under the direction of Prof. W. N. Lipscomb; we would like to thank the group, and in particular Dr R. A. Jacobson, for their help. We would like to thank the Eastman Kodak Company and the National Science Foundation for the support on one of us (K. E.).

References

EMERSON, K. (1960). Thesis: University of Minnesota.
GELLER, S. & SCHAWLOW, A. L. (1955). *J. Chem. Phys.* **23**, 779.
HARGREAVES, A. (1955). *Acta Cryst.* **8**, 12.
HEIART, R. B. & CARPENTER, G. B. (1956). *Acta Cryst.* **9**, 889.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 310.
HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
PAULING, L. (1959). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell University Press.
ROSSMAN, M. G., JACOBSON, R. A., HIRSHFELD, F. L. & LIPSCOMB, W. N. (1959). *Acta Cryst.* **12**, 530.
ROSSMAN, M. G. & LIPSCOMB, W. N. (1958). *Tetrahedron*, **4**, 291.
SUTTON, L. E. (1958). *Tables of Interatomic Distances and Configurations in Molecules and Ions*. London: Chemical Society.
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.

Acta Cryst. (1963). **16**, 118

The Crystal Structure of Cyclopentadienyl Manganese Tricarbonyl, $C_5H_5Mn(CO)_3$*

BY ALAN F. BERNDT† AND RICHARD E. MARSH

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.

(*Received* 11 *January* 1962)

The crystal structure of $C_5H_5Mn(CO)_3$ has been determined and refined by three-dimensional X-ray diffraction technique. The crystals are monoclinic with

$$a = 11{\cdot}99,\ b = 7{\cdot}07,\ c = 10{\cdot}93\ \text{Å (all } \pm 0{\cdot}03\ \text{Å) and } \beta = 117{\cdot}8 \pm 0{\cdot}2^\circ.$$

Positional and anisotropic temperature-factor parameters for all atoms except hydrogen were refined by least-squares methods, and the resulting standard deviations in the positions of the carbon and oxygen atoms are about 0·015 Å.

Within experimental error, a single axis passes through the center of the cyclopentadienyl ring, the manganese atom, and the center of the carbonyl groups. The interatomic distances indicate that the manganese atom forms approximately two electron-pair bonds with the ring and five with the three carbonyl groups.

Introduction

The determination of the crystal structure of cyclopentadienyl manganese tricarbonyl was undertaken as part of a program of structure investigations of sandwich compounds. The work reported here was begun in 1955 and the initial refinement of the positional parameters by least-squares methods was completed in 1957. The resulting molecular dimensions (which have been reported by Pauling, 1960, p. 391) were not particularly satisfactory, as the scatter in presumably equivalent values of interatomic distances suggested uncertainties of about 0·1 Å in the positions of the light atoms. More powerful computing facilities have recently become available to us, and accordingly we have continued the least-squares refinement by introducing anisotropic temperature-factor parameters for all the atoms. The resulting structure is more satisfactory, and both the experimental residuals and the scatter of equivalent interatomic distances lead to estimated standard deviations of approximately 0·015 Å in the positions of the light atoms.

Experimental

A sample of $C_5H_5Mn(CO)_3$ was supplied by Dr G. Wilkinson (see Piper, Cotton & Wilkinson, 1955). Crystals were selected directly from the sample and, because of their volatility, were mounted in lithium borate glass capillaries for photography. These crystals were irregular in shape with a maximum linear dimension of about 0·3 mm.

Two specimens were selected and oriented by means of Laue and oscillation photographs. Intensities were estimated visually from multiple-film Weissenberg photographs made with Cu $K\alpha$ radiation for layer lines 0–4 about the b axis and 0–13 about the [102] axis. The two sets of data were corrected for Lorentz and polarization factors and correlated by means of an averaging process.

---

* Contribution No. 2800 from the Gates and Crellin Laboratories of Chemistry.

† Present address: Argonne National Laboratory, Argonne, Illinois, U.S.A.

Table 1. *The final parameters and their standard deviations*

The temperature factors are expressed in the form $T = \exp\left(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl\right)$.
All values have been multiplied by 10^4

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	2876(2)	0082(2)	2623(2)	84(2)	135(3)	89(2)	16(5)	92(3)	10(5)
O_1	4778(11)	3046(17)	3803(14)	128(15)	310(34)	277(25)	−10(32)	67(28)	−75(42)
O_2	0840(10)	2885(15)	1462(12)	107(12)	328(31)	207(18)	185(30)	111(23)	89(35)
O_3	2629(14)	−0344(15)	5163(11)	255(20)	405(36)	124(13)	144(39)	281(28)	19(32)
C_1	4023(14)	1926(20)	3336(15)	117(17)	232(33)	151(21)	106(36)	105(30)	17(37)
C_2	1633(13)	1795(19)	1915(14)	96(15)	270(38)	131(18)	47(37)	97(25)	−28(37)
C_3	2676(17)	−0173(20)	4159(16)	181(22)	287(42)	142(20)	173(47)	149(34)	−2(44)
C_4	4109(14)	−1999(21)	2489(15)	119(18)	317(41)	157(22)	112(43)	150(32)	−41(43)
C_5	3556(13)	−0944(17)	1265(13)	137(17)	192(31)	125(17)	−58(35)	170(29)	−61(34)
C_6	2293(14)	−1176(20)	0606(13)	149(20)	266(37)	100(16)	40(42)	80(28)	−94(37)
C_7	1982(15)	−2371(21)	1404(16)	125(19)	313(44)	174(23)	−131(43)	162(34)	−165(47)
C_8	3123(18)	−2960(17)	2576(15)	274(33)	120(23)	166(23)	42(42)	293(45)	49(36)

Unit-cell dimensions were obtained from a Straumanis-type rotation photograph about [010] and a zero-level Weissenberg photograph about [102]. The lattice parameters (based on $\lambda(\mathrm{Cu}\,K\alpha_1) = 1{\cdot}5405$ Å), with their estimated standard deviations, are:

$$a = 11{\cdot}99 \pm 0{\cdot}03,\ b = 7{\cdot}07 \pm 0{\cdot}03,\ c = 10{\cdot}93 \pm 0{\cdot}03\ \text{Å};$$
$$\beta = 117{\cdot}8 \pm 0{\cdot}2^\circ.$$

The density calculated for $Z = 4$ (one molecule per asymmetric unit) is $1{\cdot}65 \pm 0{\cdot}01$ g.cm^{-3}.

Systematic absences of reflections ($h0l$) with h odd and ($0k0$) with k odd indicate the space group $P2_1/a$. Of approximately 2100 reflections within the sphere of reflection, less than 900 were strong enough to be observed. The absence of so many reflections results from three factors: (1) the crystals are soft and have a large temperature factor; (2) a small crystal was used for photographs about [102], necessitating long exposures which led to heavy background scattering from the capillary; (3) the contribution of the manganese atom to half the reflections is very small (see next paragraph).

Reflections with $(h+k)$ odd are, in general, weak, suggesting that the manganese atom lies either at $y = 0$ or at $x = z = 0$. The latter position seemed unlikely from packing considerations; furthermore, a Patterson projection on to (010) indicated the approximate parameters $x = 0{\cdot}04$ or $0{\cdot}29$, $z = 0{\cdot}263$ for the manganese atom, and accordingly the y parameter was initially assumed to be a zero. A calculation of some three-dimensional structure factors indicated the correct choice for the x parameter to be $0{\cdot}29$.

An electron density projection on to (010), using signs determined from the manganese position, did not give a clear indication of the structure. A three-dimensional electron density map was then calculated. Since the manganese atom assumed to lie at $y = 0$ did not contribute to reflections with $(h+k)$ odd, these reflections were omitted from the summation, giving the resulting map a false mirror plane at $y = 0$. Nevertheless, preliminary positions for the eight carbon atoms and three oxygen atoms were readily assigned.

Initial refinement of the light-atom coordinates was by electron density projections on to (010) and (100); all subsequent calculations were based on the three-dimensional data. The first set of structure factors, including a single isotropic temperature factor with $B = 3{\cdot}4$, gave an R factor of $0{\cdot}25$ for all observed reflections. Three cycles of least-squares refinement of the positional parameters were followed by a difference map from which preliminary anisotropic temperature factors for all atoms (except hydrogen) were obtained. The R factor at this stage was $0{\cdot}20$.

Coordinates for the five hydrogen atoms of the cyclopentadienyl ring were now calculated assuming a planar molecule with C–H distances of $0{\cdot}95$ Å; they were included in subsequent structure-factor calculations but were not optimized. Five more least-squares refinements of the positional parameters interspersed with a second difference map (for adjustment of the temperature factors) concluded the first stage of refinement; the R factor was now $0{\cdot}16$.

Up to this time (early 1957), structure-factor and least-squares calculations had been carried out on a Datatron 205 computer. The least-squares program, which accepted individual anisotropic parameters in calculating structure factors but permitted only positional parameters to be optimized, was based on a minimization of the quantity $\Sigma w(\Delta F)^2$. The weighting function was that of Hughes (1941), with all unobserved reflections assigned zero weight. When refinement was re-initiated in 1961, computations were carried out on a Burroughs 220 computer, and the least-squares program permitted adjustment of ten parameters for each atom—three coordinates, six temperature factors and one scale factor. The normal equations were semi-diagonalized, a 2×2 (x and z coordinates), a 1×1 (y) and a 7×7 (temperature and

Table 2. *Assumed coordinates of the hydrogen atoms*

	x	y	z
$H_1(C_4)$	0·506	−0·209	0·311
$H_2(C_5)$	0·407	−0·011	0·099
$H_3(C_6)$	0·166	−0·054	−0·029
$H_4(C_7)$	0·113	−0·273	0·116
$H_5(C_8)$	0·302	−0·385	0·322

Table 3. *Observed and calculated structure factors*

The three columns in each group contain the values of h, $10|F_o|$, and $10F_c$.
Many reflections too weak to be observed are omitted

h00		
0	---	4083
2	1058	-1291
4	489	471
6	250	-215
8	113	-95
10	177	182
12	<85	-68
h01		
$\overline{12}$	<93	41
$\overline{10}$	238	-217
$\bar{8}$	246	255
$\bar{6}$	481	-435
$\bar{4}$	117	-37
$\bar{2}$	562	-641
0	---	-74
2	513	556
4	618	-730
6	400	422
8	319	-312
10	125	142
h02		
$\overline{12}$	121	138
$\overline{10}$	227	-213
$\bar{8}$	<85	56
$\bar{6}$	295	305
$\bar{4}$	121	96
$\bar{2}$	828	984
0	877	-1066
2	206	-147
4	<52	-21
6	198	-181
8	202	222
10	121	-139
h03		
$\overline{12}$	<97	-91
$\overline{10}$	210	206
$\bar{8}$	481	-536
$\bar{6}$	577	647
$\bar{4}$	339	-378
$\bar{2}$	719	785
0	223	-210
2	210	-234
4	505	507
6	307	-320
8	271	289
10	<93	-32
h04		
$\overline{12}$	142	-153
$\overline{10}$	198	189
$\bar{8}$	<40	-9
$\bar{6}$	234	-261
$\bar{4}$	577	668
$\bar{2}$	1022	-1320
0	388	394
2	364	-362
4	150	161
6	<102	-18
8	97	-92
h05		
$\overline{12}$	102	101
$\overline{10}$	173	-166
$\bar{8}$	420	447
$\bar{6}$	311	-349
$\bar{4}$	331	330
$\bar{2}$	<65	-53
0	267	-309
2	517	485
4	271	-266
6	250	256
8	113	-119
h06		
$\overline{12}$	73	95
$\overline{10}$	102	-90
$\bar{8}$	<89	55
$\bar{6}$	121	116
$\bar{4}$	610	-646
$\bar{2}$	521	552
0	384	-354
2	271	215
4	<102	-28
6	<97	-15
h07		
$\overline{12}$	158	-174
$\overline{10}$	291	285
$\bar{8}$	379	-403
$\bar{6}$	432	457
$\bar{4}$	436	-409
$\bar{2}$	166	164
0	194	191
2	295	-294
4	206	189
6	129	-133
h08		
$\overline{12}$	<97	-72
$\overline{10}$	<69	18
$\bar{8}$	<77	43
$\bar{6}$	307	-317
$\bar{4}$	420	419
$\bar{2}$	267	-295
0	311	304
2	89	-92
4	<97	-40
h09		
$\overline{12}$	117	125
$\overline{10}$	166	-153
$\bar{8}$	133	138
$\bar{6}$	129	-81
$\bar{4}$	<102	-36
$\bar{2}$	97	82
0	186	-182
2	198	212
4	146	-157
h,0,10		
$\overline{12}$	109	117
$\overline{10}$	133	-111
$\bar{8}$	<81	-17
$\bar{6}$	218	222
$\bar{4}$	150	-161
$\bar{2}$	146	143
0	150	-154
2	<85	67
h,0,11		
$\overline{12}$	97	-99
$\overline{10}$	162	158
$\bar{8}$	246	-246
$\bar{6}$	202	184
$\bar{4}$	<97	-55
$\bar{2}$	<65	-5
0	<77	56
2	102	-87
h,0,12		
$\bar{8}$	125	136
$\bar{6}$	242	-241
$\bar{4}$	169	190
$\bar{2}$	154	-131
0	81	71
h,0,13		
$\bar{8}$	109	112
h10		
1	367	-358
2	339	-322
3	630	603
4	<29	-40
5	360	-359
6	146	165
7	416	425
8	<93	-1
9	234	-246
h11		
$\overline{11}$	121	102
$\bar{9}$	97	-82
$\bar{8}$	<93	37
$\bar{7}$	142	-130
$\bar{6}$	<33	-25
$\bar{5}$	371	351
$\bar{4}$	319	318
$\bar{3}$	771	-753
$\bar{2}$	202	-162
$\bar{1}$	808	1073
0	<33	-20
1	1054	-1122
2	630	-577
3	331	360
4	202	-191
5	<33	-12
6	40	50
7	113	-100
8	<97	-30
9	121	139
11	97	-107
h12		
$\overline{11}$	102	-120
$\bar{9}$	331	333
$\bar{8}$	<85	61
$\bar{7}$	335	-356
$\bar{6}$	85	86
$\bar{5}$	295	309
$\bar{4}$	275	243
$\bar{3}$	279	-281
$\bar{2}$	356	-390
$\bar{1}$	223	240
0	344	364
1	206	207
2	295	236
3	432	-399
4	117	107
5	396	408
7	356	-344
8	73	44
9	125	121
h13		
$\overline{11}$	146	-169
$\bar{9}$	150	163
$\bar{8}$	<36	25
$\bar{7}$	33	-1
$\bar{6}$	141	131
$\bar{5}$	271	-281
$\bar{4}$	263	-237
$\bar{3}$	371	373
$\bar{2}$	662	-760
$\bar{1}$	388	-409
0	190	-166
1	448	498
2	<65	20
3	238	-222
4	158	135
5	77	71
7	<102	90
h14		
$\overline{11}$	146	168
$\bar{9}$	323	-337
$\bar{8}$	<48	-17
$\bar{7}$	425	429
$\bar{6}$	198	181
$\bar{5}$	432	-432
$\bar{4}$	<65	-26
$\bar{3}$	105	96
$\bar{2}$	89	87
$\bar{1}$	117	134
0	173	169
1	295	-294
2	137	-116
3	311	283
4	<48	32
5	348	-370
7	214	223
h15		
$\overline{11}$	125	137
$\bar{9}$	113	-100
$\bar{8}$	<69	-56
$\bar{7}$	105	-101
$\bar{6}$	210	-207
$\bar{5}$	460	488
$\bar{4}$	154	-174
$\bar{3}$	610	-627
$\bar{2}$	218	208
$\bar{1}$	630	626
0	303	269
1	339	-307
2	52	58
3	169	158
5	<102	-62
h16		
$\overline{11}$	162	-184
$\bar{9}$	295	259
$\bar{8}$	89	63
$\bar{7}$	404	-422
$\bar{6}$	210	-196
$\bar{5}$	408	428
$\bar{4}$	<73	27
$\bar{3}$	234	-245
$\bar{2}$	77	-67
$\bar{1}$	<146	-42
0	113	-94
1	206	188
2	<65	14
3	223	-216
5	142	178
h17		
$\overline{11}$	<102	-60
$\overline{10}$	<97	-10
$\bar{9}$	<61	-18
$\bar{8}$	<109	3
$\bar{7}$	214	191
$\bar{6}$	93	-11
$\bar{5}$	379	-398
$\bar{4}$	263	255
$\bar{3}$	541	512
$\bar{2}$	117	103
$\bar{1}$	465	-474
0	146	-113
1	267	237
2	<81	-17
3	<102	-59
h18		
$\overline{11}$	146	196
$\overline{10}$	<69	-6
$\bar{9}$	214	-221
$\bar{8}$	97	-62
$\bar{7}$	231	222
$\bar{6}$	<89	-16
$\bar{5}$	93	-99
$\bar{4}$	48	50
$\bar{3}$	65	-23
$\bar{1}$	150	148
0	<77	24
1	250	-242
2	<69	-44
3	223	241
h19		
$\overline{11}$	97	73
$\overline{10}$	<89	48
$\bar{9}$	44	21
$\bar{7}$	154	-143
$\bar{6}$	125	108
$\bar{5}$	194	189
$\bar{4}$	105	-96
$\bar{3}$	173	-168
$\bar{2}$	48	-45
$\bar{1}$	125	130
0	44	36
1	<89	-87
3	<93	8
h,1,10		
$\overline{11}$	158	-149
$\overline{10}$	<73	1
$\bar{9}$	194	211
$\bar{8}$	<81	28
$\bar{7}$	182	-191
$\bar{6}$	<93	48
$\bar{5}$	<102	83
$\bar{4}$	<102	-38
$\bar{3}$	<102	-6
$\bar{2}$	56	-19
$\bar{1}$	52	-43
1	65	101
3	102	-102
h,1,11		
$\overline{10}$	<61	-16
$\bar{9}$	<97	-61
$\bar{7}$	194	199
$\bar{6}$	<69	17
$\bar{5}$	246	-251
$\bar{4}$	69	-53
$\bar{3}$	194	198
$\bar{1}$	102	-133
h,1,12		
$\overline{11}$	117	104
$\bar{9}$	146	-138
$\bar{7}$	97	115
$\bar{4}$	<85	-7
h,1,13		
7	52	-82
h20		
0	182	194
1	177	202
2	1018	-1102
3	40	44
4	573	556
5	173	159
6	113	-90
7	<89	-69
8	<97	-1
9	<109	47
10	<102	57
12	102	-126
h21		
$\overline{12}$	<89	63
$\overline{10}$	129	-130
$\bar{9}$	125	101
$\bar{8}$	348	336
$\bar{7}$	89	-88
$\bar{6}$	331	-330
$\bar{5}$	77	89
$\bar{4}$	509	481
$\bar{3}$	173	-174
$\bar{2}$	150	103
$\bar{1}$	271	-262
0	367	-357
1	65	66
2	763	760
3	<52	-43
4	662	-636
5	48	-47
6	529	497
7	194	-154
8	206	-203
10	<102	76
h22		
$\overline{12}$	97	127
$\overline{10}$	77	-72
$\bar{9}$	<102	21
$\bar{8}$	<89	60
$\bar{7}$	105	-91
$\bar{6}$	<65	-13
$\bar{5}$	69	48
$\bar{4}$	505	-503
$\bar{3}$	525	569
$\bar{2}$	177	-85
$\bar{1}$	339	-397
0	105	-39
1	367	379
2	630	659
3	<48	-22
4	125	-130
5	85	60
6	<89	-26
8	77	82
10	117	-115
h23		
$\overline{12}$	<97	-67
$\overline{11}$	<77	42
$\overline{10}$	210	245
$\bar{9}$	<125	-46
$\bar{8}$	348	-354
$\bar{7}$	214	-177
$\bar{6}$	465	479
$\bar{5}$	129	-111
$\bar{4}$	465	-496
$\bar{3}$	109	111
$\bar{2}$	125	-112
$\bar{1}$	109	97
0	121	109
1	154	-156
2	202	-196
3	113	-67
4	275	277
5	56	-47
6	291	-279
h24		
$\overline{12}$	125	-131
$\overline{11}$	<109	15
$\overline{10}$	129	106
$\bar{8}$	73	-54
$\bar{7}$	102	79
$\bar{6}$	250	-274
$\bar{5}$	<48	-23
$\bar{4}$	505	602
$\bar{3}$	133	-134
$\bar{2}$	307	-396
$\bar{1}$	214	207
0	723	733
1	52	-48
2	412	-408
3	93	-92
4	186	181
5	69	63
6	<109	14
h25		
$\overline{12}$	77	98
$\overline{11}$	109	-114
$\overline{10}$	223	-238
$\bar{9}$	65	48
$\bar{8}$	254	246
$\bar{7}$	56	28
$\bar{6}$	367	-368
$\bar{5}$	158	159
$\bar{4}$	150	144
$\bar{3}$	166	-161
$\bar{2}$	166	164
$\bar{1}$	117	93
0	258	-237
1	102	-64
2	186	170
3	<77	-20
4	295	-262
5	150	128
6	129	136
h26		
$\overline{12}$	102	122
$\overline{10}$	102	-87
$\bar{9}$	<65	21
$\bar{8}$	69	-42
$\bar{7}$	<69	5
$\bar{6}$	258	263
$\bar{5}$	<77	-47
$\bar{4}$	250	-273
$\bar{3}$	40	52
$\bar{2}$	469	473
$\bar{1}$	56	-40
0	412	-383
1	61	-41
2	190	143
3	<65	-27
4	77	-51
6	<97	-47
h27		
$\overline{12}$	125	-142
$\overline{11}$	<102	21
$\overline{10}$	238	238
$\bar{9}$	<81	27
$\bar{8}$	315	-308
$\bar{7}$	<56	-3
$\bar{6}$	331	331
$\bar{5}$	<61	11
$\bar{4}$	182	-193
$\bar{3}$	69	-79
$\bar{2}$	<65	-8
$\bar{1}$	81	70
0	137	122
1	<65	17
2	202	-187
3	73	80
4	194	175
6	109	-96
h28		
$\overline{10}$	<69	-35
$\bar{8}$	231	218
$\bar{7}$	<77	-20
$\bar{6}$	275	-256
$\bar{5}$	102	85
$\bar{4}$	291	322
$\bar{3}$	113	-116
$\bar{2}$	396	-376
$\bar{1}$	<77	-6
0	194	182
1	<109	10
2	<102	-75
h29		
$\overline{11}$	<56	11
$\overline{10}$	166	-176
$\bar{9}$	<52	11
$\bar{8}$	173	154
$\bar{7}$	102	-86
$\bar{6}$	69	-72
$\bar{5}$	117	115
$\bar{4}$	<109	-4
$\bar{2}$	113	101
0	133	-134
2	137	137
h,2,10		
$\overline{11}$	<65	11
$\overline{10}$	<97	4
$\bar{9}$	<52	-12
$\bar{8}$	69	-83
$\bar{7}$	<102	0
$\bar{6}$	77	76
$\bar{5}$	<56	-36
$\bar{4}$	142	-161
$\bar{3}$	<102	57
$\bar{2}$	133	140
$\bar{1}$	<52	2
0	97	-67
h,2,11		
$\overline{12}$	150	-140
$\overline{10}$	227	218
$\bar{8}$	190	-191
$\bar{6}$	129	130
$\bar{4}$	69	-46
0	85	74
h,2,12		
$\bar{8}$	117	102
$\bar{6}$	133	-138
$\bar{4}$	150	170
h30		
1	169	-163
2	73	50
3	477	448
4	<52	-6
5	788	-750
6	85	66
7	327	274
8	102	-84
9	169	-142
11	97	99
h31		
$\overline{11}$	121	130
$\bar{9}$	<109	-58
$\bar{8}$	<102	64
$\bar{7}$	<40	4
$\bar{6}$	89	-89
$\bar{5}$	400	348
$\bar{4}$	190	-179
$\bar{3}$	513	-480
$\bar{2}$	210	192
$\bar{1}$	654	705
0	<48	6
1	420	-459
2	206	196
3	537	484
4	52	47
5	169	-164
6	<40	10
7	73	-63
9	129	109
11	109	-118
h32		
$\overline{11}$	102	-98
$\bar{9}$	73	81
$\bar{8}$	<97	-43
$\bar{7}$	432	-383
$\bar{6}$	<52	17
$\bar{5}$	465	481
$\bar{4}$	173	-163
$\bar{3}$	169	-178
$\bar{2}$	89	94
$\bar{1}$	169	-159
0	73	74
1	238	234
2	137	-129
3	513	-534
4	65	-39
5	481	408
7	73	-90
9	125	119
h33		
$\overline{11}$	129	-123
$\bar{9}$	73	56
$\bar{8}$	<48	-3
$\bar{7}$	<77	33
$\bar{6}$	73	-51
$\bar{5}$	190	-181
$\bar{4}$	238	253
$\bar{3}$	440	512
$\bar{2}$	102	-90
$\bar{1}$	521	-593
0	379	343
1	392	430
2	<81	-45
3	444	-432
4	93	-97
5	52	26
7	73	76
9	113	-105
h34		
$\overline{11}$	109	108
$\bar{9}$	254	-251
$\bar{8}$	<56	37
$\bar{7}$	513	472
$\bar{6}$	113	-108
$\bar{5}$	392	-421
$\bar{4}$	238	229
$\bar{3}$	271	326
$\bar{2}$	263	-278
$\bar{1}$	<52	16
0	<73	5
1	158	-165
2	85	93
3	400	380
4	97	-82
5	150	-154
7	109	111
h35		
$\overline{11}$	109	108
$\bar{9}$	<65	-17
$\bar{8}$	<81	7
$\bar{7}$	121	-113
$\bar{6}$	102	88
$\bar{5}$	177	189
$\bar{4}$	166	127
$\bar{3}$	436	-486
$\bar{2}$	85	-71
$\bar{1}$	356	360
0	182	-174
1	384	-364
2	<44	-6
3	182	153
4	40	38
5	73	36
7	73	-87
h36		
$\overline{11}$	129	-130
$\overline{10}$	73	70
$\bar{9}$	388	330
$\bar{8}$	102	-100
$\bar{7}$	348	-331
$\bar{6}$	73	63
$\bar{5}$	291	311
$\bar{4}$	56	44
$\bar{3}$	158	-170
$\bar{2}$	<56	-19
$\bar{1}$	<93	-55
0	85	73
1	275	252
2	129	-115
3	234	-224
4	137	103
5	150	145
7	102	-114
h37		
$\overline{11}$	102	-87
$\overline{10}$	109	98
$\bar{9}$	<61	-19
$\bar{8}$	61	-29
$\bar{7}$	150	122
$\bar{6}$	61	-48
$\bar{5}$	267	-264
$\bar{4}$	85	-64
$\bar{3}$	379	384
$\bar{2}$	<93	-46
$\bar{1}$	360	-352
0	73	50
1	299	273
2	<81	-31
3	77	-83
h38		
$\overline{11}$	146	150
$\overline{10}$	<69	-30
$\bar{9}$	250	-239
$\bar{8}$	113	120
$\bar{7}$	177	181
$\bar{6}$	85	-85
$\bar{5}$	137	-145
$\bar{4}$	<73	-4
$\bar{3}$	<102	-21
$\bar{2}$	<109	21
$\bar{1}$	190	172
0	<52	-16
1	214	-199
3	125	125
h39		
$\overline{11}$	<97	41
$\overline{10}$	<109	-35
$\bar{9}$	<69	41
$\bar{8}$	<65	-5
$\bar{7}$	85	-85
$\bar{6}$	<97	45
$\bar{5}$	166	167
$\bar{4}$	102	-104
$\bar{3}$	223	-224
$\bar{2}$	109	128
$\bar{1}$	214	189
0	44	-46
1	102	-76
h,3,10		
$\overline{11}$	162	-156
$\bar{9}$	194	180
$\bar{8}$	<56	-18
$\bar{7}$	154	-162
$\bar{6}$	<89	11
$\bar{5}$	133	150
$\bar{3}$	<102	-32
$\bar{1}$	93	-79
h,3,11		
$\overline{10}$	<56	19
$\bar{7}$	61	69
$\bar{6}$	<65	28
$\bar{5}$	133	-130
$\bar{3}$	186	185
$\bar{1}$	105	-128
h,3,12		
$\bar{9}$	113	-112
h40		
0	634	714
1	142	120
2	477	-443
3	154	-111
4	335	300
5	113	-101
6	105	-105
7	<81	-29
8	117	-112
10	129	127
h41		
$\overline{10}$	137	-108
$\bar{8}$	177	176
$\bar{7}$	117	-107
$\bar{6}$	335	-291
$\bar{5}$	198	199
$\bar{4}$	287	244
$\bar{3}$	40	21
$\bar{2}$	36	-26
$\bar{1}$	81	84
0	194	-186
1	52	-31
2	371	336
3	93	62
4	489	-397
5	93	81
6	323	279
8	182	-218
10	102	102
h42		
$\overline{10}$	117	-127
$\bar{8}$	<109	41
$\bar{7}$	69	61
$\bar{6}$	142	145
$\bar{5}$	190	-184
$\bar{4}$	283	-266
$\bar{3}$	<56	34
$\bar{2}$	489	557
$\bar{1}$	194	-232
0	425	-485
1	<73	-18
2	238	229
3	113	-96
4	133	-151
5	48	43
6	<109	-12
8	117	89
10	56	-79
h43		
$\overline{10}$	117	104
$\bar{8}$	198	-198
$\bar{7}$	146	145
$\bar{6}$	364	333
$\bar{5}$	77	27
$\bar{4}$	371	-360
$\bar{3}$	<73	-17
$\bar{2}$	242	264
$\bar{1}$	<61	14
0	<73	12
1	81	-89
2	242	-238
3	214	198
4	231	213
5	<65	15
6	142	-146
8	129	125
h44		
$\overline{10}$	81	79
$\bar{8}$	105	86
$\bar{7}$	102	-79
$\bar{6}$	158	-154
$\bar{5}$	56	-30
$\bar{4}$	279	286
$\bar{3}$	97	88
$\bar{2}$	432	-494
$\bar{1}$	56	-40
0	371	367
1	69	-39
2	242	-236
3	<97	28
4	85	47
6	<117	60
h45		
$\overline{10}$	166	-189
$\bar{9}$	97	94
$\bar{8}$	339	310
$\bar{7}$	146	-141
$\bar{6}$	319	-297
$\bar{5}$	48	-49
$\bar{4}$	275	263
$\bar{3}$	<65	-14
$\bar{2}$	142	-152
$\bar{1}$	<85	61
0	113	-123
1	109	87
2	303	267
3	125	-98
4	194	-212
6	154	158
h46		
$\overline{10}$	117	-76
$\bar{8}$	<81	-44
$\bar{7}$	81	84
$\bar{6}$	113	113
$\bar{5}$	69	-48
$\bar{4}$	186	-209
$\bar{3}$	<73	-22
$\bar{2}$	227	232
$\bar{1}$	<97	-8
0	275	-247
1	125	119
2	190	176
3	<69	-15
4	81	-29
6	<93	-33
h47		
$\overline{10}$	186	197
$\bar{9}$	109	-105
$\bar{8}$	291	-283
$\bar{7}$	<89	43
$\bar{6}$	194	215
$\bar{5}$	<97	89
$\bar{4}$	109	-85
$\bar{3}$	73	-74
$\bar{2}$	77	-55
$\bar{1}$	56	31
0	215	178
1	89	-74
2	198	-187
4	150	161
6	93	-100
h48		
$\overline{10}$	<109	25
$\bar{9}$	<105	-22
$\bar{8}$	<89	62
$\bar{7}$	<77	-26
$\bar{6}$	206	-213
$\bar{5}$	65	48
$\bar{4}$	254	287
$\bar{3}$	<93	10
$\bar{2}$	242	-256
$\bar{1}$	<77	40
0	202	200
2	109	-97
h49		
$\overline{10}$	129	-120
$\bar{9}$	77	72
$\bar{8}$	137	150
$\bar{7}$	56	-56
$\bar{6}$	117	-122
$\bar{5}$	<69	10
$\bar{4}$	<69	32
$\bar{2}$	77	71
0	109	-100
h,4,10		
$\overline{10}$	<93	-28
$\bar{8}$	<61	-16
$\bar{7}$	<89	32
$\bar{6}$	109	97
$\bar{5}$	65	-37
$\bar{4}$	137	-143
$\bar{2}$	133	146
0	93	-81
h,4,11		
$\overline{10}$	142	128
$\bar{8}$	129	-133
$\bar{6}$	117	105
$\bar{5}$	40	30
$\bar{4}$	<93	-47
h,4,12		
$\bar{6}$	109	-108
$\bar{4}$	109	111
h50		
1	81	-96
2	<89	47
3	254	199
4	109	-116
5	125	-152
6	69	64
h51		
$\bar{6}$	61	50
$\bar{5}$	158	143
$\bar{4}$	<85	-49
$\bar{3}$	388	-369
$\bar{2}$	<85	32
$\bar{1}$	371	334
0	<65	-36
1	356	-347
2	<73	48
3	137	132
4	77	-79
h52		
$\bar{7}$	166	-136
$\bar{6}$	146	142
$\bar{5}$	146	129
$\bar{4}$	142	-119
$\bar{3}$	133	-133
$\bar{2}$	<81	13
0	<81	11
1	258	238
2	93	-100
3	113	-123
4	73	65
5	166	150
h53		
$\bar{6}$	<69	-34
$\bar{5}$	194	-188
$\bar{4}$	<77	29
$\bar{3}$	303	294
$\bar{2}$	<69	-51
$\bar{1}$	335	-365
0	61	68
1	283	295
3	44	-32
h54		
$\bar{8}$	<69	35
$\bar{7}$	166	151
$\bar{6}$	52	-70
$\bar{5}$	254	-230
$\bar{4}$	<97	-6
$\bar{3}$	186	191
$\bar{1}$	<89	-46
0	<97	-59
1	146	-138
2	97	100
3	105	115
4	69	-40
h55		
$\bar{7}$	105	-106
$\bar{6}$	<89	21
$\bar{5}$	210	195
$\bar{4}$	<97	-60
$\bar{3}$	162	-151
$\bar{2}$	73	74
$\bar{1}$	267	271
0	93	-108
2	97	95
h56		
$\bar{9}$	206	169
$\bar{8}$	<109	-41
$\bar{7}$	227	-191
$\bar{6}$	<81	31
$\bar{5}$	73	95
$\bar{4}$	<65	16
$\bar{1}$	<102	-49
0	<56	32
1	102	93
3	150	-174
h57		
$\bar{8}$	<65	16
$\bar{7}$	154	147
$\bar{6}$	56	-38
$\bar{5}$	242	-231
$\bar{4}$	<73	57
$\bar{3}$	210	207
$\bar{2}$	<97	-36
$\bar{1}$	173	-179
1	102	118
h58		
$\bar{9}$	133	-124
$\bar{8}$	73	74
$\bar{7}$	169	169
$\bar{6}$	73	-77
$\bar{5}$	<89	-44
$\bar{2}$	<73	-17
$\bar{1}$	73	67
0	<77	-9
h59		
$\bar{7}$	105	-113
$\bar{6}$	<85	36
$\bar{5}$	166	179
$\bar{4}$	48	-45
$\bar{3}$	137	-154
$\bar{2}$	44	43
h,5,10		
$\bar{9}$	97	93
$\bar{7}$	125	-115
h,5,11		
$\bar{7}$	73	76
$\bar{5}$	73	-95
h60		
0	311	324
1	<93	-107
2	242	-235
3	77	86
4	142	142
5	<81	35
h61		
$\bar{7}$	73	-80
$\bar{6}$	263	-229
$\bar{5}$	97	85
$\bar{4}$	125	139
$\bar{3}$	206	-180
$\bar{2}$	<97	-78
$\bar{1}$	83	85
0	129	-105
1	<97	3
2	166	158
3	<89	-46
4	206	-175
5	<89	14
6	223	208
h62		
$\bar{4}$	162	-171
$\bar{3}$	142	141
$\bar{2}$	299	307
$\bar{1}$	105	-107
0	291	-301
1	162	165
2	150	150
3	<81	-49
h63		
$\bar{8}$	169	-147
$\bar{7}$	<89	19
$\bar{6}$	169	163
$\bar{5}$	113	-87
$\bar{4}$	166	-161
$\bar{3}$	<97	54
$\bar{2}$	<137	85
$\bar{1}$	<73	41
0	117	86
1	97	-81
3	<69	45
4	162	157
5	117	-110
h64		
$\bar{5}$	<77	33
$\bar{4}$	186	160
$\bar{3}$	93	-89
$\bar{2}$	250	-281
$\bar{1}$	93	100
0	223	253
1	<77	-66
2	129	-137
h65		
$\bar{9}$	<52	9
$\bar{8}$	166	145
$\bar{7}$	<65	-20
$\bar{6}$	137	-126
$\bar{5}$	93	113
$\bar{4}$	137	114
$\bar{3}$	<93	-39
$\bar{2}$	73	-44
$\bar{1}$	<97	-50
0	<77	-29
2	109	120
3	<81	-31
4	129	-140
h66		
$\bar{9}$	<40	11
$\bar{6}$	117	128
$\bar{5}$	73	-71
$\bar{4}$	202	-202
$\bar{3}$	125	143
$\bar{2}$	190	203
$\bar{1}$	97	-112
0	150	-166
2	97	104
h67		
$\overline{10}$	105	102
$\bar{8}$	142	-136
$\bar{7}$	52	51
$\bar{6}$	121	131
$\bar{5}$	105	-110
$\bar{4}$	<97	-51
$\bar{3}$	48	47
$\bar{2}$	<61	-7
$\bar{1}$	<73	16
1	<56	-12
2	81	-99
h68		
$\bar{6}$	166	-156
$\bar{4}$	166	198
$\bar{2}$	117	-135
h69		
$\bar{8}$	102	101
$\bar{6}$	97	-112
h70		
1	<89	-35
3	121	136
4	<52	-18
5	218	-208
6	<56	26
h71		
$\bar{5}$	121	101
$\bar{3}$	198	-185
$\bar{2}$	113	84
$\bar{1}$	250	250
0	146	-127
1	186	-194
2	<77	52
4	<61	3
h72		
$\bar{7}$	162	-153
$\bar{6}$	65	44
$\bar{5}$	186	193
$\bar{4}$	<77	-33
$\bar{2}$	89	61
0	<65	-18
3	158	-164
4	97	51
5	142	128
h73		
$\bar{4}$	48	53
$\bar{3}$	190	182
$\bar{2}$	102	-89
$\bar{1}$	198	-213
0	<93	25
1	162	159
3	109	-101
h74		
$\bar{8}$	<48	39
$\bar{7}$	173	151
$\bar{6}$	<73	-19
$\bar{5}$	150	-141
$\bar{3}$	56	86
3	137	143
4	48	-62
h75		
$\bar{5}$	93	92
$\bar{4}$	102	-91
$\bar{3}$	186	-188
$\bar{2}$	77	91
$\bar{1}$	166	175
0	<67	-5
h76		
$\bar{9}$	121	110
$\bar{7}$	117	-122
$\bar{5}$	97	98
h77		
$\bar{5}$	117	-132
$\bar{3}$	142	156
$\bar{1}$	93	-125
h80		
1	52	-62
2	113	-145
3	<56	12
4	93	100
h81		
$\bar{6}$	77	-96
5	<44	43
4	89	-92
h82		
$\bar{4}$	133	-119
$\bar{2}$	73	104
0	73	-96
1	<77	47
2	102	107
h83		
$\bar{6}$	105	106
$\bar{4}$	81	-77
h84		
0	65	99

scale parameters) matrix being collected for each atom. Adjustments to the over-all scale factor were obtained from a weighted average of the indicated changes for the individual atoms. The quantity minimized was $\Sigma w(F_o^2 - F_c^2)^2$. Atomic form factors were those of Berghuis *et al.* (1955) for carbon and oxygen, McWeeny (1951) for hydrogen, and Freeman (1961) for manganese. A new set of coordinates for the hydrogen atoms was also calculated, this time based on a C–H distance of 1·0 Å. The contributions of the hydrogen atoms, including an isotropic temperature factor with $B = 2{\cdot}0$, were included in all subsequent structure-factor calculations but the coordinates were not optimized.

Fifteen cycles of structure-factor least-squares refinement were carried out on the Burroughs 220. The weighting function during the first seven cycles was that used earlier (Hughes, 1941). For the final eight refinement cycles the weighting scheme was changed to

$$F_o \geq 14: \; \sqrt{w} = 1/F_o^2$$
$$F_o \leq 14: \; \sqrt{w} = 1/14F_o \, ,$$

a scheme which presumably more truly reflects the uncertainties in F_o^2. Unobserved reflections were included only if the calculated value exceeded the threshold. The change in weights led to a marked decrease in the estimated standard deviations in all the parameters, and small but significant parameter shifts followed. Refinement was halted when the maximum indicated change in any parameter was less than 15% of its standard deviation; in the last cycle the sum of the squares of the weighted residuals dropped by less than 0·2%.

The final heavy-atom parameters and their estimated standard deviations calculated in the usual way are listed in Table 1; the coordinates assumed for the hydrogen atoms are listed in Table 2. The observed and calculated structure factors are given in Table 3.

Accuracy of the results

The final R factor for 827 observed reflections is 0·09, and could be reduced to about 0·08 by omitting a number of strong, low-order reflections apparently suffering from extinction. Although this figure is a bit higher than is normally obtained for a complete three-dimensional refinement, we feel that it is an adequate representation of the experimental errors in the present case.

The estimated standard deviations in the atomic coordinates of the light atoms (Table 1) are about 0·015 Å; since the standard deviations of the manganese coordinates are only about one-eighth as large, we estimate the standard deviations in the interatomic distances to be about 0·015 Å for manganese-light atom distances and about 0·02 Å for distances between pairs of light atoms. These values are consistent with the observed scatter of values for bond distances presumed to be equivalent.

Discussion of the results

(i) *The geometry of the molecule*

Cyclopentadienyl manganese tricarbonyl exists as discrete molecules in the crystal, there being no Mn–Mn bonds such as are present in the molybdenum analogue $C_5H_5Mo(CO)_3$ (Wilson & Shoemaker, 1957). The molecules possess no formal symmetry; however, a common axis passes through the center of the five-membered ring, the manganese atom, and the three carbonyl groups. Within experimental error, this is a five-fold axis when it passes through the cyclopentadienyl ring and a three-fold axis on the carbonyl side of the molecule. A view of the molecule along this axis is shown in Fig. 1. As can be seen in the figure, there is almost a vertical mirror plane, the C_3O_3 group being nearly eclipsed with respect to atom C_8 of the ring or, alternatively, the C_1O_1 group being almost opposite C_7. However, the two deviations are in opposite senses and approximately equal in magnitude (6°), and indeed the configuration is as far from symmetry m as is possible.

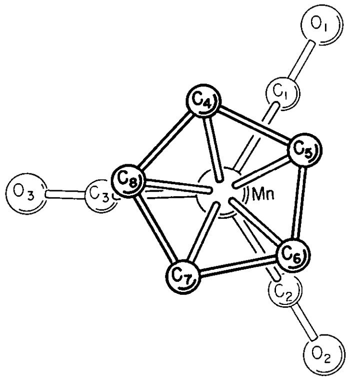


Fig. 1. The $C_5H_5Mn(CO)_3$ molecule viewed along its axis. The projection of the a^* direction is vertical.

The direction cosines of the axis of the molecule relative to a, b, and c^* are 0·366, −0·775, and −0·515. The mean plane of the cyclopentadienyl group is perpendicular to the axis and lies 1·80 Å from the manganese atom; none of the five carbon atoms is more than 0·02 Å from this plane. The three carbonyl carbon atoms are within 0·01 Å of a plane perpendicular to the axis and lying 1·00 Å on the opposite side of the manganese and the three oxygen atoms are within 0·025 Å of a plane perpendicular to the axis and lying 1·61 Å from the manganese atom.

(ii) *The temperature factors*

We choose to discuss the anisotropic temperature factors at this time because of the important effect of the implied librations on many of the interatomic distances.

In Table 4 are listed the magnitudes and direction cosines, relative to a, b, and c^*, of the principal axes of the temperature-factor ellipsoids. Although the uncertainties in these values are large (the estimated standard deviations for the carbon and oxygen atoms are about 1·0B units), the over-all pattern is so consistent and reasonable that there can be little doubt as to its reality.

The five carbon atoms of the cyclopentadienyl ring show extreme anisotropy of temperature motion, the average magnitude of the major axis being 8·8B units compared with 4·9 and 3·1 for the intermediate and minor axes. Moreover, for all five atoms the major axis is oriented nearly tangent to the ring, the maximum deviations being 28° for C_4 and 18° for C_7.

Table 4. *The magnitudes B and direction cosines q relative to abc* of the principal axes of the temperature-factor ellipsoids*

Atom	Axis i	B_i	q_{ai}	q_{bi}	q_{c^*i}
Mn	1	3·85	0·766	0·203	0·610
	2	3·05	−0·617	−0·035	0·787
	3	2·66	−0·181	0·979	−0·098
O$_1$	1	13·62	−0·615	−0·137	0·776
	2	6·23	−0·413	0·895	−0·169
	3	5·31	0·672	0·424	0·607
O$_2$	1	8·63	0·666	0·736	−0·123
	2	8·49	−0·194	0·330	0·924
	3	2·77	0·720	−0·592	0·362
O$_3$	1	12·55	0·794	0·436	0·424
	2	7·23	−0·290	0·884	−0·367
	3	2·08	−0·535	0·169	0·828
C$_1$	1	7·03	0·806	0·546	−0·229
	2	5·68	0·060	0·309	0·949
	3	3·31	0·589	−0·779	0·216
C$_2$	1	6·23	0·515	0·782	−0·351
	2	4·72	0·116	0·342	0·933
	3	3·85	0·850	−0·520	0·086
C$_3$	1	10·25	0·832	0·544	0·107
	2	5·34	0·047	−0·261	0·964
	3	3·69	0·553	−0·797	−0·243
C$_4$	1	7·91	0·560	0·820	−0·121
	2	5·99	0·252	−0·029	0·967
	3	3·08	0·789	−0·572	−0·223
C$_5$	1	6·68	0·693	−0·324	0·644
	2	3·69	0·592	0·766	−0·252
	3	3·17	−0·412	0·556	0·722
C$_6$	1	8·37	0·879	0·454	−0·147
	2	5·39	0·458	−0·717	0·525
	3	2·94	−0·133	0·529	0·838
C$_7$	1	8·87	0·243	−0·686	0·686
	2	5·08	0·853	−0·186	−0·488
	3	3·86	0·462	0·703	0·540
C$_8$	1	12·38	0·863	0·065	0·501
	2	4·24	−0·502	0·209	0·839
	3	2·27	0·050	0·976	0·213

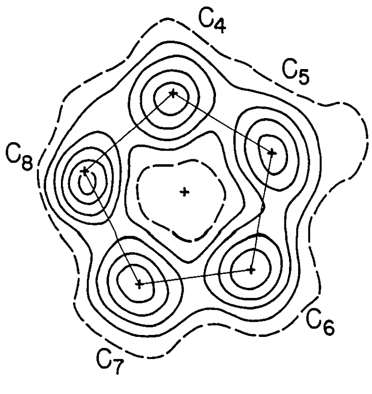


Fig. 2. The electron density in the plane of the cyclopentadienyl ring. Contours are at intervals of 1 e.Å^{-3}, the 1-electron contour being dashed. The orientation is as in Fig. 1.

The r.m.s. amplitude of the implied libration of the ring about its axis, based on a value of 5B units as the average increase in magnitude along the major axis, is 12°. For additional evidence that the ring is undergoing libration we have calculated the electron density in the plane of the ring, using all observed structure factors and the final set of signs (Table 3). This map is shown in Fig. 2. It resembles a similar map of the cyclopentadienyl ring in ferrocene (Dunitz *et al.*, 1956), which also shows pronounced libration effects.

The oxygen atoms also have large, anisotropic thermal motions, and the directions of maximum vibration are in all three cases within 10° of perpendicular to the corresponding Mn–C–O direction. The motions of the carbonyl carbon atoms are considerably smaller; we cannot say, however, whether the centers of libration of the oxygen atoms lie at the carbon atoms or at the manganese atom.

(iii) *The bond distances and angles*

The bond distances and angles are listed in Table 5. The values in parentheses have been corrected for the shortening effect of thermal librations. In correcting the distances involving the cyclopentadienyl ring we have assumed a libration of amplitude 12° (r.m.s.) about an axis passing through the center of the ring, as discussed in the preceeding section. The average C–O distance was increased somewhat arbitrarily by 0·016 Å, for we do not understand the nature of the libration of the oxygen atoms; for similar reasons, the distances between the manganese and carbonyl carbon atoms were not corrected. The uncertainties

Table 5. *Bond distances and angles*

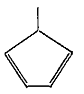
The values in parentheses have been corrected for libration effects. The uncertainties are subjective estimates of the standard deviations (see text)

Mn–C$_1$	1·788 Å	C$_1$–Mn–C$_2$	91°
Mn–C$_2$	1·791	C$_2$–Mn–C$_3$	91
Mn–C$_3$	1·812	C$_3$–Mn–C$_1$	94
Average	1·797 (1·80 ± 0·02)		
C$_1$–O$_1$	1·129	Mn–C$_1$–O$_1$	178
C$_2$–O$_2$	1·142	Mn–C$_2$–O$_2$	180
C$_3$–O$_3$	1·131	Mn–C$_3$–O$_3$	176
Average	1·134 (1·15 ± 0·03)		
Mn–C$_4$	2·139	C$_4$–Mn–C$_5$	38
Mn–C$_5$	2·127	C$_5$–Mn–C$_6$	36
Mn–C$_6$	2·169	C$_6$–Mn–C$_7$	37
Mn–C$_7$	2·145	C$_7$–Mn–C$_8$	39
Mn–C$_8$	2·176	C$_8$–Mn–C$_4$	38
Average	2·151 (2·165 ± 0·025)		
C$_4$–C$_5$	1·399	C$_4$–C$_5$–C$_6$	111
C$_5$–C$_6$	1·350	C$_5$–C$_6$–C$_7$	108
C$_6$–C$_7$	1·385	C$_6$–C$_7$–C$_8$	108
C$_7$–C$_8$	1·433	C$_7$–C$_8$–C$_4$	106
C$_8$–C$_4$	1·404	C$_8$–C$_4$–C$_5$	107
Average	1·394 (1·42 ± 0·03)		

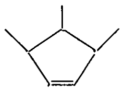
listed in Table 5 are subjective estimates of the standard deviations in the average values, and reflect our lack of confidence in the magnitudes of the libration corrections.

Since all distances and angles expected to be equivalent are indeed equal within experimental error, our discussion will be based on the average values corrected for libration.

The C–C distance, 1·42 Å, corresponds to a bond number of 1·35 (Pauling, 1960; p. 237); the Mn–C distance of 2·165 Å corresponds to a bond number of 0·41. (Here we use the familiar equation of Pauling (1960; p. 255) and a single-bond Mn–C distance of 1·93 Å.) We can explain these bond numbers quite satisfactorily by assuming that the five structures of the type (I) and the five of the type (II) all contribute equally to the resonance hybrid; the predicted bond numbers would then be 1·30 for the C–C bonds and 0·40 for the Mn–C bonds.



(I)



(II)

For the carbonyl groups, the C–O distance of 1·15 Å and the Mn–C distance of 1·80 Å correspond to bond numbers of 2·3 (Pauling, 1960; p. 266) and 1·66, suggesting that the two structures $=C=O$ and $-C\equiv O$ contribute in the ratio 2:1. Accordingly, the description of Pauling (1960; p. 391) that 'two electron pairs are involved in bond formation with the ring and five in bond formation with the carbonyl groups', which was based on the preliminary results of this investigation, is still valid.

(iv) *Packing of the molecules*

A drawing of the structure viewed down the *b* axis is shown in Fig. 3, and in Table 6 are listed all intermolecular distances (involving the heavier atoms) of 3·5 Å or under. The strongest interactions are probably between O_2 and the proton on C_5 (see Table 6) and between O_3 and the proton on C_8, where the calculated distances of 2·5 Å (based on the assumed hydrogen positions at 1·0 Å from the carbon atoms) are slightly less than the sum of Pauling's (1960; p. 260) values for the van der Waals radii of hydrogen (1·2 Å) and oxygen (1·4 Å). All other distances are greater than the sum of the van der Waals radii, and in general the packing is quite loose. This is in accord with the softness of the crystals, their volatility, and the large thermal motions of the peripheral atoms.

Table 6. *Intermolecular distances of* 3·5 Å *or less*

The atoms referred to in the first column belong to the reference molecule at x, y, z. The distances in parentheses are to the protons attached to the carbon atoms

From atom	To atom	In molecule at	Distance
O_1	O_2	$\frac{1}{2}+x, \frac{1}{2}-y, z$	3·41
O_1	O_3	$\frac{1}{2}+x, \frac{1}{2}-y, z$	3·44
O_1	O_3	$1-x, \bar{y}, 1-z$	3·36
O_1	C_3	$1-x, \bar{y}, 1-z$	3·47
O_1	C_8	$x, y+1, z$	3·35 (2·90)
O_2	O_3	$\frac{1}{2}-x, \frac{1}{2}+y, 1-z$	3·50
O_2	C_5	$\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$	3·48 (3·08)
O_2	C_5	$x-\frac{1}{2}, \frac{1}{2}-y, z$	3·42 (2·50)
O_2	C_7	$\bar{x}, \bar{y}, \bar{z}$	3·39 (2·74)
O_3	C_8	$\frac{1}{2}-x, \frac{1}{2}+y, 1-z$	3·44 (2·48)

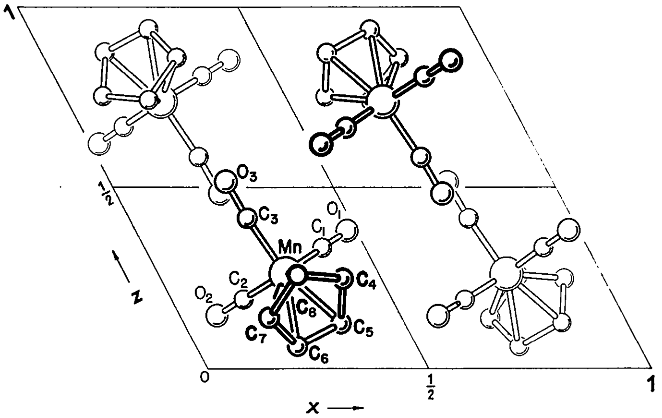


Fig. 3. The structure viewed along [010].

We are grateful to Dr V. Schomaker for many stimulating and helpful discussions. We also wish to thank Mr W. Mendell for assistance with some of the calculations and Mr D. Duchamp for a Burroughs 220 program for calculating electron density in a general plane. One of us (A. B.) is grateful to E. I. du Pont de Nemours and Company for a fellowship during the tenure of which much of this work was accomplished.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

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

Freeman, A. J. & Watson, R. E. (1961). *Acta Cryst.* **14**, 231.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd Edition. Ithaca: Cornell University Press.

Piper, T. S., Cotton, F. A. & Wilkinson, G. (1955). *J. Inorg. Nucl. Chem.* **1**, 165.

Wilson, F. C. & Shoemaker, D. P. (1957). *Acta Cryst.* **10**, 783.