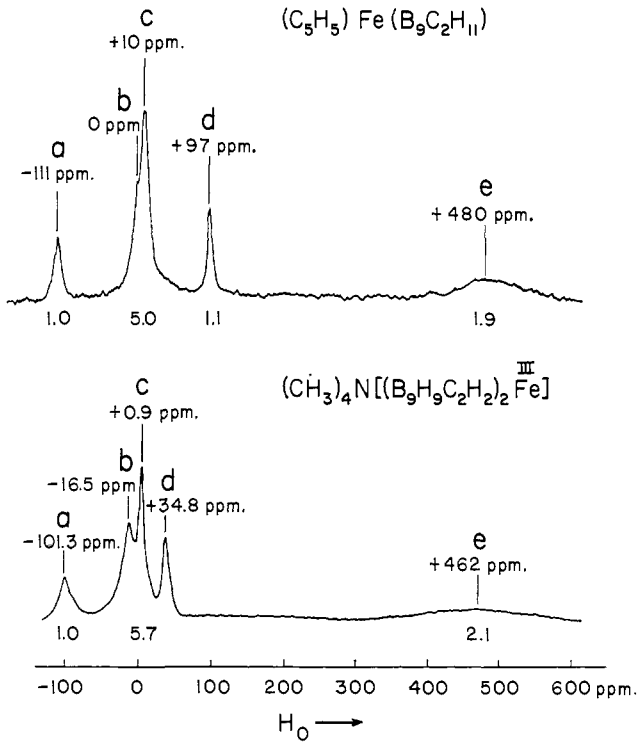

Figure 1. The 19.3-Mc./sec. ^{11}B n.m.r. spectra of VI and tetramethylammonium I determined in tetrahydrofuran and acetonitrile, respectively, with $BF_3 \cdot O(C_2H_5)_2$ standard.

Compound VI was obtained in the following manner. A solution of 20 mmoles each of disodium (1)-2,3-dicarbollide[4] and sodium cyclopentadienide was prepared from excess sodium hydride, $(CH_3)_3NHB_9C_2H_{12}$, and cyclopentadiene in tetrahydrofuran at the reflux temperature. The liberated $(CH_3)_3N$ was swept from the reaction mixture with a stream of dry nitrogen. This solution was then added to a solution of 28.5 mmoles of ferrous chloride in tetrahydrofuran at the reflux temperature. After heating for an additional 15 min., the resulting red solution was cooled and filtered, and the solvent was evaporated to yield a red gum. The crude product mixture was extracted with a mixture of 75 ml. each of benzene and water and the solvents were separated. Addition of 150 ml. of pentane to the dried benzene extractant precipitated purple needles which were recrystallized from cyclohexane–benzene to yield pure VI, m.p. 181–182°, 1.25 g., 4.95 mmoles. *Anal.* Calcd. for $(B_9C_2H_{11})Fe(C_5H_5)$: Fe, 22.04; B, 38.42; C, 33.18; H, 6.36. Found: Fe, 21.63; B, 37.64; C, 30.59; H, 6.50. Evaporation of the benzene–pentane filtrate to dryness followed by recrystallization of the residue from methanol gave ferrocene, 1.55 g., 8.35 mmoles, identified by its infrared spectrum.

The aqueous layer from the extraction was treated with excess tetramethylammonium chloride and the precipitated salt washed with ethanol. The ethanol wash was evaporated to dryness and the residue recrystallized from acetone–water to give the tetramethylammonium salt of I, 0.95 g., 2.4 mmoles, identified by its characteristic infrared spectrum.

The reduction of VI to V was carried out at room temperature in acetone solution with dilute sodium amalgam. During the course of the reduction the acetone solution changed from purple to orange. The excess amalgam was separated, the acetone solution evaporated to dryness, and the residue taken up in water. Addition of excess tetramethylammonium chloride precipitated the corresponding salt of V which was recrystallized from ethanol to yield orange plates (85%). *Anal.* Calcd. for $(CH_3)_4N(B_9C_2H_{11})Fe(C_5H_5)$: Fe, 17.05; B, 29.73; C, 40.33; N, 4.28; H, 8.61. Found: Fe, 17.86; B, 29.49; C, 37.47; N, 4.74; H, 8.55. In contrast to II, V was stable to oxidation by air. The ^1H n.m.r. spectrum of tetramethylammonium V was consistent with its assigned structure as follows[5]: a broad carborane C–H resonance of intensity 2 at −3.58 p.p.m.; a sharp singlet of intensity 12 at −3.09 p.p.m. assigned to the methyl groups in the tetramethylammonium cation; and a sharp singlet of intensity 5 at −4.37 p.p.m. assigned to cyclopentadienyl protons. In comparison, ferrocene exhibits a singlet at −4.17 p.p.m.[6] The ^{11}B n.m.r. spectrum of V closely resembles that of II and IV.

Paramagnetic VI and I gave the interesting ^{11}B n.m.r. spectra shown in Figure 1. No ^{11}B–^1H coupling was observed[7] and these spectra extended over approximately 600 p.p.m. The wide separation of the individual ^{11}B resonances is undoubtedly due to the presence of large contact shifts which involve the paramagnetic iron(III) atom. The great similarity of the two spectra presented in Figure 1 virtually proves that I bears two π-(1)-2,3-dicarbollyl[4] groups about iron as previously suggested.[1] The broad, highest-field resonances in I and VI (e) and the poorly defined (and probably quite broad) resonances in the b–c arrays must arise from the three boron atoms nearest iron(III) in I and VI.

The chemistry of the (1)-2,3- and (1)-2,4-dicarbollide ions[4] is under intensive investigation and further results will be reported at a later date.

Acknowledgments. The authors are indebted to Professor David Templeton and Dr. Allan Zalkin for the results of their structural studies received prior to publication. This research was generously supported by the Army Research Office (Durham).

(5) Relative to tetramethylsilane standard.
(6) G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).
(7) W. N. Lipscomb and A. Kaczmarczyk, *Proc. Natl. Acad. Sci. U. S.*, **47**, 1796 (1961), have observed the loss of ^{11}B–^1H coupling in ^{11}B n.m.r. spectra obtained in the presence of Fe^{III}.
(8) Alfred P. Sloan Research Fellow.

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The Crystal and Molecular Structure of $C_5H_5FeB_9C_2H_{11}$

Sir:

A compound designated π-cyclopentadienyl-π-(1)-2,3-dicarbollyliron(III) was synthesized by Hawthorne and Pilling as described in the adjacent communication.[1] We determined its crystal structure by X-ray diffraction and found a "sandwich"-type molecular structure as predicted by Hawthorne. This work is the

(1) M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, **87**, 3987 (1965).

first X-ray crystallographic confirmation of the structure of the $B_9C_2H_{11}^{-2}$ ion, and it gives support for the structures suggested previously for several other derivatives.[2,3]

Crystals of $C_5H_5FeB_9C_2H_{11}$ were received from Hawthorne and Pilling[1] as tiny flat plates. They are monoclinic, space group $P2_1/c$, with unit cell dimensions $a = 11.470$, $b = 6.629$, $c = 16.808$ Å., $\beta = 99.86°$. With four molecules in the unit cell, the density is calculated as 1.34 g./ml. We measured the intensities of 1639 independent reflections by the stationary crystal technique using Mo Kα radiation (λ 0.71069 Å.) and a scintillation detector. The Patterson function revealed the iron atom location, and a Fourier calculation phased by the iron atom showed all of the boron and carbon atoms. Carbon and boron atoms in the carborane were distinguished by the behavior of their thermal parameters when scattering factors were interchanged in least-squares calculations. The assignment was confirmed by the bond distances which resulted; they correspond to a smaller bond radius for carbon than for boron. After some refinement by least squares, a difference function showed evidence for all the hydrogen atoms. In the final refinement, isotropic thermal parameters were used for hydrogen and anisotropic parameters for all other atoms. The function $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was reduced to 0.074. In Table I are listed the final coordinates of the

Table I. Atomic Coordinates and Root-Mean-Square Amplitudes[a]

Atom	x	y	z	u
Fe	0.2244	−0.0331	0.1897	0.23
C(1R)[a]	0.0917	−0.0331	0.0909	0.35
C(2R)	0.1817	0.0862	0.0767	0.33
C(3R)	0.2779	−0.0361	0.0780	0.34
C(4R)	0.2433	−0.2285	0.0942	0.34
C(5R)	0.1278	−0.2228	0.1026	0.34
C(2)	0.3345	−0.1476	0.2871	0.25
C(3)	0.2008	−0.1537	0.2978	0.24
B(4)	0.1354	0.0749	0.2794	0.25
B(5)	0.2502	0.2337	0.2580	0.26
B(6)	0.3764	0.0795	0.2621	0.27
B(7)	0.3035	−0.1630	0.3822	0.30
B(8)	0.1786	−0.0172	0.3790	0.27
B(9)	0.2127	0.2301	0.3555	0.26
B(10)	0.3607	0.2328	0.3447	0.28
B(11)	0.4159	−0.0112	0.3609	0.30
B(12)	0.3173	0.0825	0.4194	0.28

[a] In Å.; R indicates an atom in the cyclopentadienyl ring.

heavy atoms and the root-mean-square amplitudes of thermal vibration. The standard deviations of these coordinates correspond to about 0.001 Å. for Fe and 0.01 Å. for the other atoms. These estimates of precision make no provision for systematic errors.

The thermal motion is large and anisotropic. In the cyclopentadienyl ring the largest amplitudes are tangential to the ring, and the atoms are very poorly resolved in Fourier sections. This evidence for torsional motion or internal rotation is very similar to that reported in ferrocene.[4] In the carborane part of the molecule the amplitudes are less, the bond distances are greater, and the atomic resolution is very much better. We have found no simple way of describing the thermal anisotropy of this part of the molecule.

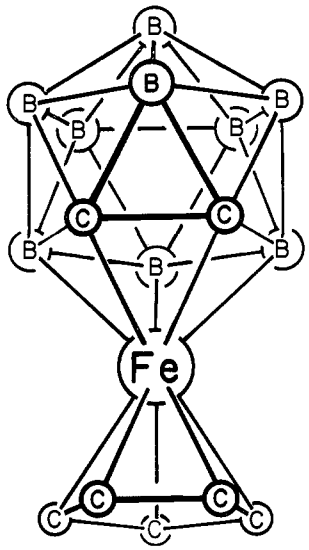

Figure 1.

Average bond distances are listed in Table II, without any correction for thermal motion. This correction may be as much as 0.05 Å. for some of the bonds,

Table II. Average Bond Distances

Atoms	Distance, Å.
Fe–B (3)[a]	2.09
Fe–C (2)	2.04
Fe–C (5)[b]	2.07
B–B (18)	1.75
B–C (6)	1.68
C–C (1)	1.58
C–C (5)[b]	1.36
B–H (9)	0.9
C–H (2)	0.8
C–H (5)[b]	0.7

[a] Number of bonds in molecule. [b] Cyclopentadienyl distances.

but we cannot estimate it with confidence. In each case the correction will increase the bond distance. Each distance in a group (except bonds to H) is within 0.03 Å. of the average value. Because of the large and uncertain thermal corrections, we give no significance to the deviations within each group. Because of the well-known tendency of the X-ray method to give short values for bond lengths to hydrogen, as well as the large thermal motion, no significance is given to the fact that the lengths of these bonds listed in Table II are shorter than accepted values.

The skeleton of the molecule is shown in Figure 1. The atoms of the carborane part are at 11 of the 12 corners of an icosahedron which is approximately regular. The iron atom is at the twelfth corner, but somewhat further away. Within the experimental accuracy of about 0.2 Å., each hydrogen atom is on the line passing through its neighbor and the opposite atom of the icosahedron. The hydrogen atom positions on the cyclopentadienyl ring are more poorly

(2) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).
(3) M. F. Hawthorne and T. D. Andrews, *ibid.*, **87**, 2496 (1965).
(4) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Cryst.*, **9**, 373 (1956).

determined, but within the large experimental uncertainty they are in the expected locations in the plane of the ring.

The iron atom is almost equidistant from the carbon atoms in the ring and the five neighbors in the icosahedron. The configuration is almost exactly eclipsed rather than staggered as in the ferrocene crystal.[4] We tested the staggered structure in the least-squares calculations but got significantly worse agreement. Because of the large twisting motion, the configuration in the crystal may have little chemical significance.[5]

(5) This work was done under the auspices of the U. S. Atomic Energy Commission.

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Sense of Helix of Poly-L-histidine[1]

Sir:

Current interest in the optical rotatory properties of synthetic polypeptides centers largely on detection of ordered structures, such as the α-helix, in these molecules. Information about the screw sense of helix and estimates of helix content may be obtained from analysis of optical rotatory dispersion (ORD) curves and circular dichroism (CD) spectra.[2–9] Until quite recently, little was known about side-chain chromophore Cotton effects and their influence on estimates of helix content and helix sense. Studies on poly-L-tyrosine[7,8] and poly-L-tryptophan[9] show, however, that in these polymers side-chain Cotton effects influence the rotatory dispersion sufficiently that not even the presence of helix is certainly established from ORD measurements in the *visible* spectrum, much less the helical sense.

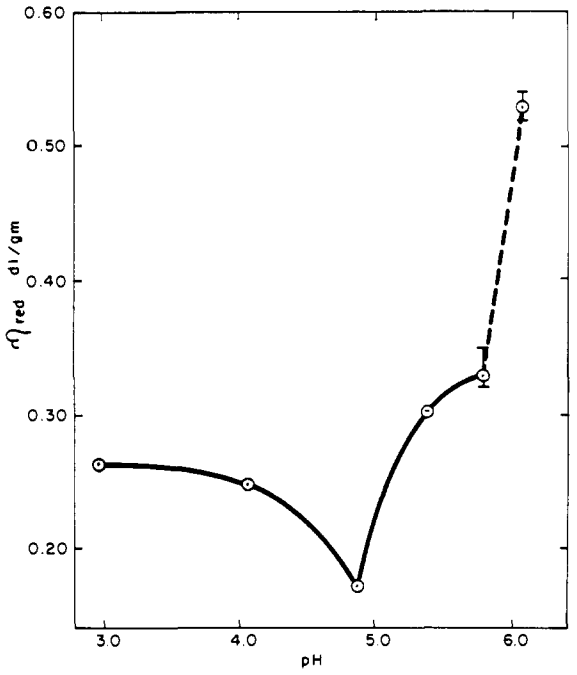

Figure 1. Reduced viscosity of poly-L-histidine at 0.5% in 0.10 *M* acetate buffer. Viscosities were measured in Cannon–Fenske viscometers with water flow times in excess of 100 sec. at 25°; the temperature was 25 ± 0.02 °.

(1) This work was supported in part by grants from the United States Public Health Service (GM 10576) and from the National Science Foundation (GB 1913).

(2) E. Schechter and E. R. Blout, *Proc. Natl. Acad. Sci. U. S.*, **51**, 794 (1964).
(3) G. Fasman, *Methods Enzymol.*, **6**, 928 (1963).
(4) J. Schellman and C. G. Schellman in "The Proteins," Vol 2, H. Neurath, Ed., Academic Press Inc., New York, N. Y., 1964, Chapter 7.
(5) E. R. Blout, I. Schmier, and N. S. Simmons, *J. Am. Chem. Soc.*, **84**, 3193 (1962).

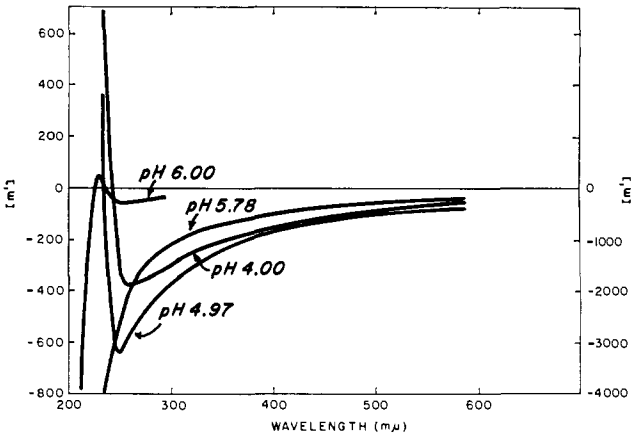

Figure 2. Optical rotatory dispersion spectra of poly-L-histidine in acetate buffer at ionic strength 0.10. The ordinate on the right is for the curve marked pH 5.78.

Norland, *et al.*,[10] have investigated the ORD of poly-L-histidine. These authors noted a marked increase in levorotation at the mercury green line associated with neutralization of the imidazolium groups. On the basis of this and other evidence, they suggested that poly-L-histidine may exist in aqueous solution as a left-handed α-helix over a narrow range of pH.

In this communication we report the CD spectra of poly-L-histidine solutions at pH values between 3.0 and 6.0. Circular dichroism spectra present narrow bands and are thus useful in resolving optically active absorption bands.[11] The CD spectra of poly-L-histidine and the viscosities indicate that in this pH interval poly-L-histidine undergoes a transition from random coil to right-handed α-helix.

Figure 1 shows the reduced viscosity at 0.5% poly-L-histidine as a function of pH. Between pH 4 and 4.9 the viscosity decreases, as expected for the random coil which is being discharged. As the pH is raised above 4.9, there is an abrupt rise in viscosity. The value at pH 6.0 was time dependent, with clearly discernible loss of solubility within a few minutes after preparation of the solution. Between pH 5.0 and 5.8, however, solutions were stable for at least 24 hr.

Figure 2 shows the ORD spectra of poly-L-histidine at the pH values indicated. There is a large change in the ORD spectrum between pH 4.97 and 5.78 both in quality and quantity. We do not believe that the minimum at 240 mμ exhibited by the solutions at pH 4 and 5 is the trough of a negative Cotton effect but

(6) G. Holzwarth, W. Gratzer, and P. Doty, *ibid.*, **84**, 3194 (1962).
(7) G. D. Fasman, E. Bodenheimer, and C. Lindblow, *Biochemistry*, **3**, 1665 (1964).
(8) S. Beychok and G. D. Fasman, *ibid.*, **3**, 1675 (1964).
(9) G. D. Fasman, M. Landsberg, and M. Buchwald, *Can. J. Chem.*, **43**, 1588 (1965).
(10) K. Norland, G. D. Fasman, E. Katchalski, and E. R. Blout, *Biopolymers*, **1**, 277 (1963).
(11) S. Beychok, *Proc. Natl. Acad. Sci. U. S.*, **53**, 999 (1965).