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THE CRYSTAL AND MOLECULAR STRUCTURE OF $C_5H_5FeB_9C_2H_{11}$

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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-dicarbollyl iron (III) was synthesized by Hawthorne and Pilling as described in the adjacent communication.[1] We determined its crystal structure

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

by X-ray diffraction and found a "sandwich" type molecular structure as predicted by Hawthorne. This work is the 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]

(2) M. F. Hawthorne, D. C. Young, and P. A. Wegner, ibid., 87, 1818 (1965).
(3) M. F. Hawthorne, and T. D. Andrews, ibid., in press.

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, β = 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 MoKα 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, which correspond to 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 $\underline{R} = \sum ||\underline{F}_{obs}|-|\underline{F}_{cal}||/\sum |\underline{F}_{obs}|$ was reduced to 0.074. In Table I are listed the final coordinates of the 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

(4) J. D. Dunitz, L. E. Orgel, and A. Rich, Acta Cryst., 9, 373 (1956).

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.

TABLE I

ATOMIC COORDINATES AND RMS AMPLITUDES

Atom	x	y	z	u, Å
Fe	.2244	-.0331	.1897	.23
C(1R)[a]	.0917	-.0331	.0909	.35
C(2R)	.1817	.0862	.0767	.33
C(3R)	.2779	-.0361	.0780	.34
C(4R)	.2433	-.2285	.0942	.34
C(5R)	.1278	-.2228	.1026	.34
C(2)	.3345	-.1476	.2871	.25
C(3)	.2008	-.1537	.2978	.24
B(4)	.1354	.0749	.2794	.25
B(5)	.2502	.2337	.2580	.26
B(6)	.3764	.0795	.2621	.27
B(7)	.3035	-.1630	.3822	.30
B(8)	.1786	-.0172	.3790	.27
B(9)	.2127	.2301	.3555	.26
B(10)	.3607	.2328	.3447	.28
B(11)	.4159	-.0112	.3609	.30
B(12)	.3173	.0825	.4194	.28

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

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.

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, 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.

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 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]

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

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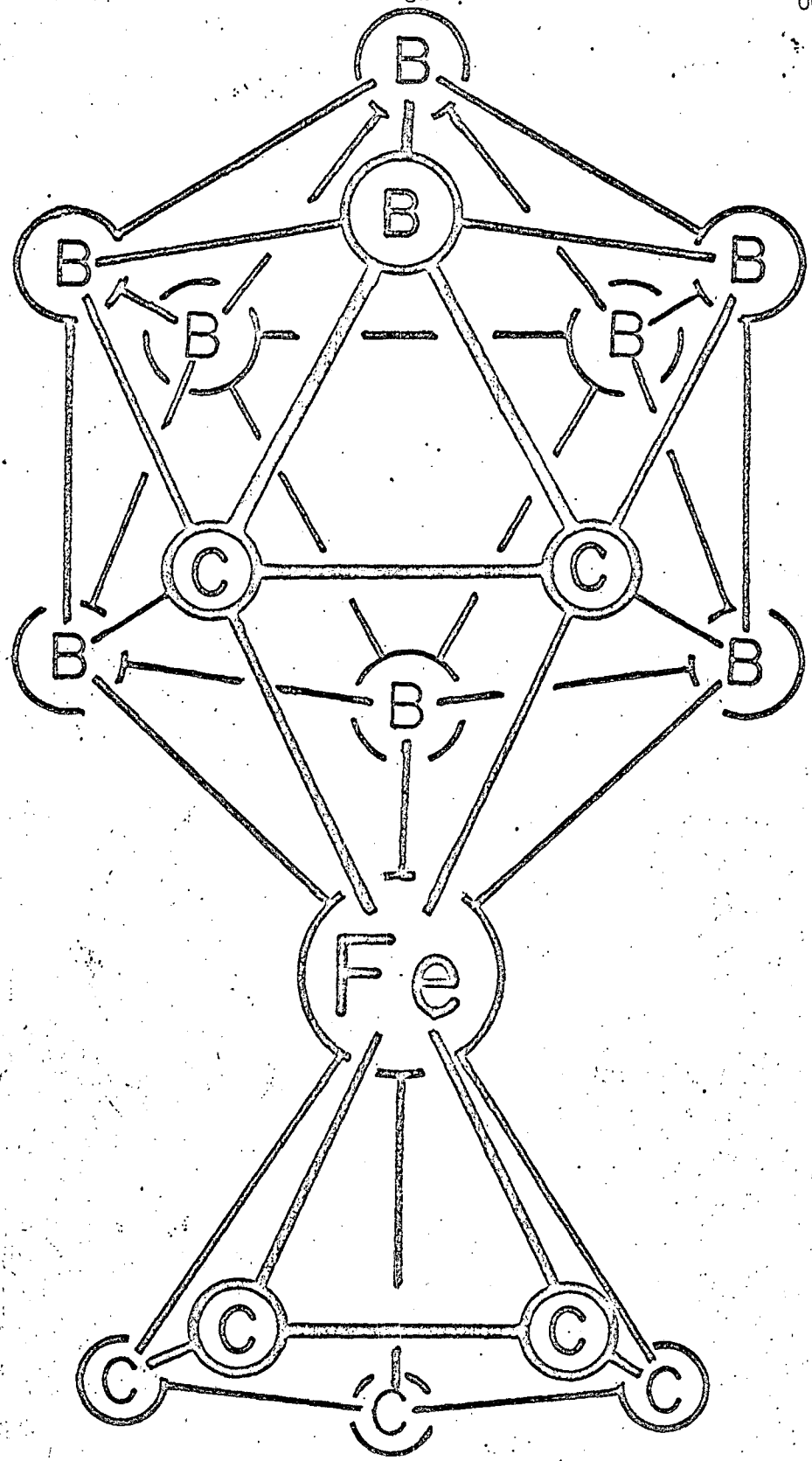

Figure 1.

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