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The Crystal and Molecular Structure of Bis(fulvalene)diiron

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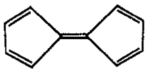
Bis(fulvalene)diiron, $(C_{10}H_8)_2Fe_2$, crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (C_{2h}^5; no. 14) with a = 9.517 ± 0.006 Å, b = 7.561 ± 0.005 Å, c = 10.604 ± 0.009 Å, β = 112.07 ± 0.08°, and Z = 2. Observed and calculated densities are 1.76 ± 0.03 and 1.728 g cm^{-3}, respectively. A single-crystal X-ray diffraction study of this complex has been completed, using counter data to $\sin\theta = 0.42$ (Mo Kα radiation). All atoms (including hydrogens) have been located, the final discrepancy index being $R_F = 7.63\%$ for the 1088 independent, nonzero reflections. A study of the intermolecular contacts ($H\cdots H \geqslant 2.39$ Å, $C\cdots H \geqslant 2.93$ Å) confirms the monomeric nature of the complex. The $(C_{10}H_8)_2Fe_2$ molecule possesses a crystallographic center of symmetry. The dihedral angle between the two five-membered rings of the fulvalene system is 2° 37′. The molecule may be regarded as 1,1′-biferrocenylene, in which each of the ferrocenylene (*i.e.*, $-C_5H_4FeC_5H_4-$) moieties takes up a conformation which is only 1° 48′ from the perfectly eclipsed arrangement. The two iron atoms are 3.984 Å apart.

Introduction

Although a number of phenyl-[2-4] and halogen-substituted[5-8] fulvalenes have been prepared, the parent compound (I) has been detected only in dilute solution.[9-14] It is interesting , therefore, that fulvalene has recently been stabilized in the complex bis(fulvalene)diiron (otherwise named as 1,1′-biferrocenylene).[15,16] This complex is of interest as a potential source both of fulvalene and of substituted fulvalenes, since it undergoes such reactions as Friedel–Crafts benzoylation.[15]



I

It has been suggested that the proton resonance spectrum of bis(fulvalene)diiron (two triplets at 3.77 and 5.27 ppm from TMS) is consistent with a structure in which "the [two] iron atoms are located off-center in their respective ferrocenylene moieties."[16] We have therefore undertaken a single-crystal X-ray diffraction study of this complex in order to establish its stereochemistry unequivocally.

Unit Cell and Space Group

A 10-mg sample of the complex was generously supplied by Professor M. D. Rausch. Crystals suitable for an X-ray diffraction study were obtained by slow cooling of a saturated solution of the complex in boiling benzene.[17] The crystals thus obtained are air stable and are not X-ray sensitive. Optical examination and the observed symmetry of the reciprocal lattice (C_{2h}; 2/m) indicated that the crystals belonged to the monoclinic system. Unit cell dimensions, obtained by a least-squares analysis of high-angle precession data, taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) and calibrated with sodium chloride (a = 5.640 Å) at 23 ± 2°, are a = 9.517 ± 0.006 Å, b = 7.561 ± 0.005 Å, c = 10.604 ± 0.009 Å, and β = 112.07 ± 0.08°. The unit cell volume is 707.2 Å^3.

A survey of $0kl$ and $1kl$ Weissenberg photographs and of $h0l$, $h1l$, $hk0$, and $hk1$ precession photographs revealed the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$, compatible only with space group $P2_1/n$ (C_{2h}^5; no. 14).[18] The observed density (ρ_{obsd} = 1.76 ± 0.03 g cm^{-3} by flotation in aqueous zinc iodide) is consistent with the presence of two molecules per unit cell (ρ_{calcd} = 1.728 g cm^{-3} for M = 368.03, Z = 2). Thus, in the absence of disorder, the molecule is required to possess a center of symmetry.

Collection and Reduction of the X-Ray Diffraction Data

Two crystals were used during the course of data collection. Crystal I, a regular parallelepiped of dimensions 0.44 × 0.10 × 0.12 mm (referred to the [100], [011], [0$\bar{1}$1] axes), was mounted along its extended a direction. Crystal II, an irregular plate of dimensions 0.08 × 0.22 × 0.26 mm (referred to the [100], [011], [01$\bar{1}$] axes), was mounted along its b axis. Each crystal was sealed into a 0.3-mm diameter thin-walled lithium borate capillary tube.

Intensity data were collected with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) on a 0.01°-incrementing Supper-Pace Buerger automated diffractometer. Details of the "stationary-background, ω scan, stationary-background" counting sequence have been described pre-

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[1] Research Fellow of the Alfred P. Sloan Foundation, 1968–1970.
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[14] E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968).
[15] M. D. Rausch, R. F. Kovar, and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **91**, 1259 (1969).
[16] F. L. Hedberg and H. Rosenberg, *ibid.*, **91**, 1258 (1969).
[17] The complex has a remarkably low solubility. Professor M. D. Rausch has estimated its solubility in boiling benzene as approximately 0.5 g/1000 ml. [Hedberg and Rosenberg[16] claimed a solubility of *ca.* 0.2 g/1000 ml in *cold* benzene.]
[18] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 99.

viously.[19] Experimental details specific to the present structural investigation include the following. (i) The X-ray generator was operated at 49.0 kV/19.0 mA. (ii) The angle scanned was chosen as $\omega = [2.0 + (1.0/L)]°$, where $(1/L)$ is the Lorentz factor. (iii) The speed of the ω scan was 2°/min. (iv) Initial and final backgrounds (B_1 and B_2 counts, respectively) were measured for one-fourth the time of the ω scan (C counts). (v) Within each level, a carefully preselected check reflection was remeasured after each batch of 20 reflections had been collected. [The absence of significant (*i.e.*, >1–2%) deviations from the mean value confirmed the stability of the crystal, the stability of the crystal toward X-rays, and the continued alignment of the crystal.] (vi) The intensity of a reflection *hkl* was calculated as: $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$.

Equiinclination Weissenberg geometry was used in collecting data for the quadrants Hkl and $Hk\bar{l}$ (H = 0–9) from the a-mounted crystal I and for quadrants hKl and $\bar{h}Kl$ (K = 0–8) from the b-mounted crystal II. [The set of data collected from crystal II is complete to $\sin\theta = 0.42$ (the limit of observable reflections on long-exposure Weissenberg photographs) save for the few reflections with $\theta \leqslant 4°$, which are shielded from the counter by a Pb backstop.]

Data were assigned standard deviations according to the following scheme, where $\delta(hkl) = 3[C(hkl) + B_1(hkl) + B_2(hkl)]^{1/2}$: $I(hkl) \geqslant 1225$, $\sigma\{I(hkl)\} = 0.1[I(hkl)]$; $1225 > I(hkl) \geqslant \delta(hkl)$, $\sigma\{I(hkl)\} = 3.5[I(hkl)]^{1/2}$; $I(hkl) < \delta(hkl)$, reflection rejected.

Of the 1237 reflections collected from crystal I, 158 were rejected; of the 1277 reflections collected from crystal II, 206 were rejected. Intensities were corrected for Lorentz and polarization effects $[(\mathrm{Lp})^{-1} = 2\cos^2\bar{\mu}\sin\Upsilon/(1 + \cos^2 2\theta)]$,[20] and absorption corrections were applied[21] (μ = 21.30 cm^{-1} for Mo Kα radiation). Transmission coefficients were found to range from 0.766 to 0.819 for data from crystal I (volume 0.0055 mm^3) and from 0.752 to 0.855 for data from crystal II (volume 0.0020 mm^3). A least-squares analysis of common reflections[22] was used to merge the 19 zones of data to a common scale. The resulting 1088 independent, nonzero reflections were used in a Wilson plot,[23] which yielded the approximate absolute scale and the over-all isotropic thermal parameter (B = 1.41 Å^2).

Elucidation and Refinement of the Structure

A three-dimensional Patterson synthesis,[24] which had been sharpened such that the average intensity was no longer θ dependent, revealed a set of vectors consistent with an iron atom at $x = 0.1995$, $y = 0.0423$, $z = 0.4710$. A three-dimensional Fourier synthesis, phased only by the iron atom ($R_F = 40.4\%$)[25] yielded the approximate positions of all ten carbon atoms in the asymmetric unit. Four cycles of full-matrix least-squares refinement[26] of individual positional and isotropic thermal parameters for the eleven independent nonhydrogen atoms resulted in convergence at $R_F = 12.09\%$ and $R_{wF^2} = 7.35\%$. A further cycle of refinement, in which the thermal motion of the iron atom was considered anisotropic, led to the reduced discrepancy indices $R_F = 10.41\%$ and $R_{wF^2} = 5.39\%$. Hydrogen atoms were now introduced in calculated positions,[27] and a structure factor calculation showed significantly better agreement with $R_F = 9.85\%$ and $R_{wF^2} = 4.80\%$. Four cycles of full-matrix refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms led to convergence ((suggested shift)/σ < 0.07 for each parameter) at $R_F = 7.63\%$ and $R_{wF^2} = 3.20\%$.

Finally, a difference-Fourier synthesis calculated by omitting hydrogen atoms ($R_F = 8.51\%$, $R_{wF^2} = 4.29\%$) revealed peaks of height 0.47–0.82 e$^-$ Å^{-3} close to each of the calculated positions for hydrogen atoms. A final F_o electron density synthesis showed carbon atoms to have maxima ranging from 5.87 to 7.26 e$^-$ Å^{-3}.

It should be noted that Hamilton R-factor ratio tests[28] confirm that (i) anisotropic thermal parameter refinement for the iron atom, (ii) anisotropic thermal parameter refinement for the carbon atoms, and (iii) the inclusion of hydrogen atoms each results in an improvement which is significant at a confidence level greater than 99.5%. At the completion of the analysis, the standard error in an observation of unit weight was 1.9.

Scattering factors for *neutral* carbon and hydrogen[29a] were used throughout the analysis; the Thomas–Fermi–Dirac values for *neutral* iron[29b] were corrected for dispersion ($\Delta f' = +0.4$ e$^-$, $\Delta f'' = +1.0$ e$^-$).[29c] Observed and calculated structure factors are collected in Table I. Final atomic coordinates are shown in Table II. Thermal parameters are given in Table III; the associated atomic vibration ellipsoids are listed in Table IV and displayed pictorially[30] in Figure 1.

The Molecular Structure

Interatomic distances with their estimated standard deviations (esd's) are collected in Table V; bond angles (with esd's) are shown in Table VI. The stereochemistry of the bis(fulvalene)diiron molecule and the system for labeling atoms are each illustrated in Figure 1. [Hydrogen atoms, omitted from this figure for the sake of clarity, bear the same numbers as the carbon atoms to which they are bonded. Atoms in the basic asym-

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(19) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 1123 (1968).

(20) $\bar{\mu}$ is the equiinclination angle, Υ is the vertical Weissenberg coordinate, and θ is the Bragg angle (all in degrees).

(21) Using a local modification of the IBM 7094 program GNABS; see C. W. Burnham, *Am. Mineralogist*, **51**, 159 (1966).

(22) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

(23) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

(24) All crystallographic computations were (unless otherwise stated) performed under the CRYM system. CRYM is an integrated sequence of crystallographic routines for the IBM 7094, written by Professor R. E. Marsh and his coworkers at the California Institute of Technology.

(25) $R_F = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

(26) The over-all scale parameter for F_o was refined in all least-squares refinement processes. Throughout the analysis, the residual minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$.

(27) Hydrogen atom positions were calculated with d(C–H) = 1.080 Å and the idealized geometry for attachment to a planar pentagonal ring. Each hydrogen atom was assigned an isotropic thermal parameter of B = 4.0 Å^2. Neither positions nor thermal parameters were refined. Positions were, however, redefined with respect to the up-dated carbon positions at the end of the refinement procedure.

(28) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(29) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 211; (c) p 216.

(30) Atomic vibration ellipsoids have been drawn using OTLIPS, a program for the IBM 1620 (with on-line CALCOMP plotter) written by Dr. P. H. Bird.

Table I

Observed and Calculated Structure Factors (in electrons × 10.00) for Bis(fulvalene)diiron

K	L	FO	FC
H = -11			
1	4	49	11
1	5	74	38
H = -10			
0	2	190	171
0	4	161	191
0	6	242	239
0	8	171	171
1	1	180	169
1	3	203	190
1	5	194	195
1	7	166	179
1	8	95	48
1	9	104	102
2	2	166	168
2	3	51	10
2	4	187	177
2	6	91	123
2	8	110	99
3	1	76	105
3	2	82	4
3	3	148	158
3	5	104	113
3	6	76	56
3	7	141	103
4	4	140	125
4	5	331	86
H = -9			
0	1	176	186
0	3	262	246
0	5	156	142
0	7	294	272
0	9	222	190
1	1	64	37
1	2	195	201
1	3	58	65
1	4	187	181
1	5	24	13
1	6	223	209
1	8	246	230
1	9	48	26
1	10	179	175
2	1	65	18
2	2	154	144
2	3	175	174
2	4	71	67
2	5	159	153
2	6	96	102
2	7	189	176
2	9	185	140
2	10	87	44
3	1	253	265
3	3	197	190
3	4	95	119
3	5	139	141
3	6	69	66
3	7	85	109
3	8	133	132
3	9	79	74
4	2	198	197
4	3	59	53
4	4	102	100
4	5	64	59
4	6	127	116
4	7	72	71
4	8	91	95
5	2	91	29
5	3	145	134
5	4	77	46
5	5	85	77
5	6	96	86
H = -8			
0	2	60	47
0	4	312	334
0	6	213	236
0	8	130	42
0	10	95	76
1	1	165	167
1	3	211	226
1	4	119	127
1	5	275	274
1	6	78	82
1	7	108	14
1	8	102	36
1	10	89	51
1	11	40	38
2	1	93	91
2	2	225	233
2	4	163	155
2	5	115	130
2	6	33	10
2	7	212	204
2	8	38	36
2	10	70	39
2	11	123	125
3	1	116	125
3	2	142	168
3	3	139	138
3	4	164	169
3	6	321	265
3	8	156	150
3	10	168	154
4	1	180	176
4	2	154	154
4	3	201	212
4	4	82	98
4	5	197	206
4	6	83	13
4	7	169	166
4	8	73	49
4	9	152	154
5	1	71	67
5	2	148	153
5	3	162	145
5	4	227	230
5	5	92	67
5	6	198	195
5	8	173	166
6	1	84	60
6	2	46	38
6	3	163	160
6	4	70	35
6	5	234	242
H = -7			
0	1	468	466
0	3	339	357
0	5	446	472
0	7	389	374
0	9	209	216
0	11	199	197
1	1	71	58
1	2	457	470
1	3	36	34
1	4	366	389
1	6	441	454
1	7	162	156
1	8	284	282
1	10	204	209
1	11	40	32
2	1	329	340
2	2	84	96
2	3	352	363
2	4	107	111
2	5	275	264
2	6	128	121
2	7	321	319
2	8	147	134
2	9	269	273
2	10	90	35
2	11	145	130
3	1	231	237
3	2	252	264
3	3	137	118
3	4	93	71
3	5	78	77
3	6	83	79
3	8	298	310
3	10	189	178
3	11	105	71
4	1	182	177
4	2	61	32
4	3	168	170
4	4	52	23
4	6	135	137
4	7	191	191
4	8	102	83
4	9	192	190
4	10	84	72
5	1	131	113
5	2	167	179
5	3	50	28
5	4	161	159
5	5	62	49
5	6	127	131
5	7	131	101
5	8	99	112
5	9	87	70
6	1	40	17
6	2	115	112
6	3	81	55
6	4	61	7
6	5	40	39
6	6	54	23
6	7	77	24
H = -6			
0	2	111	98
0	4	96	100
0	6	224	191
0	8	109	93
0	10	82	70
0	12	239	240
1	1	92	89
1	2	50	11
1	3	169	164
1	5	190	197
1	7	200	183
1	9	58	43
1	10	181	166
1	11	232	230
1	12	64	76
2	1	272	282
2	2	121	114
2	3	262	267
2	4	44	37
2	5	297	297
2	6	310	311
2	7	47	36
2	8	214	211
2	10	244	233
2	11	142	157
3	1	39	45
3	2	319	329
3	3	101	85
3	4	482	478
3	5	72	68
3	4	302	279
3	7	120	129
3	8	170	170
3	9	180	180
3	10	171	165
3	11	117	132
4	1	199	191
4	2	54	63
4	3	246	247
4	4	78	48
4	5	328	328
4	6	81	31
4	7	203	213
4	8	95	89
4	9	207	210
4	10	42	71
5	1	123	104
5	2	150	152
5	4	301	305
5	5	83	62
5	6	259	264
5	7	112	109
5	8	192	191
6	1	199	210
6	2	108	16
6	3	313	312
6	4	61	41
6	5	327	335
6	6	71	52
6	7	199	184
6	8	36	12
7	1	42	18
7	2	245	229
7	3	48	35
7	4	256	261
7	6	186	189
H = -5			
0	1	644	660
0	3	287	313
0	5	379	373
0	7	546	538
0	9	297	311
0	11	75	76
1	1	300	289
1	2	508	530
1	3	73	71
1	4	371	396
1	5	114	90
1	6	399	412
1	8	338	345
1	9	100	89
1	10	62	49
1	11	113	118
2	1	467	485
2	2	217	213
2	3	526	535
2	4	98	99
2	5	317	335
2	6	86	93
2	7	282	292
2	8	177	171
2	9	33	49
2	10	182	194
2	11	84	14
2	12	86	80
3	1	84	63
3	2	414	421
3	3	73	92
3	4	308	314
3	5	192	185
3	6	254	261
3	7	171	175
3	8	192	200
3	9	235	242
3	10	74	34
3	11	91	90
4	1	371	328
4	2	55	53
4	3	290	284
4	4	116	114
4	5	199	196
4	7	217	226
4	8	186	182
4	9	90	86
4	10	160	157
4	11	104	95
5	2	227	230
5	3	91	84
5	5	184	154
5	6	122	128
5	7	161	171
5	8	41	20
5	9	310	230
6	1	85	61
6	2	158	86
6	3	126	116
6	4	181	183
6	5	62	60
6	6	187	185
6	8	234	230
7	1	144	62
7	2	143	135
7	3	130	138
7	4	160	170
7	5	83	48
7	6	72	29
7	7	117	111
8	2	102	122
H = -4			
0	2	81	35
0	4	384	359
0	6	472	475
0	8	407	392
0	10	328	338
0	12	289	275
1	1	172	181
1	2	59	40
1	3	311	312
1	4	108	111
1	5	573	568
1	6	149	153
1	7	444	440
1	9	309	319
1	10	62	17
1	11	271	263
2	1	269	243
2	2	184	183
2	3	403	391
2	4	594	591
2	5	304	298
2	6	412	423
2	7	121	103
2	8	255	256
2	10	242	251
2	12	207	198
3	1	122	131
3	2	558	557
3	3	285	295
3	4	429	423
3	5	297	303
3	6	160	167
3	7	91	97
3	8	97	101
3	9	159	171
3	10	49	49
3	11	209	225
4	1	387	394
4	2	199	196
4	3	421	426
4	4	207	171
4	5	121	127
4	6	141	126
4	7	163	169
4	8	83	70
4	9	178	165
4	10	187	179
4	11	55	87
5	1	159	163
5	2	316	317
5	4	172	163
5	5	148	143
5	6	70	55
5	7	149	156
5	8	130	133
5	9	110	76
5	10	107	61
6	1	280	275
6	3	213	227
6	4	69	72
6	5	145	146
6	6	109	124
6	7	66	65
6	8	63	27
7	1	88	49
7	2	228	225
7	3	111	119
7	4	263	268
7	5	69	31
7	6	186	187
8	1	213	210
8	2	224	45
8	3	200	199
8	4	46	21
H = -3			
0	1	698	686
0	3	456	319
0	5	466	438
0	7	209	209
0	11	84	76
1	1	165	167
1	2	505	499
1	3	53	26
1	4	197	212
1	5	50	31
1	6	276	266
1	7	133	106
1	8	53	43
1	9	59	16
1	11	102	83
2	1	476	463
2	2	301	296
2	3	263	280
2	4	190	201
2	5	86	86
2	6	237	246
2	7	86	50
2	8	177	171
2	9	132	154
2	10	92	45
2	11	92	86
2	12	116	113
3	1	272	271
3	2	540	530
3	3	476	466
3	4	172	176
3	5	269	292
3	6	148	163
3	7	311	338
3	8	78	70
3	9	203	188
3	10	96	110
3	11	134	129
4	1	321	318
4	2	383	385
4	3	304	304
4	4	416	419
4	5	198	190
4	6	267	274
4	7	136	146
4	8	376	381
4	9	52	17
4	10	231	227
4	11	58	41
5	1	162	167
5	2	53	52
5	3	374	373
5	4	137	129
5	5	297	300
5	6	33	12
5	7	355	362
5	8	55	58
5	9	302	310
5	10	45	65
6	1	92	81
6	2	172	176
6	3	138	50
6	4	273	285
6	5	71	30
6	6	323	321
6	7	88	101
6	8	291	297
6	9	90	36
7	1	178	182
7	2	95	96
7	3	175	179
7	4	42	90
7	5	256	258
7	6	73	75
7	7	250	247
8	2	161	174
8	3	91	81
8	4	176	166
8	5	84	90
H = -2			
0	2	1023	1278
0	4	795	770
0	6	925	920
0	8	444	431
0	10	360	372
0	12	215	223
1	1	841	1003
1	2	29	10
1	3	646	638
1	4	138	131
1	5	721	725
1	6	52	44
1	7	580	580
1	8	133	131
1	9	284	291
1	11	272	279
1	12	119	114
2	1	260	251
2	2	543	552
2	3	122	112
2	4	340	357
2	5	237	211
2	6	389	367
2	7	160	162
2	8	291	291
2	9	45	61
2	10	266	218
2	11	100	83
3	1	588	580
3	2	156	158
3	3	497	498
3	4	174	171
3	5	246	242
3	6	103	95
3	7	215	219
3	8	58	58
3	9	232	251
3	10	71	22
3	11	137	146
4	1	349	352
4	2	438	433
4	3	33	4
4	4	340	330
4	5	79	71
4	6	167	176
4	7	65	53
4	8	191	182
4	10	140	144
4	11	79	92
5	1	121	129
5	2	89	96
5	3	113	123
5	4	88	73
5	5	210	213
5	7	80	80
5	9	36	47
5	10	73	86
6	1	202	179
6	2	79	56
6	3	86	60
6	4	60	73
6	5	81	31
6	6	88	92
6	7	90	79
6	8	40	13
6	9	102	70
7	1	53	38
7	2	181	181
7	3	95	103
7	4	153	123
8	1	157	138
8	2	122	133
8	3	122	129
8	4	142	135
8	5	78	59
H = -1			
0	3	42	16
0	5	333	315
0	7	309	295
0	9	33	24
0	11	151	157
1	10	133	132
1	3	121	119
1	5	142	139
1	6	312	308
1	7	92	78
1	8	154	153
1	11	95	100
2	1	225	213
2	2	214	206
2	3	134	148
2	4	319	307
2	5	149	154
2	6	226	231
2	7	183	193
2	8	42	14
2	9	237	251
2	10	125	143
2	11	189	188
3	1	454	458
3	2	188	176
3	3	459	452
3	4	189	191
3	5	523	520
3	6	120	110
3	7	257	262
3	8	214	208
3	9	158	166
3	10	241	243
3	11	127	129
4	1	129	121
4	2	645	650
4	3	40	24
4	4	574	563
4	5	121	117
4	6	422	438
4	8	289	298
4	9	188	177
4	10	152	160
5	1	395	419
5	2	123	118
5	3	446	452
5	5	330	336
5	6	61	8
5	7	313	313
5	8	66	12
5	9	211	200
6	2	288	292
6	4	297	296
6	5	134	115
6	6	206	225
6	8	208	207
7	1	275	293
7	3	381	394
7	4	88	93
7	5	256	260
7	6	79	58
7	7	170	179
8	1	46	9
8	2	318	314
8	3	53	14
8	4	303	297
H = 0			
0	4	708	691
0	6	544	530
0	8	291	260
0	10	252	244
1	2	845	849
1	3	258	271
1	4	241	230
1	5	650	646
1	6	204	186
1	7	326	321
1	8	103	48
1	9	222	228
1	10	145	134
1	11	89	87
2	0	443	435
2	1	690	605
2	2	85	63
2	3	197	188
2	4	431	429
2	5	60	85
2	6	414	411
2	7	123	111
2	8	149	147
2	9	86	94
2	10	71	60
2	11	192	198
3	1	435	426
3	2	186	179
3	3	453	446
3	4	87	57
3	5	370	377
3	6	192	182
3	7	203	202
3	8	113	108
3	10	162	164
4	0	376	371
4	1	101	97
4	2	404	394
4	3	97	100
4	4	319	286
4	5	214	223
4	6	266	268
4	7	246	248
4	8	98	81
4	9	178	173
4	10	63	10
5	1	165	166
5	2	64	57
5	3	89	88
5	4	126	110
5	5	167	133
5	6	235	223
5	7	143	149
5	8	231	229
5	9	72	15
6	0	173	161
6	1	68	27
6	2	70	37
6	3	91	40
6	4	79	71
6	5	100	63
6	6	94	16
6	7	215	202
6	8	84	22
7	1	74	62
7	2	175	175
7	3	88	92
7	4	116	115
7	5	110	112
7	6	153	137
7	7	88	79
8	0	110	126
8	1	136	133
8	2	129	125
8	3	194	191
8	4	107	99
8	5	109	99
H = 1			
0	3	361	349
0	5	547	559
0	7	288	300
0	9	338	357
0	11	205	188
1	2	83	48
1	3	131	110
1	4	437	427
1	5	83	79
1	6	344	356
1	7	81	13
1	8	283	282
1	9	59	15
1	10	322	317
1	11	83	70
2	0	75	74
2	1	303	278
2	2	247	228
2	4	374	369
2	5	484	491
2	6	180	187
2	7	200	202
2	8	152	144
2	9	291	287
3	0	37	16
3	1	302	302
3	2	426	415
3	3	594	600
3	4	810	830
3	5	344	350
3	6	267	276
3	7	176	184
3	8	149	157
3	9	151	146
3	10	156	168
4	0	849	848
4	1	53	50
4	2	735	738
4	3	535	549
4	4	375	387
4	5	259	280
4	7	86	84
4	8	104	107
4	9	125	103
5	0	61	48
5	1	514	524
5	3	451	456
5	4	46	5
5	6	62	11
5	8	92	83
5	9	92	67
6	0	233	232
6	2	360	368
6	3	102	60
6	4	195	201
6	5	75	75
6	6	116	101
6	8	124	114
7	0	70	87
7	1	284	287
7	3	246	259
7	4	44	39
7	5	199	167
8	0	231	223
8	1	85	76
8	2	224	217
8	3	84	70
8	4	190	148
H = 2			
0	0	956	1111
0	2	407	388
0	4	482	452
0	6	81	42
0	8	195	149
1	0	424	415
1	1	384	376
1	2	269	263
1	3	430	413
1	4	293	279
1	5	322	308
1	6	235	221
1	8	56	30
1	9	82	82
1	10	78	33
2	0	381	371
2	1	223	230
2	2	206	222
2	3	122	126
2	4	270	265
2	5	354	341
2	6	187	188
2	7	225	222
2	8	69	7
2	9	97	84
2	10	76	46
3	0	363	359
3	1	328	330
3	2	173	184
3	3	51	28
3	4	307	304
3	5	85	82
3	6	275	276
3	7	64	70
3	8	233	228
3	9	67	31
4	0	407	396
4	1	434	36
4	2	105	111
4	3	395	407
4	4	67	59
4	5	241	251
4	6	155	130
4	7	216	207
4	9	199	193
5	0	333	325
5	1	109	117
5	2	334	324
5	3	75	60
5	4	203	197
5	5	222	251
5	6	194	175
5	8	249	242
6	0	109	34
6	1	237	227
6	2	78	63
6	3	134	125
6	5	162	167
6	6	147	36
6	7	310	304
7	0	275	273
7	2	262	260
7	3	118	108
7	4	172	180
7	5	84	94
7	6	313	317
8	0	55	31
8	1	269	271
8	2	69	89
8	3	187	195
H = 3			
0	1	791	753
0	3	898	896
0	5	415	431
0	7	229	224
0	9	249	236
1	0	441	440
1	1	107	98
1	2	644	637
1	3	68	57
1	4	574	575
1	5	125	128
1	6	268	275
1	7	72	56
1	8	296	296
2	0	298	286
2	1	252	266
2	2	239	226
2	3	532	526
2	4	74	49
2	5	315	307
2	6	37	35
2	7	267	264
2	8	109	32
2	9	274	268
3	0	389	384
3	1	316	317
3	2	459	477
3	3	200	197
3	4	380	392
3	6	173	150
3	7	114	103
3	8	227	185
3	9	46	29
4	0	188	193
4	1	290	294
4	2	198	201
4	3	321	334
4	4	91	105
4	5	196	207
4	6	83	24
4	7	103	105
4	8	89	25
5	0	67	38
5	1	204	206
5	2	88	65
5	4	158	138
5	5	98	96
5	6	141	132
5	7	48	22
6	0	166	171
6	1	65	8
6	2	193	213
6	3	62	35
6	4	59	65
6	5	71	49
7	1	141	188
7	2	46	32
7	3	94	113
7	4	61	59
8	0	193	173
8	1	46	37
8	2	61	78
H = 4			
0	0	228	225
0	2	179	149
0	4	243	71
0	6	154	151
0	8	195	189
1	0	57	66
1	1	111	113
1	2	86	99
1	3	48	41
1	7	147	208
1	8	56	52
1	9	138	122
2	0	171	141
2	1	272	270
2	2	45	52
2	3	164	167
2	5	182	189
2	6	60	75
2	7	134	146
2	8	193	195
3	0	337	344
3	1	61	79
3	2	334	351
3	3	45	36
3	4	277	274
3	5	63	61
3	6	304	314
3	7	113	110
3	8	151	154
4	0	197	169
4	1	330	349
4	2	76	14
4	3	322	333
4	4	54	38
4	5	258	242
4	6	70	57
4	7	203	200
5	0	286	293
5	1	61	20
5	2	334	335
5	4	232	232
5	5	61	16
5	6	212	203
5	7	88	41
6	1	317	321
6	2	97	86
6	3	270	264
6	4	87	20
6	5	213	233
7	0	304	318
7	1	94	96
7	2	269	263
7	3	47	38
7	4	226	209
8	0	77	34
8	1	226	219
H = 5			
0	1	766	786
0	3	420	422
0	5	364	294
0	7	149	152
1	0	684	763
1	2	502	516
1	3	163	92
1	4	336	322
1	5	41	39
1	6	219	223
1	8	139	126
2	0	179	171
2	1	319	324
2	2	142	136
2	3	297	290
2	4	64	50
2	5	197	240
2	6	109	92
2	7	136	138
3	0	182	192
3	1	44	43
3	2	183	181
3	3	187	165
3	4	172	172
3	5	79	85
3	6	74	72
3	7	126	117
4	0	137	26
4	3	182	192
4	4	183	169
4	5	64	93
4	6	112	104
4	7	228	84
5	1	285	269
5	2	93	92
5	3	115	101
5	4	131	117
5	5	112	101
5	6	79	68
6	0	92	74
6	2	52	52
6	4	77	87
7	0	95	60
7	1	94	66
7	2	95	54
H = 6			
0	0	197	184
0	2	320	309
0	4	106	100
0	6	200	143
1	1	287	285
1	2	98	97
1	3	211	204
1	4	60	27
1	5	156	168
1	6	47	19
1	7	186	160
2	0	63	46
2	1	128	130
2	2	196	192
2	4	220	222
2	5	105	101
2	6	185	194
3	0	333	345
3	1	53	73
3	2	196	195
3	3	182	190
3	4	158	163
3	5	155	187
3	6	114	103
4	0	59	59
4	1	332	334
4	2	68	51
4	3	278	276
4	4	174	167
4	5	157	140
5	0	208	214
5	1	84	80
5	2	299	301
5	3	71	97
5	4	173	171
6	0	74	78
6	1	208	216
6	3	152	164
7	0	193	182
H = 7			
0	1	178	186
0	3	294	295
0	5	225	226
1	0	260	273
1	1	55	23
1	2	114	113
1	3	65	57
1	4	218	217
1	5	112	98
2	0	192	196
2	1	83	72
2	3	61	56
2	4	76	83
3	0	165	161
3	1	228	237
3	2	98	101
3	3	98	105
3	5	156	166
4	0	171	172
4	1	121	130
4	2	145	146
4	3	92	75
4	4	138	147
5	0	77	51
5	1	175	167
5	3	173	158
6	0	215	203
6	1	82	35
H = 8			
0	0	150	151
0	2	277	276
0	4	268	265
1	0	119	83
1	1	252	253
1	2	82	72
1	3	263	257
1	4	66	18
2	0	213	213
2	1	66	44
2	2	234	231
2	3	43	25
2	4	137	133
3	0	163	109
3	1	151	148
3	2	63	58
3	3	168	161
4	0	123	83
4	1	130	138
4	2	149	161
5	0	114	100
5	1	97	98
H = 9			
0	1	69	33
0	3	96	52
1	3	48	51
2	0	183	178
2	1	44	66
2	2	75	79
3	1	132	122
3	2	91	67
4	0	109	109
H = 10			
0	0	220	203
2	0	115	125

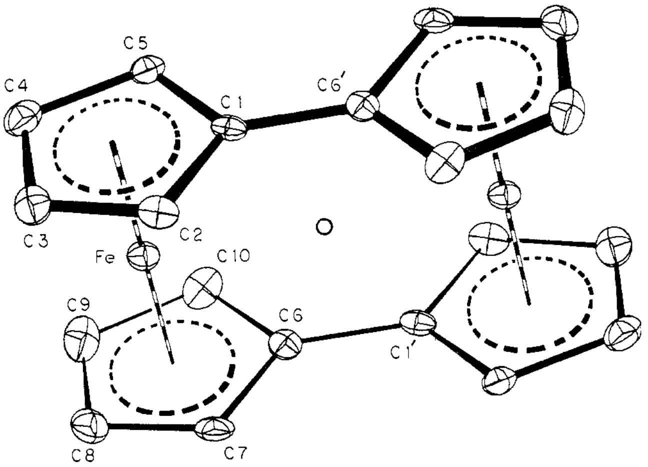

Figure 1.—Numbering of atoms in the bis(fulvalene)diiron molecule. The center of symmetry of the molecule (at 0, 0, $^1/_2$) is indicated by a small circle. The diagram also shows the 68% probability envelopes for the atomic vibration ellipsoids (OTLIPS[31] diagram).

metric unit are labeled without superscripts; those atoms in the other half of the molecule, related to the basic unit by the transformation ($x' = -x, y' = -y, z' = 1 - z$), are labeled with a prime.]

As had been anticipated[15,16] the molecule consists of two ferrocenylene (*i.e.*, $-C_5H_4FeC_5H_4-$) units. These are linked to each other by the bonds C(1)–C(6′) and C(6)–C(1′) and are related to each other *via* a crystallographically imposed center of symmetry. The molecule may also be named 1,1′-biferrocenylene. The two iron atoms in the molecule are 3.984 ± 0.004 Å apart [*cf.* the longest reported covalent iron–iron bond distance of 2.88 Å in the $Fe_2(CO)_8^{2-}$ dianion[31,31a]]. Contrary to the suggestion of Hedberg and Rosenberg,[16] the two iron atoms in bis(fulvalene)diiron apparently do not interact to any appreciable extent; the two iron atoms are symmetrically located in the center of their respective ferrocenylene moieties.

The π-cyclopentadienyl system defined by C(1)–C(2)–C(3)–C(4)–C(5) has a root-mean-square (rms) deviation of 0.007 Å from the least-squares plane $0.1539X - 0.7294Y + 0.6665Z - 4.5832 = 0$[32] [see Table VII]. The other crystallographically independent π-cyclopentadienyl system, defined by C(6)–

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[31] O. S. Mills, personal communication—reported in *J. Am. Chem. Soc.*, **84**, 4639 (1962).

[31a] Note Added in Proof.—An Fe–Fe bond length of 3.05 Å (average) has recently been found in $[Fe(NO)_2I]_2$: L. F. Dahl, E. R. de Gil, and R. D. Feltham, *ibid.*, **91**, 1653 (1969).

[32] Cartesian coordinates; see Table VII.

TABLE II

FINAL ATOMIC COORDINATES (WITH ESD'S) FOR BIS(FULVALENE)DIIRON[a-c]

Atom	x	y	z
Fe	0.19883 (11)	0.03975 (13)	0.48254 (10)
C(1)	0.1494 (8)	−0.1430 (8)	0.6038 (7)
C(2)	0.2652 (9)	−0.0232 (10)	0.6840 (7)
C(3)	0.3899 (9)	−0.0371 (11)	0.6413 (9)
C(4)	0.3543 (9)	−0.1625 (11)	0.5346 (9)
C(5)	0.2008 (8)	−0.2287 (9)	0.5085 (7)
C(6)	−0.0016 (8)	0.1710 (9)	0.3838 (7)
C(7)	0.1150 (8)	0.2923 (9)	0.4645 (8)
C(8)	0.2364 (9)	0.2844 (11)	0.4154 (10)
C(9)	0.1985 (9)	0.1585 (12)	0.3074 (8)
C(10)	0.0504 (9)	0.0879 (11)	0.2870 (8)
H(2)	0.2592	0.0614	0.7639
H(3)	0.4950	0.0358	0.6830
H(4)	0.4261	−0.2013	0.4812
H(5)	0.1390	−0.3256	0.4332
H(7)	0.1104	0.3747	0.5461
H(8)	0.3401	0.3601	0.4546
H(9)	0.2675	0.1229	0.2506
H(10)	−0.0108	−0.0099	0.2123

[a] Esd's appear in parentheses after each parameter; they are right-adjusted to the least significant digit of the preceding number. [b] Only atoms of the basic asymmetric unit are listed. Atoms in the other half of the molecule are related to these by inversion through the center of symmetry at (0, 0, $^1/_2$) such that $x' = -x, y' = -y, z' = 1 - z$. [c] A hydrogen atom is numbered similarly to the carbon atom to which it is attached.[27]

C(7)–C(8)–C(9)–C(10), has an rms deviation of only 0.004 Å from the least-squares plane $0.1951X - 0.7276Y + 0.6575Z - 1.2410 = 0$. The dihedral angle between these planes is 2° 37′—*i.e.*, they are very close to being parallel. [As a result of the center of symmetry in the molecule, it follows that the angle between the two five-membered rings in either fulvalene system is also 2° 37′.]

Individual carbon–carbon bond lengths within the two five-membered rings range from 1.416 ± 0.012 Å [for C(3)–C(4)] to 1.468 ± 0.011 Å [for C(4)–C(5)]. The average value for the ten independent measurements is 1.436 Å. [Wheatley[33] has made a survey of such carbon–carbon bond lengths in π-cyclopentadienyl complexes as have been determined by X-ray diffraction techniques. The mean value (from a total of 23 compounds) is 1.419 Å. However, it is believed that this "X-ray value" is systematically reduced from the true value because of librational motions of the π-cyclopentadienyl system about its C_5 axis. An electron diffraction study of ferrocene shows a carbon–carbon bond distance of 1.431 Å.[34] Similarly, more recent X-ray diffraction studies on complexes in which libration of the π-cyclopentadienyl system is restrained by bulky and inflexible substituents show carbon–carbon bond distances which are increased from Wheatley's mean value. Thus, the average carbon–carbon bond distance in the π-cyclopentadienyl system of $(C_{10}H_8)_2Fe_4(CO)_{10}$ is 1.423 Å,[35,36] in $C_{10}H_8Fe_2(CO)_5$ it is 1.427 Å,[37,38] and in $(C_{10}H_8)_2Fe$ it is 1.430 Å.[39,40]]

C–C–C bond angles within the five-membered rings vary from 106.9 to 109.0° and from 107.6 to 108.8°, averaging 108.0, the value appropriate to a regular planar pentagon, in each case. None of the observed bond

TABLE III

ANISOTROPIC THERMAL PARAMETERS (WITH ESD'S) FOR BIS(FULVALENE)DIIRON[a,b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	82.1 (1.7)	85.2 (2.2)	52.5 (1.3)	4.6 (2.6)	50.5 (2.0)	16.6 (2.3)
C(1)	93 (10)	65 (11)	54 (7)	−2 (17)	37 (14)	32 (15)
C(2)	115 (11)	109 (13)	49 (8)	−16 (20)	38 (15)	3 (16)
C(3)	93 (11)	162 (16)	82 (9)	35 (22)	49 (16)	72 (21)
C(4)	120 (11)	124 (16)	98 (10)	84 (21)	97 (18)	50 (19)
C(5)	97 (10)	81 (12)	69 (8)	38 (17)	78 (16)	15 (16)
C(6)	89 (9)	94 (12)	51 (7)	14 (17)	60 (14)	48 (15)
C(7)	101 (10)	61 (11)	90 (9)	15 (19)	31 (16)	51 (17)
C(8)	105 (11)	129 (14)	127 (12)	5 (22)	86 (19)	97 (22)
C(9)	112 (11)	227 (20)	87 (9)	74 (24)	105 (17)	127 (22)
C(10)	119 (12)	176 (16)	49 (8)	77 (22)	58 (16)	27 (18)

[a] The anisotropic thermal parameter (T) is defined as: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Esd's are shown in parentheses.

TABLE IV

VIBRATION ELLIPSOIDS FOR ATOMS IN THE BIS(FULVALENE)DIIRON MOLECULE[a,b]

Atom	B_{maj}, Å^2	B_{med}, Å^2	B_{min}, Å^2
Fe	2.57	2.22	1.72
C(1)	3.23	2.29	1.21
C(2)	3.94	2.45	1.90
C(3)	4.55	3.24	2.21
C(4)	4.67	3.36	2.06
C(5)	3.27	2.39	1.66
C(6)	2.89	2.58	1.28
C(7)	4.59	2.94	1.14
C(8)	5.79	3.25	2.12
C(9)	6.36	3.02	1.82
C(10)	4.93	2.93	1.80

[a] Major, median, and minor axes of the atomic vibration ellipsoid are defined in terms of the isotropic thermal parameter, B. The transformation to root-mean-square displacement, $(\bar{U^2})^{1/2}$, is: $(\bar{U^2})^{1/2} = [B/8\pi^2]^{1/2}$. [b] The atomic vibration ellipsoids are illustrated in Figure 1.

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TABLE V
INTERATOMIC DISTANCES WITHIN THE BIS(FULVALENE)DIIRON MOLECULE[a]

Atoms	Dist, Å	Atoms	Dist, Å
Fe–C(1)	2.058 (6)	Fe–C(6)	2.053 (7)
Fe–C(2)	2.043 (7)	Fe–C(7)	2.050 (7)
Fe–C(3)	2.044 (8)	Fe–C(8)	2.060 (9)
Fe–C(4)	2.053 (8)	Fe–C(9)	2.061 (8)
Fe–C(5)	2.047 (7)	Fe–C(10)	2.056 (8)
C(1)–C(2)	1.433 (10)	C(6)–C(7)	1.446 (10)
C(2)–C(3)	1.423 (11)	C(7)–C(8)	1.436 (11)
C(3)–C(4)	1.416 (12)	C(8)–C(9)	1.427 (12)
C(4)–C(5)	1.468 (11)	C(9)–C(10)	1.445 (12)
C(5)–C(1)	1.432 (10)	C(10)–C(6)	1.440 (10)
C(1)–C(6′)	1.476 (9)	Fe···Fe′	3.984 (4)

[a] Esd's, shown in parentheses, are right-adjusted to the least significant digit of the preceding number. They include contributions from errors in the unit cell dimensions.

TABLE VI
BOND ANGLES WITHIN THE BIS(FULVALENE)DIIRON MOLECULE[a]

Atoms	Angle, deg	Atoms	Angle, deg
C(1)–Fe–C(2)	40.9 (0.3)	C(6)–Fe–C(7)	41.3 (0.3)
C(2)–Fe–C(3)	40.8 (0.3)	C(7)–Fe–C(8)	40.9 (0.3)
C(3)–Fe–C(4)	40.5 (0.3)	C(8)–Fe–C(9)	40.5 (0.4)
C(4)–Fe–C(5)	42.0 (0.3)	C(9)–Fe–C(10)	41.1 (0.3)
C(5)–Fe–C(1)	40.8 (0.3)	C(10)–Fe–C(6)	41.0 (0.3)
C(1)–C(2)–C(3)	108.2 (0.7)	C(6)–C(7)–C(8)	107.6 (0.7)
C(2)–C(3)–C(4)	109.0 (0.7)	C(7)–C(8)–C(9)	108.8 (0.8)
C(3)–C(4)–C(5)	107.6 (0.7)	C(8)–C(9)–C(10)	107.8 (0.8)
C(4)–C(5)–C(1)	106.9 (0.6)	C(9)–C(10)–C(6)	107.9 (0.7)
C(5)–C(1)–C(2)	108.3 (0.6)	C(10)–C(6)–C(7)	107.8 (0.6)
C(2)–C(1)–C(6′)	125.7 (0.7)	C(7)–C(6)–C(1′)	125.7 (0.6)
C(5)–C(1)–C(6′)	125.9 (0.6)	C(10)–C(6)–C(1′)	126.5 (0.7)

[a] See footnote *a* to Table V.

TABLE VII
LEAST-SQUARES PLANES WITHIN THE ASYMMETRIC UNIT OF BIS(FULVALENE)DIIRON[a–c]

Atom	Dist, Å	Atom	Dist, Å
(A) $0.1539X - 0.7294Y + 0.6665Z - 4.5832 = 0$			
C(1)*	+0.009 (7)	C(4)*	+0.006 (9)
C(2)*	−0.006 (8)	C(5)*	−0.009 (7)
C(3)*	0.000 (9)	Fe	−1.646 (1)
(B) $0.1951X - 0.7276Y + 0.6575Z - 1.2410 = 0$			
C(6)*	−0.003 (7)	C(9)*	−0.003 (9)
C(7)*	+0.005 (8)	C(10)*	0.000 (8)
C(8)*	−0.005 (9)	Fe	+1.652 (1)

[a] All planes are expressed in Cartesian coordinates. The transformations are: $X = xa + zc \cos \beta$, $Y = yb$, $Z = zc \sin \beta$. [b] A plane is derived using unit weights for atoms with asterisks and zero weights for other atoms. [c] The angle between planes A and B is 2° 37′.

distances or bond angles within the five-membered ring is significantly different (at the 3σ level) from the mean values. Thus the carbon skeleton of each five-membered ring has D_{5h} symmetry within the limits of experimental error.

Individual iron–carbon distances vary from 2.043 ± 0.007 to 2.058 ± 0.006 Å for atoms of plane A [C(1) through C(5)] and from 2.050 ± 0.007 to 2.061 ± 0.008 Å for atoms of plane B [C(6) through C(10)]. The mean of the ten independent distances is 2.053 Å (*cf.* the iron–carbon distance of 2.058 ± 0.002 Å obtained from an electron diffraction study of ferrocene).[34] The iron atom in bis(fulvalene)diiron lies 1.646 Å from plane A and 1.652 Å from plane B (see Table VII).

The two π-cyclopentadienyl rings are forced to adopt an almost perfectly eclipsed conformation, the mean rotational displacement of one ring from the other (ω) being 1.8°. [Although ferrocene is known to have a perfectly staggered conformation (*i.e.*, $\omega = 36°$) in the solid state, the various substituted ferrocenes take up a variety of different conformations.[41]]

Finally, it may be noted that the symmetry-related bridging bonds, C(1)–C(6′) and C(6)–C(1′), are each 1.476 ± 0.009 Å in length. This is in good agreement with the accepted sp^2–sp^2 single-bond distance of 1.465 ± 0.005 Å[42] and with the bridging bond distance of 1.48 Å found by Kaluski[43] for bisferrocenyl, $(\pi\text{-}C_5H_5)Fe(C_5H_4C_5H_4)Fe(\pi\text{-}C_5H_5)$.

Crystal Packing

Figure 2 illustrates the packing of molecules in the bis(fulvalene)diiron crystal, projected onto (010). The closest contacts (of each type) are 2.39 Å for a hydrogen···hydrogen and 2.93 Å for a carbon···hydrogen interaction, thus confirming the monomeric nature of the complex.

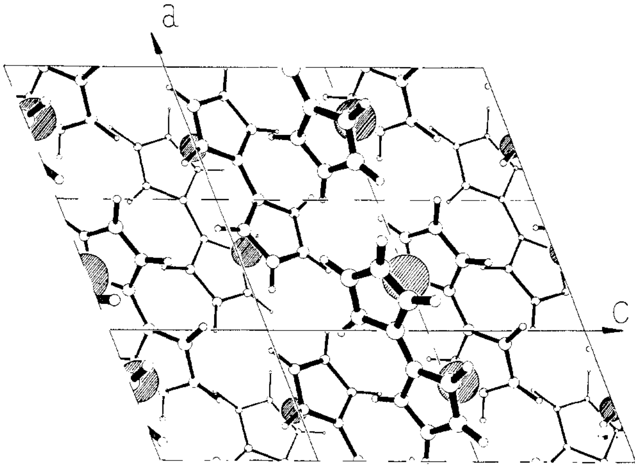

Figure 2.—Packing of molecules within the bis(fulvalene)diiron crystal. The crystal structure is viewed down *b*.

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(41) The known conformations of ferrocene derivatives have recently been tabulated—see Table VIII of ref 40.

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