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The Structure of Diferrocenyl Ketone

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Crystals of diferrocenyl ketone, C_5H_5 . Fe . C_5H_4 . CO . C_5H_4 . Fe . C_5H_5, are monoclinic, $a=10·50$, $b=6·18$, $c=13·05$ Å, $\beta=111°0'$. The space group is $P2/c$ and there are two molecules in the unit cell, the molecule having a C_2 axis coincident with the diad axis of the space group. The intensities of the reflexions were measured with a scintillation counter using Fe $K\alpha$ radiation; the iron, oxygen and carbon atom positions were determined by Patterson and electron-density methods, the hydrogen atoms were located from an (F_o-F_c) synthesis, and all the positional and thermal parameters were refined by least-squares methods. The final R value for 664 observed reflexions is 0·063.

Each iron atom is sandwiched between two five-membered rings which are planar, parallel, separated by 3·30 Å, and rotated only 5° from an eclipsed orientation. The ferrocenyl groups are rotated 17° out of the carbonyl plane. The mean bond distances are Fe–C 2·05 Å, C–C (cyclopentadienyl rings) 1·43 Å, C–C (exocyclic) 1·45 Å, C=O 1·23 Å, C–H 1·1 Å, and the mean angle in the five-membered rings is 108°. The intermolecular separations correspond to van der Waals interactions.

Introduction

Crystal structure analyses of cyclopentadienyl compounds have shown that the five-membered rings are staggered in ferrocene (Dunitz, Orgel & Rich, 1956) and some of its derivatives, but eclipsed in ruthenocene (Hardgrove & Templeton, 1959) and its derivatives (Trotter, 1963). This difference in orientation could be a result of differences in bonding orbitals of the metal atoms, or of different *intra*molecular steric forces. A more recent analysis of biferrocenyl (Macdonald & Trotter, 1964; Kaluski, Struchkov & Avoyan, 1964) has shown that the orientation in this molecule is about midway between eclipsed and staggered, and this result, when compared with that of ferrocene, suggests that the orientations are strongly dependent on *inter*molecular forces (see also Edwards, Kington & Mason, 1960). The structure of ferrocenyl ruthenocenyl ketone, where both ferrocene and ruthenocene entities are present in the same molecule, has been investigated (Small & Trotter, 1964), but disorder in the crystal precluded an accurate determination of the structure.

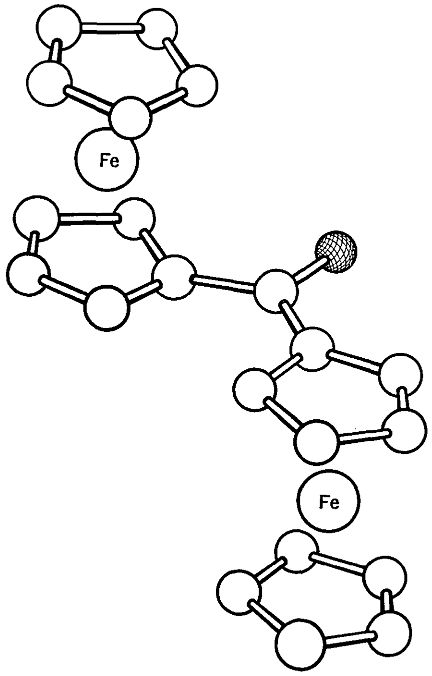

Fig. 1. Diferrocenyl ketone.

The present paper describes an analysis of diferrocenyl ketone (Fig. 1), the most important object of the investigation being the determination of the orientation of the cyclopentadienyl rings.

Experimental

Crystals of diferrocenyl ketone (Rausch, Fischer & Grubert, 1960) are red-violet plates elongated along **b** with (100) developed. The density was measured by flotation in aqueous silver nitrate, and the unit-cell dimensions and space group were determined from various rotation and Weissenberg photographs, and on a General Electric Spectrogoniometer. The crystals are isomorphous with those of ferrocenyl ruthenocenyl ketone.

Crystal data (λ, Cu $K\alpha=1·5418$ Å; λ, Fe $K\alpha=1·9373$ Å)
Diferrocenyl ketone, $C_{21}H_{18}OFe_2$; M.W. 398·0; m.p. 204 °C (decomp.).
Monoclinic, $a=10·50\pm0·02$, $b=6·18\pm0·01$, $c=13·05\pm0·03$ Å, $\beta=111°\ 0'\pm5'$.
$U=790·6$ Å^3.
$D_m=1·64$, $Z=2$, $D_x=1·67$ g.cm^{-3}.
Absorption coefficients for X-rays, μ(Cu $K\alpha$) $=150$ cm^{-1}, μ(Fe $K\alpha$) $=42$ cm^{-1}.

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$F(000)=408$.

Absent reflexions: $h0l$ when l is odd. Space group is Pc (C_s^2) or $P2/c$ (C_{2h}^4). $P2/c$ from structure analysis.

The intensities of the reflexions were measured on a General Electric XRD 5 Spectrogoniometer with Single Crystal Orienter, using a scintillation counter, approximately monochromatic Fe $K\alpha$ radiation (manganese filter and pulse height analyser), and the moving-crystal moving-counter method (Furnas, 1957). Of 790 reflexions in the range $0<2\theta(\text{Fe}\,K\alpha)\leq 146°$ (corresponding to a minimum interplanar spacing $d=1{\cdot}0$ Å), 664 (84%) had a measurable intensity. The intensities were corrected for background, which was found to be approximately a function of θ only. The crystal used was mounted with **b** parallel to the φ axis of the goniostat, and had dimensions $0{\cdot}05\times0{\cdot}6\times0{\cdot}4$ mm parallel to **a***, **b**, **c** respectively. Efforts to cut the

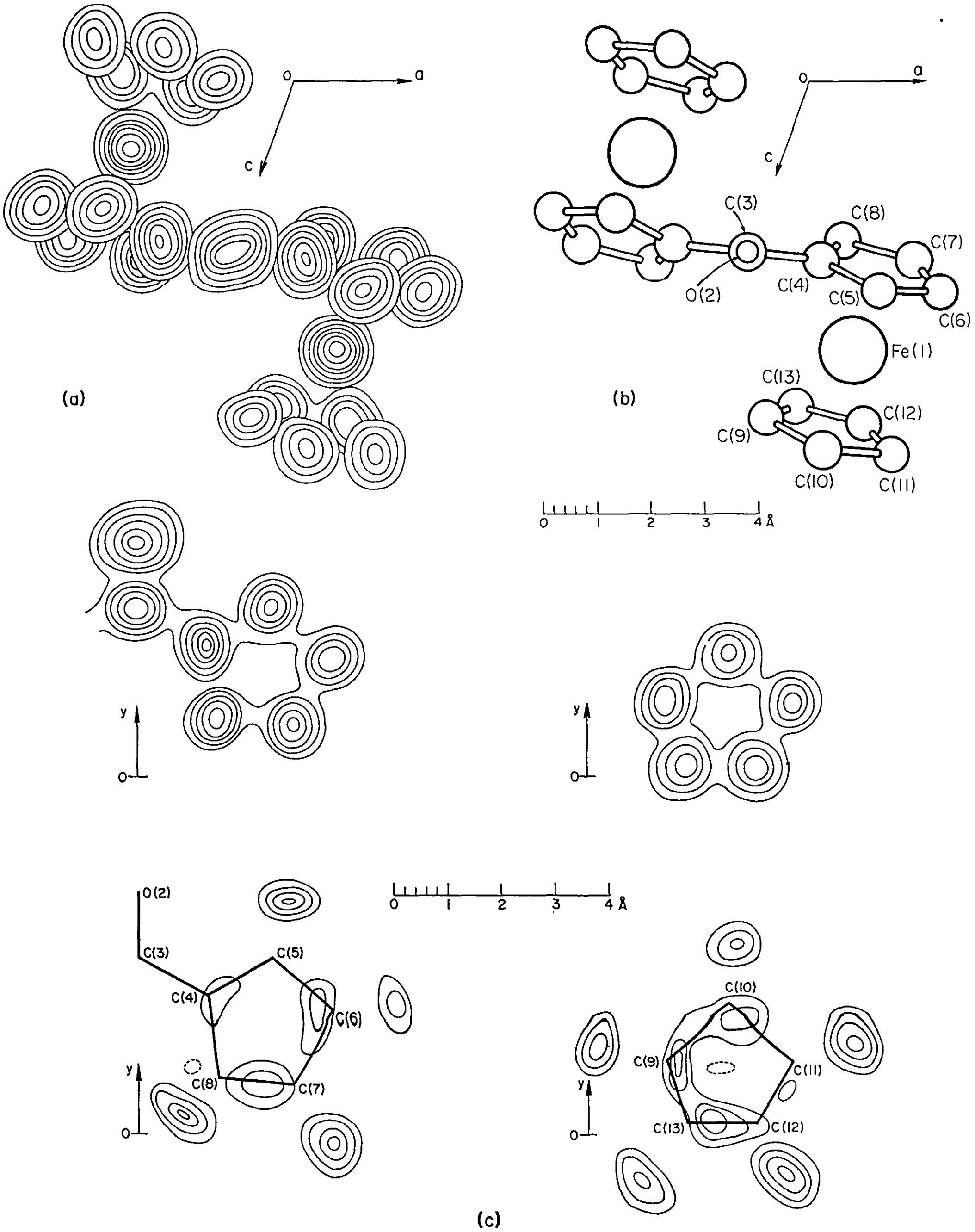

Fig. 2. (*a*) Superimposed sections of the final three-dimensional electron-density distribution, taken through the atomic centres parallel to (010). Contour intervals: iron, 5 e.Å^{-3} starting at 5 e.Å^{-3}; other atoms 1 e.Å^{-3} starting at 2 e.Å^{-3}. (*b*) Drawing of the molecule. (*c*) Sections of the electron-density distribution, and of the (F_o-F_c) synthesis in the mean ring planes. Contours as in (*a*) for the electron-density, and at $\pm0{\cdot}2$, $0{\cdot}3$, $0{\cdot}4$, $0{\cdot}5$ e.Å^{-3} for the difference density.

crystals to more uniform dimensions were unsuccessful, and the use of molybdenum radiation was impractical since this would have reduced the intensities by a factor of twenty ($\{1{\cdot}94/0{\cdot}71\}^3$). It was therefore important to apply corrections for absorption errors. Because of the thinness of the crystal plate, absorption is serious only for planes in a few very narrow regions of reciprocal space (Buerger, 1960), and approximate corrections were applied for planes in these regions of high absorption by considering the path lengths in the crystal of beams reflected from the centre (Albrecht, 1939). The maximum correction was 40% in intensity. Lorentz and polarization factors were applied and the structure amplitudes were derived.

Structure analysis

The iron atom position was determined from the three-dimensional Patterson function and positional parameters were derived for the C=O group and for the atoms of the five-membered ring bonded to it, by assuming a structure in space group $P2/c$ similar to that of ferrocenyl ruthenocenyl ketone (Small & Trotter, 1964). Structure factors were calculated, using the Fe, C, O scattering factors of *International Tables for X-ray Crystallography* (1962), and a Fourier series was summed. The resulting electron-density distribution had, of course, symmetry $P2/c$, and the good resolution of all the atoms and the absence of false peaks confirmed that $P2/c$ was the true space group. The map gave positions for all the Fe, C and O atoms in the molecule.

The positional and thermal parameters were refined by (block-diagonal) least-squares methods, minimizing $\Sigma w(F_o-F_c)^2$. Since the intensity measurements were considered to be least reliable for the very strong and for the very weak reflexions, the weighting scheme used was $\sqrt{w}=|F_o|/F^*$ when $|F_o|<F^*$ and $\sqrt{w}=F^*/|F_o|$ when $|F_o|\geq F^*$; F^* was taken as 12. After four cycles with isotropic thermal parameters and five cycles with anisotropic thermal parameters, the shifts were small

Table 1. *Measured and calculated structure factors*

Columns are h, $10|F_o|$, $10F_c$

h	$10\lvert F_o\rvert$	$10F_c$
H0L		
L= 0		
1	241	230
2	1538	-1557
3	250	252
4	487	513
5	49	-41
6	223	-241
7	226	210
8	544	509
9	65	-49
L= 2		
-9	367	-342
-8	<45	12
-7	225	234
-6	207	-208
-5	556	-547
-4	63	105
-3	569	614
-2	611	-598
-1	1259	-1271
0	113	122
1	542	570
2	424	-423
3	847	-871
4	93	121
5	571	552
6	208	-201
7	511	-485
8	39	-47
L= 4		
-9	92	-79
-8	199	-195
-7	420	437
-6	700	709
-5	482	-459
-4	457	-468
-3	285	295
-2	266	-234
-1	700	698
0	576	534
1	184	230
2	719	727
3	370	-330
4	620	-647
5	292	294
6	512	492
7	81	87
8	159	-156
L= 6		
-10	155	150
-9	114	124
-8	383	-411
-7	325	-338
-6	432	444
-5	259	249
-4	630	-615
-3	351	-358
-2	356	343
-1	125	123
0	701	-696
1	363	-364
2	390	391
3	104	120
4	361	-365
5	133	-131
6	224	209
L= 8		
-9	329	322
-8	49	-54
-7	156	-148
-6	122	113
-5	399	392
-4	117	123
-3	833	-805
-2	51	-66
-1	967	989
0	163	133
1	302	-314
2	99	105
3	208	204
4	117	-123
5	257	-241
L=10		
-8	144	154
-7	114	-142
-6	298	-279
-5	58	53
-4	350	338
-3	137	-140
-2	421	-452
-1	<45	18
0	289	272
1	89	-102
2	294	-310
L=12		
-5	231	-220
-4	147	159
-3	174	147
-2	93	-76
0	227	244
H1L		
L= 0		
0	35	6
1	122	-131
2	169	-158
3	118	-107
4	263	-233
5	<35	-9
6	159	142
7	59	-55
8	209	-192
9	48	-36
L= 1		
-9	273	-262
-8	238	-223
-7	353	340
-6	198	216
-5	175	-215
-4	34	-98
-3	700	738
-2	775	808
-1	1188	-1233
0	884	-869
1	1179	1239
2	640	625
3	377	-386
4	75	-121
5	477	497
6	197	205
7	385	-379
8	127	-119
L= 2		
-9	112	104
-8	52	46
-7	<45	-26
-6	170	154
-5	79	54
-4	48	-38
-3	131	122
-2	166	-147
-1	269	251
0	661	617
1	32	49
2	52	39
3	30	-21
4	83	-66
5	154	133
6	84	69
7	25	6
8	68	81
L= 3		
-9	32	-39
-8	364	-363
-7	<45	-30
-6	532	576
-5	<34	-5
-4	834	-861
-3	249	-258
-2	97	165
-1	77	-82
0	96	-167
1	217	-218
2	575	593
3	86	71
4	795	-830
5	227	-230
6	365	347
7	128	118
L= 4		
-9	150	-154
-8	203	-209
-7	74	75
-6	146	167
-5	167	-165
-4	100	-99
-3	135	135
-2	439	-419
-1	509	-507
0	238	205
1	113	110
2	144	-130
3	139	-144
4	76	-108
5	46	41
6	63	59
7	113	-117
L= 5		
-9	250	242
-8	<45	22
-7	521	-538
-6	72	96
-5	846	850
-4	35	-22
-3	470	-490
-2	112	114
-1	371	380
0	<31	26
1	580	-593
2	200	188
3	653	692
4	<46	34
5	355	-344
6	41	-29
L= 6		
-9	146	149
-8	51	-73
-7	26	-24
-6	149	131
-5	<40	5
-4	53	40
-3	<36	-3
-2	<33	15
-1	293	287
0	102	101
1	48	37
2	86	103
3	74	-53
4	37	-43
5	85	67
6	88	83
L= 7		
-9	64	61
-8	269	263
-7	106	-102
-6	346	-335
-5	160	157
-4	522	520
-3	489	-475
-2	938	-960
-1	456	446
0	634	623
1	279	-286
2	307	-329
3	79	90
4	168	160
5	217	-212
L= 8		
-9	118	-120
-8	41	[illegible]
-7	45	44
-6	<46	-18
-5	<45	-30
-4	203	201
-3	23	-32
-2	477	-476
-1	78	-63
0	218	220
1	88	-94
2	70	-78
3	43	34
4	43	-59
L= 9		
-9	90	-80
-8	182	190
-7	89	94
-6	122	-120
-5	151	-154
-4	309	321
-3	365	370
-2	428	-425
-1	289	-277
0	258	256
1	212	222
2	100	-122
3	141	-133
4	218	221
L=10		
-7	<39	28
-6	34	-24
-5	51	-18
-4	64	71
-3	<45	20
-2	45	55
-1	68	61
0	49	46
1	61	67
2	<34	-11
L=11		
-6	96	99
-5	244	-226
-4	71	-59
-3	96	75
-2	52	35
-1	184	-176
0	104	-120
1	291	299
L=12		
-4	130	161
-3	120	-147
H2L		
L= 0		
0	814	-814
1	39	8
2	437	464
3	44	36
4	358	-397
5	67	-53
6	366	388
7	26	-18
8	393	-354
9	53	46
L= 1		
-8	<41	58
-7	142	-152
-6	<45	-22
-5	66	63
-4	241	-226
-3	61	-54
-2	141	120
-1	100	-91
0	151	-129
1	151	-135
2	165	170
3	68	-57
4	318	-293
5	<40	16
6	<46	0
7	108	-106
8	71	66
L= 2		
-9	246	223
-8	300	-300
-7	324	-321
-6	325	317
-5	453	489
-4	138	-168
-3	514	-543
-2	180	170
-1	551	544
0	248	-249
1	542	-573
2	172	180
3	549	578
4	233	-244
5	373	-392
6	281	280
7	230	204
8	179	-179
L= 3		
-9	77	-74
-8	61	-65
-7	37	28
-6	78	80
-5	227	226
-4	56	40
-3	126	-121
-2	106	90
-1	37	-28
0	34	4
1	63	97
2	94	111
3	191	207
4	69	-66
5	88	-93
6	161	154
7	31	38
L= 4		
-9	235	220
-8	180	173
-7	376	-361
-6	388	-403
-5	459	494
-4	535	565
-3	514	-506
-2	522	-499
-1	331	347
0	542	552
1	515	-522
2	537	-549
3	481	512
4	313	316
5	326	-314
6	170	-147
7	120	121
L= 5		
-9	137	173
-8	<42	-10
-7	165	-172
-6	45	23
-5	39	-27
-4	184	-179
-3	<37	-9
-2	96	90
-1	104	103
0	193	-199
1	53	-49
2	132	130
3	117	-131
4	110	-89
5	35	44
6	56	-68
L= 6		
-9	190	-212
-8	168	156
-7	207	208
-6	339	-345
-5	188	-196
-4	636	624
-3	343	332
-2	745	-751
-1	448	-449
0	672	675
1	262	261
2	441	-430
3	155	-170
4	247	240
5	185	169
6	211	-198
L= 7		
-8	40	-2
-7	36	22
-6	113	110
-5	124	104
-4	49	43
-3	77	57
-2	190	-181
-1	130	-125
0	149	150
1	<46	35
2	88	71
3	89	98
4	56	-41
L= 8		
-9	203	-195
-8	89	-99
-7	154	185
-6	86	76
-5	311	-294
-4	46	-39
-3	553	554
-2	<46	17
-1	506	-497
0	<46	-2
1	282	277
2	107	119
3	223	-220
L= 9		
-7	22	-4
-6	<43	-39
-5	144	-140
-4	26	-20
-3	84	87
-2	84	91
-1	58	-79
0	51	-67
1	104	106
2	31	-70
L=10		
-8	275	-277
-7	<34	30
-6	242	240
-5	23	0
-4	158	-135
-3	55	46
-2	86	63
-1	83	-76
0	228	-215
1	<35	11
L=11		
-5	20	-31
-4	88	109
-3	30	32
-2	176	-200
-1	44	-40
H3L		
L= 0		
0	<33	-38
1	52	-79
2	114	123
3	81	86
4	118	-108
5	26	55
6	117	132
7	78	-126
8	75	-68
L= 1		
-8	117	93
-7	359	-345
-6	227	-227
-5	329	325
-4	282	302
-3	305	-349
-2	351	-359
-1	468	448
0	79	111
1	609	-599
2	323	-359
3	276	295
4	344	345
5	258	-261
6	247	-248
7	231	209
L= 2		
-8	59	-66
-7	35	47
-6	59	-18
-5	111	95
-4	197	195
-3	278	-293
-2	294	-272
-1	190	177
0	290	273
1	83	-82
2	311	-301
3	172	173
4	79	44
5	231	-231
6	135	148
7	142	143
L= 3		
-8	303	303
-7	140	132
-6	403	-390
-5	238	-257
-4	489	523
-3	244	225
-2	554	-553
-1	94	91
0	701	690
1	204	219
2	514	-542
3	159	-178
4	433	444
5	81	70
6	267	-258
L= 4		
-9	101	88
-8	52	-38
-7	93	-87
-6	26	-30
-5	37	-9
-4	104	104
-3	71	81
-2	115	-119
-1	58	51
0	74	49
1	95	-88
2	33	-13
3	<46	15
4	26	-4
5	54	69
6	28	-31
L= 5		
-8	<36	-9
-7	265	247
-6	74	-99
-5	350	-402
-4	131	128
-3	511	502
-2	48	-60
-1	618	-595
0	84	-73
1	460	462
2	122	-115
3	314	-356
4	114	108
5	268	252
L= 6		
-8	20	-23
-7	<41	16
-6	36	3
-5	143	152
-4	88	65
-3	118	-114
-2	174	-178
-1	26	4
0	241	237
1	75	-72
2	45	-36
3	147	142
4	129	-141
L= 7		
-7	172	175
-6	142	160
-5	249	-245
-4	279	-269
-3	183	183
-2	455	457
-1	88	-93
0	291	-287
1	174	174
2	202	203
3	113	-111
L= 8		
-7	<36	-22
-6	47	-40
-5	75	-71
-4	44	52
-3	83	80
-2	<45	0
-1	73	-57
0	44	-49
1	34	33
2	<38	-6
L= 9		
-6	176	184
-5	235	228
-4	186	-204
-3	175	-177
-2	245	238
-1	122	104
0	244	-252
1	185	-209
L=10		
-5	34	45
-4	47	-25
-3	<37	15
-2	63	-90
-1	<35	12
H4L		
L= 0		
0	571	557
1	57	42
2	422	-412
3	59	40
4	477	485
5	136	132
6	247	-236
7	<30	-29
L= 1		
-6	23	26
-5	<44	19
-4	106	75
-3	53	-53
-2	86	-79
-1	189	191
0	234	226
1	111	101
2	53	-52
3	53	-11
4	78	57
5	81	-83
6	51	43
L= 2		
-7	283	270
-6	47	45
-5	484	-490
-4	99	-103
-3	370	392
-2	340	-337
-1	465	-449
0	390	378
1	382	384
2	177	-192
3	517	-550
4	138	-133
5	317	295
L= 3		
-7	98	-102
-6	103	-91
-5	102	-81
-4	103	109
-3	138	121
-2	155	-136
-1	154	-150
0	95	-98
1	53	-60
2	65	-66
3	36	-42
4	136	116
5	<36	5
L= 4		
-7	133	113
-6	313	304
-5	36	-84
-4	230	-225
-3	328	314
-2	343	335
-1	247	-243
0	253	-246
1	299	298
2	314	317
3	156	-151
4	179	-155
L= 5		
-6	45	8
-5	55	-49
-4	58	37
-3	64	35
-2	46	5
-1	46	-16
0	180	174
1	165	166
2	86	-64
3	65	-43
4	19	-19
L= 6		
-6	218	234
-5	117	-106
-4	287	-268
-3	205	-192
-2	101	67
-1	228	239
0	186	-161
1	113	-114
2	143	156
3	60	-65
L= 7		
-7	45	-49
-6	28	-15
-5	44	-46
-4	41	11
-3	54	52
-2	65	62
-1	94	-103
0	172	-175
1	<38	11
2	19	19
L= 8		
-5	298	303
-4	67	50
-3	239	-228
-2	44	-35
-1	281	287
0	50	50
H5L		
L= 0		
0	112	137
1	36	-33
2	171	-172
3	136	-133
4	158	-153
5	70	-73
L= 1		
-4	169	-197
-3	249	248
-2	127	104
-1	331	-319
0	67	-34
1	301	286
2	180	194
3	181	-175
4	258	-272
L= 2		
-4	174	172
-3	201	203
-2	86	-63
-1	71	-15
0	169	171
1	55	34
2	41	5
3	111	111
L= 3		
-4	254	-267
-3	133	-108
-2	401	395
-1	55	-46
0	439	-417
1	33	-24
2	268	302
3	104	101
L= 4		
-4	138	-182
-3	55	-38
-2	87	-72
-1	82	-70
0	57	8
1	83	52
2	35	-29
L= 5		
-4	56	-30
-3	270	-267
-2	73	-82
-1	318	296
0	43	42
1	229	-235
L= 6		
-2	52	42
-1	112	121
H6L		
L= 0		
0	65	-50
1	28	4

and in random directions, the maximum parameter shift in the final cycle being one-third of a standard deviation, so that the refinement was considered to have converged. The R value was 0·081 for the 664 observed reflexions. Final three-dimensional F_o and (F_o-F_c) syntheses were computed. Superimposed sections of the final electron-density distribution are shown in Fig. 2(*a*), and a drawing of the molecule with the atom numbering used is shown in Fig. 2(*b*). The electron densities in the mean plane of each cyclopentadienyl ring are shown in Fig. 2(*c*). As is clear from Fig. 2(*a*) and (*c*) all the atoms are very well resolved. The difference electron densities in the mean ring planes are also shown in Fig. 2(*c*); the most significant features are nine well-resolved peaks corresponding to the nine hydrogen atoms in the asymmetric unit. The rest of the three-dimensional difference map contained no fluctuations greater than ± 0·4 e.Å^{-3}.

Hydrogen atom positions were obtained from the three-dimensional difference map, and their contributions were included in the structure factors, taking $B=5$ Å^2; R was reduced to 0·072. Before the refinement was continued, the suitability of the weighting scheme was considered by examining the values of (F_o-F_c). These values were largest for the very weak, and for some of the strong reflexions, but they suggested that the weights assigned to the strong reflexions were somewhat low. F^* was therefore increased to 20, and refinement was then completed by four further cycles, refining positional and anisotropic ther-

Table 2. *Final fractional positional parameters* ($\times 10^4$ *for* C, O, Fe *atoms*, $\times 10^3$ *for* H *atoms*; O(2), C(3) *are in* 2(*e*), *other atoms in* 4(*g*) *of* $P2/c$), *standard deviations* (Å $\times 10^3$), *thermal parameters and standard deviations* (U_{ij} *in* Å$^2\times 10^2$; B *in* Å^2), *and deviations*, Δ, *from the ring planes* (Å)

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	Δ_1	Δ_2
Fe(1)	2497	2423	4040	2·5	3·4	2·6	+1·647	−1·647
O(2)	0	7028	$\frac{1}{4}$	0	16	0	−0·329	—
C(3)	0	5031	$\frac{1}{4}$	0	23	0	−0·002	—
C(4)	1286	3962	2653	15	16	15	0	—
C(5)	2579	4959	3074	17	17	17	−0·003	—
C(6)	3614	3469	3120	18	18	17	+0·005	—
C(7)	2983	1466	2707	16	18	15	−0·005	—
C(8)	1508	1692	2409	17	15	16	+0·003	—
C(9)	1443	2336	5093	17	25	15	—	+0·003
C(10)	2685	3586	5566	20	22	17	—	0
C(11)	3787	2214	5639	17	23	16	—	−0·003
C(12)	3249	0134	5224	18	20	17	—	+0·005
C(13)	1819	0218	4882	18	20	17	—	−0·005
H(5)	277	649	322	Mean $\sigma(x)=0·16$ Å	$\sigma(y)=0·22$	$\sigma(z)=0·18$	−0·1	—
H(6)	475	333	347				+0·1	—
H(7)	363	−033	274				+0·1	—
H(8)	077	084	194				−0·2	—
H(9)	032	265	462				—	−0·3
H(10)	282	506	572				—	−0·1
H(11)	495	267	584				—	−0·2
H(12)	379	−102	526				—	+0·1
H(13)	105	−129	437				—	−0·1

Atom	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	Mean $\sigma(U)$
Fe(1)	4·51	−0·33	−1·40	3·47	0·09	3·51	0·13
O(2)	7·52	0	−6·45	1·01	0	9·67	1·2
C(3)	5·12	0	−2·17	1·04	0	2·67	1·3
C(4)	3·35	0·25	−1·10	2·34	0·44	2·28	0·9
C(5)	4·53	−0·29	−1·00	2·38	0·95	2·77	0·9
C(6)	4·59	−1·09	−0·89	3·28	1·14	2·56	0·9
C(7)	3·68	0·54	0·28	3·95	0·97	1·85	0·9
C(8)	4·26	0·33	−0·56	1·63	−0·11	1·87	0·8
C(9)	6·17	0·94	1·15	7·07	0·94	2·94	1·0
C(10)	6·75	−0·35	−0·27	6·47	−0·32	2·10	1·1
C(11)	5·27	−0·53	−1·13	6·23	−0·18	2·07	1·0
C(12)	5·65	−0·02	−0·19	4·62	1·26	2·29	1·0
C(13)	5·50	−1·58	−0·11	4·85	1·71	2·97	1·0
H(5)	$B=4$ Å^2, mean $\sigma(B)\simeq 5$ Å^2						
H(6)	3						
H(7)	1						
H(8)	10						
H(9)	6						
H(10)	8						
H(11)	1						
H(12)	2						
H(13)	3						

mal parameters for the iron, carbon, and oxygen atoms, and positional and isotropic thermal parameters for the hydrogen atoms. In the final cycles the shifts were in random directions, and the maximum shift in the last cycle in a heavier atom parameter was 0·3σ. The hydrogen atoms behaved reasonably well in the refinement, although their thermal parameters show a rather wide variation, and the maximum shift in a hydrogen parameter in the last cycle was about one-third of a standard deviation. The final measured and calculated structure factors are listed in Table 1 (R=0·063 for the 664 observed reflexions). A final (F_o-F_c) synthesis showed a trough of $-$0·4 e.Å^{-3} at the iron atom position, with two adjacent small peaks of +0·4 e.Å^{-3}. These fluctuations indicate that minor adjustments are required in the iron scattering factor, probably small changes in thermal parameters, but since the fluctuations are small, no adjustments were made. The rest of the difference map showed no significant features, the difference density not exceeding $\pm\frac{1}{4}$ e.Å^{-3}.

Coordinates and molecular dimensions

The final positional and thermal parameters are given in Table 2, together with their standard deviations estimated from the inverses of the diagonals of the matrix of the least-squares normal equations. x, y, and z are fractional coordinates referred to the monoclinic crystal axes, and U_{ij} are the components of the vibration tensors, written in matrix form and referred to orthogonal axes a, b, and c^*.

The bond distances and valency angles, and their standard deviations from the least-squares residuals, are given in Table 3. The standard deviations of the bond lengths, computed from the least-squares coordinate standard deviations, vary from 0·015–0·019 Å for individual Fe–C bonds, and from 0·023–0·032 Å for individual C–C bonds. Since there are ten independent Fe–C bonds and ten independent C–C ring bonds, the standard deviations may also be estimated by assuming that the ten bonds of each type have equal lengths, and computing the root mean square deviations from the mean values. The values of σ derived in this manner are 0·012 Å for individual Fe–C bonds and 0·024 Å for C–C bonds, so that the least-squares values are a reasonable, and actually slightly pessimistic, estimate of the errors. The standard deviations of the mean Fe–C and C–C distances, from the least-squares σ's, are 0·005 Å and 0·008 Å respectively. Similar considerations apply to the standard deviations of the angles, the standard deviation of the individual values being 1·5° from the least-squares σ's, and 1·3° from the root mean square deviation from the mean. The standard deviations of the C–H bond distances are about 0·2 Å.

The planes of the five-membered carbon rings have equations:

Ring 1 [C(4)–C(8)]:

$$-0{\cdot}2706X'-0{\cdot}2654Y+0{\cdot}9254Z'=2{\cdot}3117,$$

Ring 2 [C(9)–C(13)]:

$$-0{\cdot}2880X'-0{\cdot}2825Y+0{\cdot}9150Z'=5{\cdot}5170,$$

where X', Y, Z' are coordinates in Å referred to orthogonal axes a, b and c^*. These planes are very nearly parallel (the angle between their normals is $\cos^{-1}0{\cdot}9996=0°$ within experimental error), and the distance be-

Table 3. *Bond distances and valency angles, and standard deviations*

Bond	l	$\sigma(l)$
Fe–C(4)	2·037 Å	0·015 Å
Fe–C(5)	2·032	0·017
Fe–C(6)	2·060	0·018
Fe–C(7)	2·067	0·017
Fe–C(8)	2·056	0·016
Fe–C(9)	2·052	0·017
Fe–C(10)	2·061	0·019
Fe–C(11)	2·045	0·017
Fe–C(12)	2·035	0·019
Fe–C(13)	2·034	0·019
Mean Fe–C	2·048	
C(4)—C(5)	1·412	0·023
C(5)—C(6)	1·409	0·024
C(6)—C(7)	1·416	0·024
C(7)—C(8)	1·463	0·023
C(8)—C(4)	1·476	0·023
C(9)—C(10)	1·450	0·030
C(10)-C(11)	1·410	0·028
C(11)-C(12)	1·430	0·030
C(12)-C(13)	1·406	0·025
C(13)-C(9)	1·422	0·032
Mean C–C	1·429	
C(3)—C(4)	1·451	0·021
C(3)—O(2)	1·235	0·028

Atoms	Angle	Mean σ
C(4)—C(5)—C(6)	111°	1·5°
C(5)—C(6)—C(7)	108	
C(6)—C(7)—C(8)	109	
C(7)—C(8)—C(4)	106	
C(8)—C(4)—C(5)	107	
C(9)—C(10)-C(11)	107	
C(10)-C(11)-C(12)	108	
C(11)-C(12)-C(13)	109	
C(12)-C(13)-C(9)	108	
C(13)-C(9)—C(10)	108	
Mean C-C-C	108	
C(5)—C(4)—C(3)	125	
C(8)—C(4)—C(3)	128	
C(4)—C(3)—O(2)	117	
C(4)—C(3)—C(4′)	126	

Bond	l	Atoms	Angle
C(5)—H	1·0 Å	C-C-H	111°–139°
C(6)—H	1·1	Mean	125°
C(7)—H	1·3		
C(8)—H	1·0		
C(9)—H	1·1		
C(10)-H	0·9		
C(11)-H	1·2		
C(12)-H	0·9		
C(13)-H	1·3		
Mean C–H	1·1		

Table 4. *Shorter intermolecular distances*

All distances ≤4 Å between a standard half-molecule (I) and neighbouring molecules were calculated; only the most significant contacts are listed.

I······II		*d*
C(7)	C(12)	3·49 Å
H(7)	C(11)	3·0
I······III		
H(6)	H(12)	2·3
H(7)	H(11)	2·4
H(11)	H(12)	2·5
I······IV		
H(9)	H(13)	2·4
I······V		*d*
H(6)	H(6)	2·8
I······VI		
O(2)	H(8)	2·7
O(2)	H(13)	2·5
H(5)	H(7)	2·3

Molecule I at	x	y	z
II	x	$-y$	$-\frac{1}{2}+z$
III	$1-x$	$-y$	$1-z$
IV	$-x$	$-y$	$1-z$
V	$1-x$	y	$\frac{1}{2}-z$
VI	x	$1+y$	z

tween them is 3·30 Å. The deviations of the atoms from the planes are included in Table 2.

All the shorter intermolecular contacts are listed in Table 4, and the packing of the molecules is shown in Fig. 3.

Discussion

The analysis has shown that the molecule has symmetry C_2 (Figs. 1, 2, 3), with each iron atom sandwiched between two cyclopentadienyl rings. These rings are planar within experimental error (maximum displacement from mean planes is only 0·005 Å), almost exactly parallel, and separated by 3·30 Å.

The carbon atom of the carbonyl group lies on the planes of each of the rings to which it is bonded (displacement only 0·002 Å), but each ring is rotated, by 17° about the C(3)–C(4) bond, out of the carbonyl plane [C(4), C(3), O(2), C(4′)]. These rotations are the result of intramolecular steric interference between atoms H(8) and H(8′), the distance between which would be only about 1·7 Å in a coplanar model, but is increased to $2{\cdot}5_5$ Å by the rotations from planarity. As a result of the rotations the oxygen atom is displaced from the ring planes by 0·33 Å.

The primary object of the investigation was the determination of the relation between the cyclopentadienyl rings. This is illustrated in Figs. 1, 2 and 3, and more clearly in Fig. 4, which shows a view of half of the molecule along the normal to the planes of the rings. The orientation is very nearly eclipsed, and can be more precisely described in terms of the rotation of one of the rings from the fully eclipsed position as given by the angles between the projections, on the mean plane of a cyclopentadienyl ring, either of the

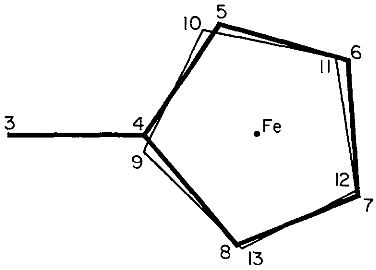

Fig. 4. View of half of the molecule along the normal to the planes of the rings. Heavier lines are nearer the viewer.

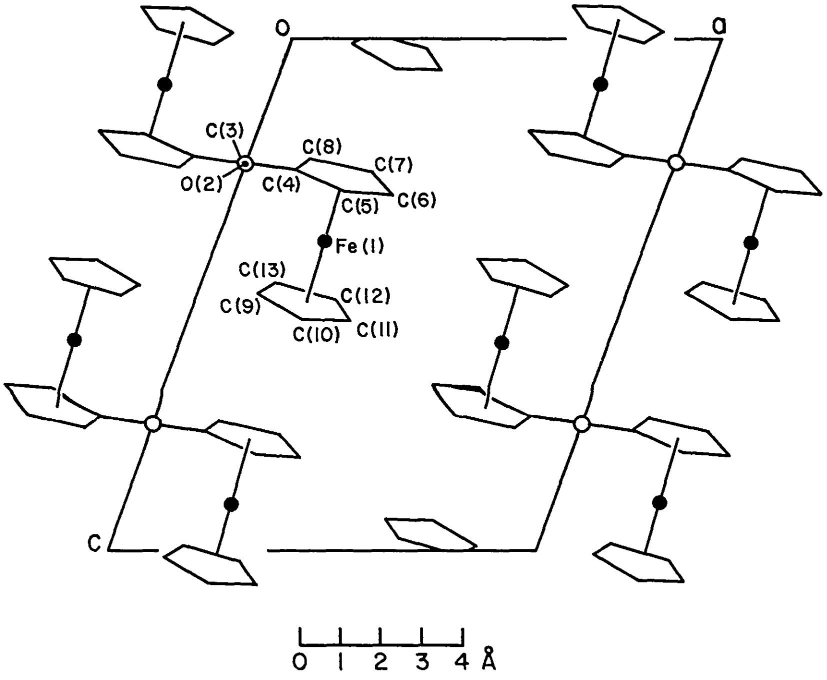

Fig. 3. Projection of the structure along **b**.

Fe–C bonds or of the vectors from each carbon atom to the mean centre of each ring:

C(4)–Fe–C(9) = 8·3° C(4)–centre–C(9) = 6·8°
C(5)–Fe–C(10) = 7·6 C(5)–centre–C(10) = 4·7
C(6)–Fe–C(11) = 5·8 C(6)–centre–C(11) = 5·2
C(7)–Fe–C(12) = 1·0 C(7)–centre–C(12) = 3·8
C(8)–Fe–C(13) = 3·4 C(8)–centre–C(13) = 5·4
Mean 5·2 Mean 5·2

The mean rotation from the eclipsed position is only 5·2°, in comparison with 36° for the fully staggered position. This nearly eclipsed orientation may be compared with that in ferrocene (Dunitz, Orgel & Rich, 1956), where the rings are staggered, and with that in biferrocenyl (Macdonald & Trotter, 1964), where the arrangement is about midway between eclipsed and staggered. Since the inter-ring distances are similar in all three molecules (Table 5), these results suggest that the orientations must be strongly dependent on intermolecular forces.

The mean bond distances in diferrocenyl ketone are very similar to those in related molecules (Table 5). The average Fe–C distance is 2·05 Å (mean standard deviation of individual values is 0·017 Å), the average C–C distance in the rings is 1·43 Å (mean σ is 0·026 Å), the exocyclic C–C bond measures 1·45 Å (σ, 0·021 Å), and the C=O bond 1·235 Å (σ, 0·028 Å). There are apparent deviations from pentagonal symmetry in the measured C–C bond distances, but since the maximum difference from the mean value is only $1{\cdot}9\sigma$ [for C(8)–C(4)], the deviations cannot be considered as significant. The mean angle in the rings is, of course, 108°, and the angles at the carbonyl group (117° and 126°) do not differ from normal values. The mean C–H bond distance is 1·1 Å ($\sigma = 0{\cdot}2$ Å for individual bonds), and none of the lengths is significantly different from the mean value. Variations in C–C–H angle are also not significant, the mean angle being 125°. The fact that the hydrogen atoms have been located indicates that the experimental data are quite reliable, as also indicated by the physically reasonable thermal parameters described below.

The thermal vibrations are analysed in Table 6 in terms of the mean square atomic displacements. For each ring the thermal motion is smallest normal to the ring plane. The in-plane vibrations are largest for the outer ring [C(9)–C(13)], and this ring shows a small amount of rotational oscillation about its normal; the mean square tangential vibration is 0·065 Å^2, in comparison with a mean square radial displacement of 0·050 Å^2. The rings bonded to the carbonyl group have smaller thermal motions, and exhibit only slight libration, the tangential and radial vibration being 0·036 and 0·030 Å^2 respectively. The rotational motion is thus not very great for either ring, as suggested also by Fig. 2(*c*) where the electron-density contours are not as elongated as in several other compounds of this type (see for example Dunitz, Orgel & Rich, 1956; Jones, Marsh & Richards, 1965). The carbonyl group thermal vibration is smallest parallel to the C–O bond, and large in directions perpendicular to the bond, the thermal motion of the oxygen atom being greater as might be expected.

Table 6. *Mean square vibrations* ($\overline{u^2}$ *in* Å^2) *in various directions*

Atom	Parallel to plane normals	In plane Radial	In plane Tangential
C(4)	0·027	0·026	0·026
C(5)	0·029	0·029	0·040
C(6)	0·025	0·036	0·043
C(7)	0·016	0·035	0·043
C(8)	0·024	0·026	0·028
C(9)	0·026	0·057	0·079
C(10)	0·030	0·059	0·064
C(11)	0·032	0·041	0·063
C(12)	0·022	0·051	0·053
C(13)	0·023	0·043	0·067
Atom	Parallel to C=O bond	Parallel to **a**	Parallel to **c***
O(2)	0·010	0·075	0·097
C(3)	0·010	0·051	0·027

All the intermolecular contacts (Table 4 and Fig. 3) correspond to van der Waals interactions. The shortest contacts all involve hydrogen atoms.

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Table 5. *Average distances in ferrocene derivatives* (Å)

Compound	Fe–C	C–C*	Inter-ring distance	Reference
Ferrocene	2·05	1·40	3·32	Dunitz, Orgel & Rich (1956)
Dibenzoylferrocene	2·05	1·41		Struchkov & Khotsyanova (1957)
Biferrocenyl	2·04	1·40	3·32	Macdonald & Trotter (1964)
α-Keto-1,1′-trimethyleneferrocene	2·04	1·43		Jones, Marsh & Richards (1965)
1,1′-Tetramethylethyleneferrocene	2·04	1·44		Laing & Trueblood (1965)
Diferrocenyl ketone	2·05	1·43	3·30	This paper

* None of the distances have been corrected for thermal librations.

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The Crystal and Molecular Structure of 1,2-*O*-Aminoisopropylidene-α-D-glucopyranose Hydroiodide

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Crystals of 1,2-*O*-aminoisopropylidene-α-D-glucopyranose hydroiodide are monoclinic, $a = 10{\cdot}09$, $b = 7{\cdot}88$, $c = 8{\cdot}16$ Å, $\beta = 100{\cdot}6°$, $Z = 2$, space group $P2_1$. The intensities of 1360 reflexions were measured with a scintillation counter and Mo $K\alpha$ radiation. The iodide ion position was determined by Patterson methods, and all carbon, nitrogen, and oxygen atoms were located from two three-dimensional electron-density distributions. The positional and anisotropic thermal parameters of the seventeen I, C, N, O, atoms in the asymmetric unit were refined by least-squares, and all the hydrogen atoms (except those of the CH_3 group) were located from an $(F_o - F_c)$ synthesis; the final R value is 0·089.

The previously unknown configuration of the asymmetric dioxolane 2-carbon atom is determined, and the absolute configuration is established since the compound is derived from D-glucose. The five-membered ring has an envelope conformation, with the dioxolane 2-carbon atom displaced 0·36 Å from the plane of the other four atoms, and the pyranose ring has a flattened chair conformation. The dihedral angles are different from those deduced from a previous proton magnetic resonance (p.m.r.) study, but the p.m.r. data can be reinterpreted in terms of a conformation similar to that found in the present analysis. The bond distances and valency angles are normal. The crystal is held together by a system of O–H · · · O (2·69 Å), N–H · · · O (2·74, 2·85, 3·03 Å), and O–H · · · I^- (3·39, 3·47 Å) hydrogen bonds.

Introduction

In a study of the proton magnetic resonance (p.m.r.) spectra of a series of 1,2-*O*-alkylidene-α-D-glucopyranoses, Coxon & Hall (1964) suggested that the pyranose ring in these derivatives adopts, not the expected flattened chair, but essentially a skewed boat conformation. This deduction was made by measuring the vicinal proton-coupling constants, and using the Karplus (1959, 1963) equation,

$$J = J_0 \cos^2 \varphi - K$$

to calculate the dihedral angles† (φ) from the coupling constants (J), J_0 and K being empirically derived constants. Since this equation involves a $\cos^2\varphi$ dependence, two angles may be calculated for each coupling constant, and Coxon & Hall chose acute dihedral angles between H(1) and H(2), between H(2) and H(3), and between H(3) and H(4), with values in the range about 40–60° for the various compounds, and angles close to 180° for the H(4), H(5) dihedral angles. These choices were made by comparison with compounds of known chair conformation, in which the dihedral angles are

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* Alfred P. Sloan Foundation Fellow.

† The dihedral angle between two hydrogen atoms on adjacent carbon atoms is the angle between the C–H bonds when they are viewed along the axis of the C–C bond.