1.912	C(8B)	1.913	0.001
H(1A)	1.30	H(1B)	1.29	0.01
H(2A)	2.25	H(2B)	2.27	0.02
H(3A)	3.41	H(3B)	3.42	0.01
H(4A)	2.42	H(4B)	2.41	0.01
H(5A)	2.29	H(5B)	2.34	0.05
H(6A)	2.63	H(6B)	2.52	0.11

(B) Least-Squares Planes within the Bis(pentalenyl)iron Molecule[c,d]

Atom	Dev, Å	Atom	Dev, Å
Plane I: $0.3858X + 0.6261Y + 0.6776Z - 4.108 = 0$			
C(4A*)	−0.014	C(1A)	−0.333
C(5A*)	+0.005	C(2A)	−0.219
C(6A*)	+0.006	C(3A)	−0.076
C(7A*)	−0.015		
C(8A*)	+0.018	Fe	−1.641
H(4A)	−0.02		
H(5A)	+0.03		
H(6A)	+0.01		
Plane II: $0.1974X + 0.3518Y + 0.9150Z - 0.1095 = 0$			
C(4B*)	+0.011	C(1B)	+0.331
C(5B*)	−0.003	C(2B)	+0.222
C(6B*)	−0.007	C(3B)	+0.081
C(7B*)	+0.014		
C(8B*)	−0.016	Fe	+1.638
H(4B)	+0.05		
H(5B)	−0.06		
H(6B)	+0.07		

Dihedral angle I/II = 23.59°

[a] All calculations were performed using the program PLOD by B. G. DeBoer. [b] Δ is the difference between the two (C_2 related) entries on the line. [c] Cartesian coordinates $[X, Y, Z] = [xa, yb, zc]$. [d] Atoms marked with an asterisk were given unit weight; all other atoms were assigned zero weight.

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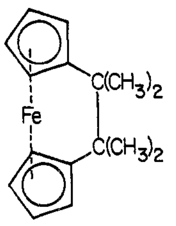
(19) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956); R. K. Bohn and A. Haaland, *J. Organometal. Chem.*, **5**, 470 (1966).

is 1,1′-tetramethylethyleneferrocene (X), studied by Laing



X

and Trueblood,[20] which also has a two-carbon-atom bridge across the ferrocene system. In this molecule the interplanar angle is 23.2° and the CpA-Fe-CpB angle is 163.4°.

The relative tilt of the two (substituted) π-cyclopentadienyl systems in the bis(pentalenyl)iron molecule manifests itself in a number of ways. Iron-carbon distances vary systematically and significantly around the five-membered rings, conserving overall C_2 molecular symmetry. The shortest distances are those adjacent to the C(1A)-C(1B) bridge. Thus (in pairs, related by the molecular C_2 axis), Fe-C(7A) = 1.988 (5) and Fe-C(7B) = 1.974 (4) Å, Fe-C(8A) = 2.048 (5) and Fe-C(8B) = 2.050 (5) Å, Fe-C(4A) = 2.077 (5) and Fe-C(4B) = 2.088 (5) Å, Fe-C(5A) = 2.063 (5) and Fe-C(5B) = 2.069 (5) Å, Fe-C(6A) = 2.018 (5) and Fe-C(6B) = 2.015 (5) Å.

As shown in Figure 3, the ferrocene moiety is closer to an eclipsed than to a staggered conformation, the mean rotational angle being ~10° (*cf.* 0° for an eclipsed conformation, 36° for a staggered conformation, and a value of ~9° for 1,1′-tetramethylethyleneferrocene[20]). We may note at this point that a compilation of the conformations of ferrocene derivatives has appeared previously[21] and that species are known with perfectly staggered and perfectly eclipsed geometries; many intermediate situations have also been reported.

Carbon···carbon distances across the ferrocene system of the present molecule vary appreciably, with C(7A)···C(7B) = 2.723 (6) [adjacent to the C(1A)-C(1B) bond], C(6A)···C(8B) = 3.116 (7) and C(8A)···C(6B) = 3.117 (7), C(5A)···C(4B) = 3.647 (7) and C(4A)···C(5B) = 3.639 (7) Å. Carbon-iron-carbon angles involving these pairs of carbon atoms show similarly large variations, *viz.*, C(7A)-Fe-C(7B) = 86.9 (2), C(6A)-Fe-C(8B) = 100.0 (2) and C(8A)-Fe-C(6B) = 100.2 (2), C(5A)-Fe-C(4B) = 122.9 (2) and C(4A)-Fe-C(5B) = 122.8 (2)°.

Carbon-carbon distances within the π-cyclopentadienyl ring of pentalene system A range from 1.411 (8) to 1.433 (8) Å (average = 1.420 Å) and within the π-cyclopentadienyl ring of system B range from 1.407 (7) to 1.432 (8) Å (average = 1.425 Å). These average values may be compared with the accepted C-C(π-cyclopentadienyl) bond length of ~1.43 Å. Other carbon-carbon distances are also close to the appropriate recognized values. Thus, the olefinic bonds, C(2A)-C(3A) and C(2B)-C(3B), are 1.323 (8) and 1.329 (9) Å in length [*cf.* the recognized C=C distance of 1.335 ± 0.005 Å[22]]; the bond lengths C(7A)-C(1A) = 1.524 (7), C(1A)-C(2A) = 1.510 (8), C(7B)-C(1B) = 1.544 (7), and C(1B)-C(2B) = 1.508 (8) Å are all close to the recognized C(sp^2)-C(sp^3) single bond distance of 1.510 ± 0.005 Å;[22] the bond lengths C(3A)-C(8A) = 1.474 (8) and C(3B)-C(8B) = 1.464 (8) Å are close to the recognized C(sp^2)-C(sp^2) single bond distance of 1.465 ± 0.005 Å.[22]

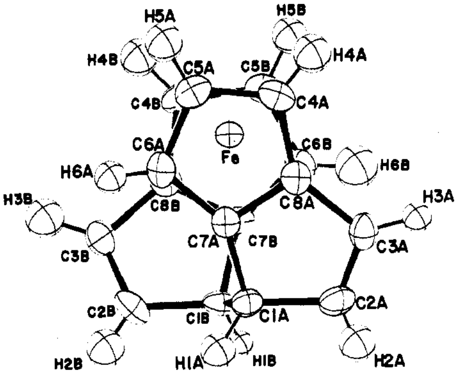


Figure 3. The bis(pentalenyl)iron molecule projected onto the plane which bisects the dihedral angle between the two π-cyclopentadienyl systems. The molecular C_2 axis is vertical.

Finally, we may note that the bridging C(1A)-C(1B) distance of 1.568 (7) Å is significantly (~4σ) longer than the normal C(sp^3)-C(sp^3) distance of 1.537 ± 0.005 Å.[22] Similar, but less statistically significant increases have been found in other bridged systems, *viz.*, 1.585 (15) Å for the C(azulene)-C(azulene) bridge in $(C_{10}H_8)_2Fe$,[18] 1.584 (14) Å for the $C(CH_3)_2$-$C(CH_3)_2$ bridge in 1,1′-tetramethylethyleneferrocene,[20] 1.567 (12) Å for the C(azulene)-C(azulene) bridge in $(C_{10}H_8)_2Fe_4(CO)_{10}\cdot C_2H_4Cl_2$,[23] and 1.561 (18) Å for the C(azulene)-C(azulene) bridge in $[(C_{10}H_8)Mo(CO)_3CH_3]_2$.[24]

The 12 independent carbon-hydrogen bond distances range from C(2A)-H(2A) = 0.86 (5) to C(3B)-H(3B) = 1.05 (6) Å, the mean value being 0.966 Å. This value appears to be typical for a carbon-hydrogen distance determined from X-ray diffraction studies (*cf.* ref 25) and is contracted by ~0.11 Å from the recognized inter*nuclear* distance of 1.08 Å. Angles of the type H-C(sp^3)-C range from 107 (2) to 117 (3)° (average = 112°), while H-C(sp^2)-C angles vary from 118 (4) to 129 (4)° (average = 125°; the angle expected as the external bisector of a regular pentagon is 126°).

Acknowledgments. We thank Professor T. J. Katz for providing samples of the complex investigated. This work was made possible by financial support from the National Science Foundation (Grant No. GP-33018, to M. R. C.) and a generous allocation of computer time on an IBM 370/155 from the Computer Center, University of Illinois at Chicago Circle.

Registry No. $(C_8H_6)_2Fe$, 38959-96-5.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St. N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2274.

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[20] M. B. Laing and K. N. Trueblood, *Acta Crystallogr.*, 19, 373 (1965).

[21] See Table VIII of ref 18.

[22] L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 18, S14s (1965).

[23] M. R. Churchill and P. H. Bird, *Inorg. Chem.*, 8, 1941 (1969).

[24] P. H. Bird and M. R. Churchill, *Inorg. Chem.*, 7, 349 (1968).

[25] M. R. Churchill, *Inorg. Chem.*, 12, 1213 (1973).