730. *The* X-*Ray Analysis of Tricarbonylcyclo-octa-*1,3,5-*trienyl-chromium.*

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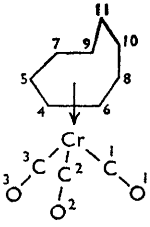
The crystal structure of tricarbonylcyclo-octa-1,3,5-trienylchromium $(CO)_3C_8H_{10}Cr$, has been determined and refined by least-squares analysis of partial three-dimensional data. The structure resembes that of tricarbonyltropylidenemolybdenum,[2] the conjugate system of the hydrocarbon being approximately planar and situated on the opposite side of the metal atom to the carbonyl groups; these lie in a pyramidal configuration. The methylene groups of the hydrocarbon are on the opposite side of the conjugate system to the metal atom.

On the basis of dipole-moment and magnetic-susceptibility measurements Fischer *et al.*[1] suggested that tricarbonylcyclo-octa-1,3,5-trienylchromium, $(CO)_3C_8H_{10}Cr$, was a metal–arene complex of the ferrocene type (I). In such a complex the conjugate system of the cyclo-octatriene must be approximately planar, with the methylene groups as far as possible from the metal atom. A similar arrangement has been found by Dunitz and Pauling [2] for tricarbonyltropylidenylmolybdenum, but the distortions of the trigonal planar and tetrahedral angles required if tropylidene is to be planar are considerably less than those required for cyclo-octa-1,3,5-triene. Indeed it has been suggested [3] that free tropylidene is itself planar.



(I)

Tricarbonylcyclo-octa-1,3,5-trienylchromium forms deep red prismatic crystals stable in dry air but slowly decomposed by an *X*-ray beam over a period of some weeks.

Crystal Data.—$C_{11}H_{10}CrO_3$. $M = 242{\cdot}1$. Monoclinic sphenoidal. $a = 7{\cdot}04 \pm 0{\cdot}02$, $b = 7{\cdot}31 \pm 0{\cdot}02$, $c = 10{\cdot}31 \pm 0{\cdot}02$ Å; $\gamma = 106{\cdot}5° \pm 0{\cdot}1°$; $U = 510{\cdot}9$ Å^3; $D_m = 1{\cdot}585 \pm 0{\cdot}005$ (by flotation); $Z = 2$; $D_c = 1{\cdot}577$; $F(000) = 248$; $\mu = 91{\cdot}4$ cm.$^{-1}$; space group $P2_1$ (C_2^2, No. 4); Cu-K_α radiation; single-crystal oscillation and Weissenberg photographs. Optically biaxial.

Structure Analysis.—Systematic absences were observed only for $00l$ reflections with l odd, indicating that the space group was $P2_1$ or $P2_1/m$. The latter form is centrosymmetric with a four-fold general position and requires the molecule to possess a mirror plane, the chromium atom and one carbonyl group lying in this plane. The former is non-centrosymmetric and imposes no symmetry restrictions on the molecule.

A three-dimensional Patterson function, sharpened to " atoms at rest," was computed by using 812 independent terms. Approximate positions were thus readily assigned to the

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[1] Fischer, Palen, and Fritz, *Chem. Ber.*, 1959, **92**, 2645.

[2] Dunitz and Pauling, *Helv. Chim. Acta*, 1960, **273**, 2189.

[3] Abel, Bennett, and Wilkinson, *Proc. Chem. Soc.*, 1958, 152.

chromium atoms, and further details of the function gave preliminary positions for the other atoms (except hydrogen) provided the space group were taken as $P2_1$. However, only atoms C(10) and C(11) were not in or related by a mirror plane. The refinement proceeded first by a three-dimensional F_o synthesis and then by difference synthesis, which to some extent broke up the false symmetry. The space parameters were then improved by three cycles of least-squares refinement, a block diagonal approximation to the normal matrix being used and only half the calculated shift applied. The block diagonal approximation is not strictly valid for an atomic arrangement with a near-mirror plane, and the calculated shifts for a majority of the atoms were consistently too large. A weighting scheme of the form $\sqrt{\omega} = |F_o|/F^*$ if $|F_o| < F^*$, otherwise $\sqrt{\omega} = F^*/|F_o|$, was used, F^* being given the value of 15·0 on an absolute scale.

After approximate positions of hydrogen had been deduced from a three-dimensional difference synthesis the space and the temperature parameters of all atoms except hydrogen were further refined by assuming first isotropic and then anisotropic thermal motion. The two iteration sequences converged at residuals of 0·137 and 0·127, respectively.

DISCUSSION

The space parameters obtained from the two refinements were very similar, except for atoms C(8) and C(9) which also appeared to have a highly anisotropic thermal motion. The standard deviations in space parameters were of the same order from both refinements, those derived on the assumption of anisotropic thermal motion being rather lower except where the motion was highly anisotropic. The isotropic refinement gave interatomic distances that were, on average, nearer the accepted values. In view of the somewhat inadequate refinement it is believed that the isotropic refinement, giving the chemically more acceptable structure and involving fewer parameters, should be accepted as the better. This is clearly a case where the full matrix least-squares technique would be most advantageous but no programme was available.

Table 1 lists the final atomic co-ordinates with standard deviations and temperature factors. The standard deviations are minimum values, owing to the assumptions of the block diagonal normal matrix from which they were deduced. Table 2 lists the observed

TABLE 1.

Atomic co-ordinates, with standard deviations ($\times 10^5$) in parentheses, and isotropic temperature factors.

	x/*a*		*y*/*b*		*z*/*c*		*B*
Cr	0·0803	(41)	0·2271	(37)	0·2657	(28)	1·72
O(1)	−0·1955	(201)	0·8274	(188)	0·2470	(243)	4·52
O(2)	−0·1887	(256)	0·3676	(241)	0·4296	(186)	3·96
O(3)	−0·1752	(256)	0·3603	(238)	0·0669	(187)	4·33
C(1)	−0·0879	(249)	0·9852	(225)	0·2736	(395)	2·86
C(2)	−0·0701	(299)	0·3255	(263)	0·3633	(213)	2·35
C(3)	−0·0744	(296)	0·3065	(253)	0·1371	(192)	1·84
C(4)	0·3673	(310)	0·4288	(294)	0·3209	(218)	2·54
C(5)	0·3719	(329)	0·4128	(313)	0·1802	(233)	3·18
C(6)	0·2985	(316)	0·2759	(283)	0·4125	(228)	2·61
C(7)	0·2908	(358)	0·2651	(326)	0·0931	(244)	3·66
C(8)	0·2410	(363)	0·0715	(338)	0·4141	(267)	3·55
C(9)	0·2543	(380)	0·0663	(351)	0·1324	(272)	4·19
C(10)	0·3180	(345)	0·9294	(319)	0·3275	(238)	3·67
C(11)	0·4104	(339)	0·0199	(310)	0·2032	(241)	3·15
H(4)	0·380		0·550		0·370		2·5
H(5)	0·328		0·541		0·160		3·2
H(6)	0·300		0·301		0·504		2·6
H(7)	0·220		0·320		0·020		3·7
H(8)	0·130		0·020		0·470		3·6
H(9)	0·120		0·990		0·110		4·2
H(10)a	0·230		0·882		0·290		3·7
H(10)b	0·394		0·863		0·354		3·7
H(11)a	0·460		0·932		0·160		3·2
H(11)b	0·430		0·137		0·237		3·2

and calculated structure amplitudes; Table 3 lists the atomic co-ordinates referred to orthogonal axes; and Table 4 lists some bond angles. On average, the standard deviation of interatomic distances is 0·03 Å and in bond angle 2° calculated by the formulæ of Cruikshank and Ahmed and of Darlow.[4]

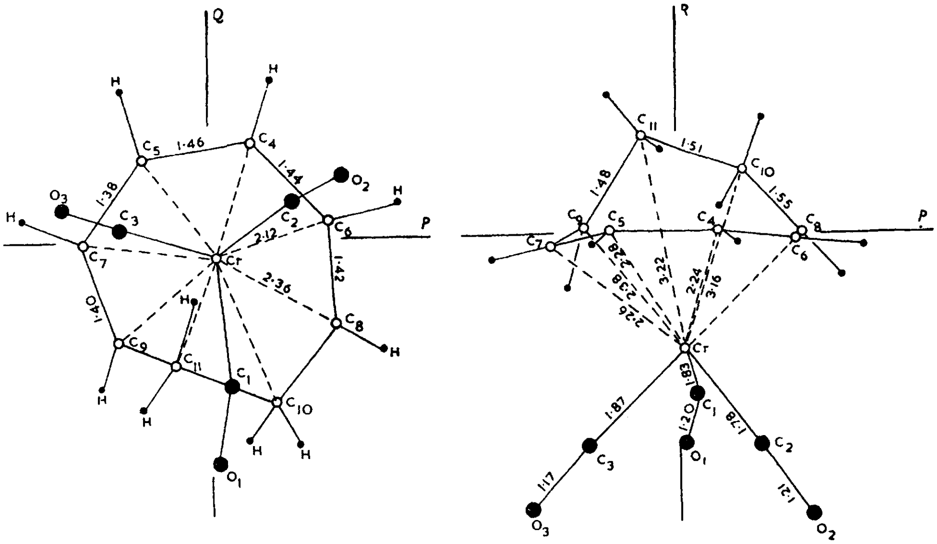

FIG. 1. The tricarbonylcyclo-octatrienylchromium molecule projected on to the best plane through the six near-planar carbon atoms of the conjugate system and a projection perpendicular to this plane. Some interatomic distances are given (in Å).

The molecular structure of tricarbonylcyclo-octa-1,3,5-trienylchromium is that proposed by Fisher *et al.* and is analogous to that of tricarbonyltropylidenylmolybdenum.[2] Fig. 1 shows the molecule projected on to the best plane through the six near-planar carbon atoms and a projection perpendicular to this plane. The axes P and Q in the plane and R normal to the plane have their origin at $x/a = 0{\cdot}304$, $y/b = 0{\cdot}253$, $z/c = 0{\cdot}259$. The transformation matrix from the co-ordinates in Table 3 to co-ordinates referred to axes P, Q, and R is:

$$\begin{array}{ccc} -0{\cdot}0168 & -0{\cdot}0746 & 0{\cdot}9971 \\ 0{\cdot}0442 & 0{\cdot}9962 & 0{\cdot}0753 \\ 0{\cdot}9989 & 0{\cdot}0453 & 0{\cdot}0135 \end{array}$$

The maximum deviation from the plane is 0·14 Å and the mean deviation 0·07 Å. The bond lengths within the conjugate system are irregular but approximate more closely to all bonds' being equivalent than to alternating double and single bonds. The mean bond length is rather longer than in the tropylidene system, which shows this alternation. The methylene groups completing the 8-membered ring are on the opposite side of the conjugate system to the chromium atom. The ring is highly strained to adopt this configuration and the bond angles, although generally larger than the unstrained values, vary irregularly. This is, in part, due to the impossibility of obtaining a structure in which the saturated carbon atoms are arranged symmetrically with respect to the unsaturated section of the ring if this section is to be planar. The configuration adopted by the saturated carbon atoms is such that the hydrogen atoms attached to the one atom are staggered with respect

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[4] Cruickshank and Ahmed, *Acta Cryst.*, 1953, **6**, 385; Darlow, *ibid.*, 1960, **13**, 683.

TABLE 2.

Observed and calculated structure amplitudes for *hkl*. In each set of three columns the first gives *l*, the second $10F_{\text{obs.}}$, and the third $10F_{\text{calc.}}$. The values are rounded from the computer figures used to calculate *R*.

0 0 *l*		
2	595	656
4	140	122
6	427	369
8	218	194
10	123	124
12	118	122
0 1 *l*		
0	182	185
1	600	732
2	303	316
3	228	184
4	190	160
5	256	220
6	122	97
7	281	237
8	125	143
11	97	110
13	59	86
0 2 *l*		
0	302	296
1	303	309
2	160	129
3	165	185
4	262	229
6	342	299
7	132	106
8	239	220
10	150	147
12	95	87
0 3 *l*		
0	230	229
1	222	216
2	282	230
3	289	289
4	249	230
5	239	224
6	84	78
7	214	196
8	93	80
9	165	150
11	103	102
0 4 *l*		
0	1923	164
1	53	58
2	267	258
3	295	268
4	220	193
5	114	117
6	183	168
8	165	147
10	81	84
11	81	66
0 5 *l*		
0	195	146
1	236	195
2	255	208
3	194	168
4	255	229
5	137	116
6	107	105
7	152	142
8	254	48
9	44	57
10	84	82
0 6 *l*		
0	153	119
1	111	96
2	107	84
3	124	96
5	142	131
6	58	909
7	54	65
9	59	59
0 7 *l*		
0	99	87
1	111	93
2	83	73
3	91	75
4	87	97
5	110	105
6	93	95
7	74	78
8	61	64
0 8 *l*		
0	34	15
1	100	88
3	108	111
4	62	69
5	100	107
6	41	69
1 0 *l*		
0	391	452
1	525	421
2	250	254
3	60	37
4	308	306
5	125	123
6	345	320
7	97	83
8	277	260
10	192	189
12	79	90
13	68	74
1 1 *l*		
0	265	325
1	373	492
2	173	168
3	164	153
4	34	98
5	213	181
6	157	131
7	247	194
8	109	81
9	163	147
11	86	91
1 −1 *l*		
0	453	413
1	208	266
2	355	441
3	393	439
4	303	308
5	206	187
6	269	252
7	191	155
8	223	182
9	232	199
11	123	123
12	109	98
13	46	54
1 2 *l*		
0	519	748
1	54	40
2	300	300
3	79	67
4	189	169
5	202	161
6	319	264
7	165	148
8	215	182
9	53	65
1 −2 *l*		
0	184	155
1	52	69
2	372	445
3	251	255
4	210	175
5	239	212
6	139	133
7	197	154
8	52	49
9	81	94
11	80	95
12	60	53
1 3 *l*		
0	173	177
1	314	323
2	130	142
3	261	216
5	237	190
6	115	86
7	160	151
9	164	165
11	93	113
1 −3 *l*		
0	171	147
1	276	270
2	203	189
3	335	372
4	282	281
5	112	84
6	246	222
7	147	116
9	86	82
10	49	66
12	100	93
1 4 *l*		
0	314	256
1	156	127
2	355	357
3	171	145
4	331	293
6	136	139
8	123	134
9	48	26
10	129	146
1 −4 *l*		
1	236	180
2	97	54
3	142	97
4	83	79
5	342	309
6	161	151
7	216	184
8	168	143
11	103	90
1 5 *l*		
0	123	123
1	120	101
2	114	93
3	244	237
4	167	152
5	111	112
6	68	49
8	60	48
9	103	115
1 −5		
0	341	325
1	104	84
2	152	119
3	90	59
4	197	158
5	151	128
6	287	260
7	161	128
8	123	126
1 6 *l*		
0	53	34
1	87	76
2	168	159
4	153	157
6	94	100
8	104	110
1 −6 *l*		
0	67	23
1	322	279
3	153	131
5	205	172
6	51	60
7	133	128
9	68	73
1 7 *l*		
0	98	72
1	125	99
2	99	77
3	157	152
4	104	84
5	115	115
6	53	49
7	97	103
1 −7 *l*		
0	172	172
2	124	113
4	90	84
5	86	67
6	90	83
1 8 *l*		
0	46	33
1	111	106
2	61	73
3	68	65
4	68	89
1 −8 *l*		
1	128	134
3	130	125
5	106	97
1 −9 *l*		
0	67	85
2	61	92
2 0 *l*		
0	216	257
1	274	348
2	316	325
3	342	326
4	251	213
5	232	217
6	55	57
7	176	187
8	110	119
9	132	144
10	92	122
11	45	93
2 1 *l*		
0	34	23
1	232	233
2	341	407
3	265	238
4	303	284
5	86	85
6	158	159
7	49	70
8	197	187
9	131	142
10	76	91
11	35	80
12	39	68
2 −1 *l*		
0	100	38
1	137	150
2	336	393
3	485	628
4	427	504
5	117	98
6	230	216
7	98	94
8	127	140
9	142	150
10	117	142
11	45	61
12	84	108
2 2 *l*		
0	383	523
1	181	201
2	243	252
3	258	284
4	87	93
6	110	112
7	92	97
8	100	116
9	78	97
10	72	113
11	23	72
12	23	55
2 −2 *l*		
0	357	452
1	461	483
2	27	32
3	392	518
5	361	344
6	62	81
7	83	99
8	107	94
9	68	98
10	41	26
11	111	126
2 3 *l*		
0	178	182
1	289	337
2	247	280
3	61	63
4	164	176
5	126	151
6	41	46
7	141	171
8	52	72
9	112	136
10	55	85
11	47	80
2 −3 *l*		
0	344	329
1	71	66
2	139	135
3	65	100
4	238	224
6	209	195
7	71	84
10	78	98
11	33	17
12	68	96
2 4 *l*		
0	263	280
1	60	58
2	153	164
3	56	89
4	127	159
5	30	40
6	163	187
8	112	154
10	80	110
2 −4 *l*		
0	49	36
1	324	310
2	82	85
3	136	128
4	63	68
5	287	278
7	199	196
8	52	82
9	95	127
11	73	104
2 5 *l*		
1	79	86
3	85	118
4	30	52
5	67	118
7	53	91
9	63	97
2 −5 *l*		
0	289	248
2	163	160
3	48	61
4	185	177
6	195	177
7	120	105
8	107	128
9	57	56
10	85	103
11	30	5
2 6 *l*		
0	111	102
2	127	157
4	120	164
6	75	111
8	72	105
2 −6 *l*		
0	185	162
1	190	169
2	94	93
3	214	207
4	43	50
5	170	173
7	120	137
8	70	65
9	96	114
10	19	7
2 7 *l*		
1	98	120
3	99	139
5	65	91
2 −7 *l*		
0	73	66
1	172	157
2	119	121
3	59	64
4	107	111
6	43	68
7	79	66
8	60	83
2 −8 *l*		
0	64	80
1	113	121
3	97	104
6	24	39
2 −9 *l*		
0	96	126
1	52	66
2	67	93
3	41	38
3 0 *l*		
0	39	33
1	219	234
2	124	109
3	386	429
4	137	116
5	266	271
6	116	124
7	78	63
9	82	94
11	92	112
3 1 *l*		
0	118	118
1	75	74
2	346	365
3	147	166
4	346	333
6	125	139
7	40	84
8	92	123
10	94	124
3 −1 *l*		
0	117	110
1	164	167
2	220	214
3	84	10
4	325	344
5	46	49
6	229	199
7	106	90
8	82	91
10	86	117
11	33	15
3 2 *l*		
0	29	3
1	168	200
3	300	330
5	132	165
6	56	66
7	123	161
8	87	92

TABLE 2. (*Continued.*)

9	109	131
3 −2 *l*		
0	60	34
1	203	237
2	189	177
3	243	282
4	151	149
5	392	435
6	81	52
7	270	271
9	158	183
10	38	61
11	97	129
3 3 *l*		
0	118	94
1	207	213
2	206	217
3	59	87
4	153	168
5	107	107
6	120	143
7	119	146
8	129	165
9	35	84
10	58	86
3 −3 *l*		
0	223	133
1	171	179
2	83	75
3	216	214
4	191	183
5	35	82
6	184	197
7	90	92
8	124	140
9	130	129
10	93	112
3 4 *l*		
0	233	27
3	81	108
6	103	119
7	93	103
8	73	86
3 −4 *l*		
0	176	127
1	268	248
2	166	146
3	279	276
5	129	139
8	115	107
9	93	84
3 5 *l*		
0	162	155
1	172	192
2	139	155
4	105	120
5	38	59
6	75	76
3 −5 *l*		
0	158	100
1	225	218
2	282	257
3	150	133
4	207	204
7	107	89
8	77	75
9	68	82
10	101	107
3 6 *l*		
0	211	204
2	109	115
3	70	76
4	66	73
3 −6 *l*		
0	120	85
1	81	78
2	115	98
3	223	207
4	65	87
6	97	96
8	104	110
9	118	120
3 −7 *l*		
0	58	41
1	100	106
2	107	108
3	120	115
4	39	72
5	122	132
7	109	123
3 −8 *l*		
0	87	114
2	85	81
4	62	81
3 −9 *l*		
0	50	60
1	83	104
4 0 *l*		
0	175	166
1	283	277
2	212	198
3	121	125
4	140	139
5	274	278
7	170	152
9	37	67
10	66	70
11	79	91
4 1 *l*		
0	145	149
1	116	118
2	105	96
3	76	82
4	223	232
5	110	106
6	241	241
7	39	28
8	81	97
9	36	52
10	68	99
11	22	38
4 −1 *l*		
0	321	342
1	124	130
2	85	56
3	262	224
4	88	84
6	219	202
7	54	46
8	67	113
9	116	110
10	58	59
11	33	53
4 2 *l*		
0	81	77
1	169	173
3	209	229
5	254	274
6	73	84
7	152	178
9	69	100
4 −2 *l*		
0	104	69
1	293	345
2	135	118
3	149	140
4	69	53
5	241	209
6	68	84
7	167	148
8	206	181
9	65	92
10	66	97
11	53	73
4 3		
0	148	147
1	104	83
2	154	164
3	108	99
4	128	140
6	115	131
8	57	87
10	34	57
4 −3 *l*		
0	217	197
1	219	249
2	190	190
3	253	254
4	175	153
5	123	106
6	134	108
7	223	202
8	819	687
9	166	175
10	50	65
11	42	70
4 4 *l*		
1	156	166
3	128	122
4	60	50
5	94	97
6	60	51
7	88	118
4 −4 *l*		
0	257	191
1	76	36
2	240	225
3	116	98
4	116	109
6	67	88
7	73	87
8	140	118
9	87	76
10	63	82
4 5 *l*		
0	208	185
1	78	44
2	155	154
4	102	98
5	48	23
6	98	107
7	46	56
4 −5 *l*		
0	55	3
1	179	169
2	101	88
3	181	177
4	60	76
5	110	104
6	61	74
7	96	94
8	107	109
9	92	109
10	54	58
4 6		
0	41	69
4 −6 *l*		
0	154	150
1	128	115
2	169	157
4	169	148
6	112	103
7	34	42
8	90	97
4 −7 *l*		
0	156	152
1	155	161
2	46	55
3	148	144
4	67	40
5	126	122
4 −8 *l*		
0	109	102
2	112	110
3	57	60
4	106	117
5	17	33
6	88	97
4 −9 *l*		
0	20	5
1	37	40
2	30	25
5 0 *l*		
0	138	153
1	87	83
2	167	145
3	57	49
4	91	113
5	189	164
6	134	143
7	125	114
8	148	149
10	62	82
5 1 *l*		
0	173	172
1	138	116
2	102	88
3	131	130
4	161	149
5	159	152
6	136	147
7	132	143
9	81	97
5 −1 *l*		
0	38	34
1	265	299
2	30	58
3	166	147
4	112	99
5	83	79
6	89	113
7	195	183
9	97	113
5 2 *l*		
0	107	83
1	160	146
3	157	155
4	61	74
5	161	175
6	89	101
7	46	70
8	36	44
9	33	60
5 −2 *l*		
0	297	334
1	47	41
2	211	207
3	140	121
4	47	26
5	33	63
6	113	96
8	122	115
5 3 *l*		
0	66	60
1	135	133
2	94	100
3	50	28
4	119	136
5	79	83
6	32	62
7	28	47
8	32	29
5 −3 *l*		
0	34	52
1	315	336
2	136	140
33	162	154
4	101	88
5	153	136
7	168	159
8	59	53
9	89	104
10	42	44
5 4 *l*		
0	141	144
1	120	112
2	67	46
3	150	157
4	44	43
5	109	112
6	64	84
5 −4 *l*		
0	220	232
2	138	141
4	152	147
5	79	83
6	209	204
8	123	156
10	84	115
5 5 *l*		
0	49	57
2	78	100
4	92	109
5 −5 *l*		
0	144	115
1	137	117
3	65	61
4	115	98
5	155	152
7	116	136
9	63	91
5 −6 *l*		
0	268	226
1	36	31
2	126	133
3	135	112
4	108	115
6	120	133
7	45	36
8	56	77
5 −7 *l*		
0	42	12
1	136	147
2	89	90
3	77	85
4	79	75
5	102	109
6	44	17
7	72	95
5 −8 *l*		
0	85	100
2	79	93
3	74	80
4	85	94
6 0 *l*		
0	226	204
1	28	20
2	230	194
3	95	78
4	119	105
5	31	16
6	122	122
7	28	40
8	144	147
6 1 *l*		
0	66	68
1	219	206
2	86	91
3	183	171
4	72	88
6 −1 *l*		
0	130	120
3	115	128
4	66	52
5	92	116
6	76	77
7	115	160
6 2 *l*		
0	72	76
1	33	28
2	105	123
6 −2 *l*		
0	168	177
6 3 *l*		
0	39	31
6 −3 *l*		
0	83	68
6 4		
0	43	64
6 −4 *l*		
0	278	285
6 −5 *l*		
0	58	30
6 −6 *l*		
0	76	82
6 −7 *l*		
0	70	74
6 −8 *l*		
0	14	30
7 0 *l*		
0	186	171
1	56	79
2	186	159
3	24	25
4	101	102
5	53	52
6	64	82
7 1 *l*		
0	79	82
1	114	117
2	25	31
3	93	96
7 −1 *l*		
0	40	52
7 2 *l*		
0	65	93
1	26	45
2	90	111
7 −2 *l*		
0	110	116
7 3 *l*		
0	31	45
7 −3 *l*		
0	25	8
7 −4 *l*		
0	69	71
7 −5 *l*		
0	135	145
7 −6 *l*		
0	40	33
7 −7 *l*		
0	65	80
8 0 *l*		
0	118	117
1	40	45
2	43	61
3	71	80
4	31	48
8 1 *l*		
0	24	43
8 − *l*		
0	68	72
8 −2 *l*		
0	81	90
8 −3 *l*		
0	35	33
8 −4 *l*		
0	23	12
8 −5 *l*		
0	63	63
8 −6 *l*		
0	58	81

to those attached to the other. The ends of the unsaturated system have different environments.

The chromium atom lies close to the normal to the plane of the conjugate system through its centroid. The chromium–carbon distances for atoms in the plane are between 2·12 and 2·38 Å and for the methylene carbon atoms between 3·16 and 3·22 Å. The chromium–carbon distance observed in dibenzenechromium [5] is 2·19 Å.

TABLE 3.

Atomic co-ordinates (Å) referred to the orthogonal axes parallel to *a*, *b**, *c*.

	X′	*Y′*	*Z*		*X′*	*Y′*	*Z*		*X′*	*Y′*	*Z*
Cr	0·0936	1·5933	2·7404	C(2)	−1·1710	2·3156	3·7569	C(7)	1·4990	1·8406	0·9858
O(1)	−1·2212	−0·5100	2·5861	C(3)	−1·1561	2·0966	1·4494	C(8)	1·5615	0·5246	4·2518
O(2)	−2·1181	2·6370	4·4300	C(4)	1·7203	3·0139	3·2990	C(9)	1·6759	0·4997	1·3416
O(3)	−1·9613	2·4591	0·6892	C(5)	1·7623	2·9015	1·8428	C(10)	2·3813	−0·4784	3·4007
C(1)	−0·5870	−0·1093	2·7903	C(6)	1·5379	1·9420	4·2470	C(11)	2·8762	0·1164	2·1072

TABLE 4.

Some interatomic angles.

C(1)–Cr–C(2)	95·4°	Cr–C(2)–O(2)	170·9°	C(4)–C(6)–C(8)	138·0°	C(7)–C(9)–C(11)	118·9°
C(1)–Cr–C(3)	91·0°	Cr–C(3)–O(3)	176·5°	C(5)–C(7)–C(9)	123·8°	C(8)–C(10)–C(11)	113·0°
C(2)–Cr–C(3)	78·8°	C(5)–C(4)–C(6)	126·8°	C(6)–C(8)–C(10)	130·8°	C(9)–C(11)–C(10)	106·9°
Cr–C(1)–O(1)	168·6°	C(4)–C(5)–C(7)	132·6°				

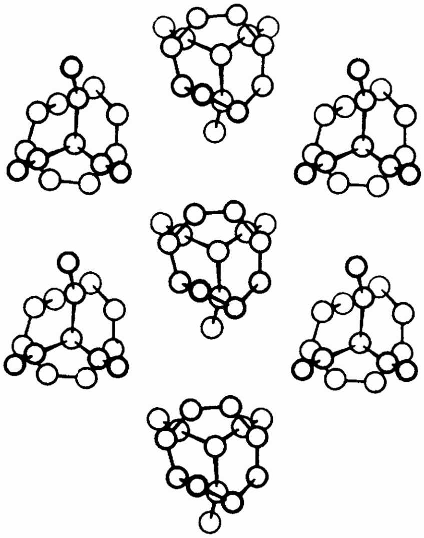

FIG. 2. Tricarbonylcyclo-octatrienylchromium, showing the crystal structure projected perpendicular to the (100) plane.

The carbonyl groups form an irregular pyramid. The plane through the three carbonyl carbon atoms is inclined at an angle of 20° to the plane of the hydrocarbon. The chromium–carbon distances here (1·78, 1·83, and 1·87 Å) are rather shorter than that (1·92 Å) observed in hexacarbonylchromium [6] by electron-diffraction techniques. The oxygen atoms of the carbonyl groups have markedly high temperature factors, consistent with the ease of bending of the metal–carbonyl system.

The molecules are packed in the crystal lattice in a body-centred arrangement (Fig. 2) with shortest approach distances of about 3·4 Å between the oxygen atoms and the hydrocarbon.

[5] Weiss and Fischer, *Z. anorg. Chem.*, 1956, **286**, 142.

[6] Brockway, Ewens, and Lister, *Trans. Faraday Soc.*, 1938, **34**, 1350.

EXPERIMENTAL

Preparation.—Dr. M. Whiting kindly supplied a sample of the compound, prepared by refluxing a mixture of hexacarbonylchromium and cyclo-octa-1,3,5-triene in 1,2-dimethoxyethane under nitrogen.[7] The crude product was recrystallised from light petroleum (b. p. 80—100°) by slow evaporation and gave crystals up to a few mm. long.

X-*Ray Photography.*—The unit-cell dimensions were obtained from zero-layer Weissenberg films about the *b*- and the *c*-axis, calibrated with the powder diffraction pattern of a copper wire. The *X*-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg films taken about the *b*- and *c*-axes for crystals about 0·02 cm. thick. The intensities were corrected for Lorentz and polarisation factors, and a common scale was obtained by the method of Rollett and Sparks.[8] No absorption or extinction corrections were applied.

Calculations.—Calculations were carried out on a Ferranti " Mercury " electronic computer. Structure factors and rounds of least-squares refinement were calculated by using the " SFLS " programme of J. S. Rollett.[9] Atomic scattering factors for carbon and oxygen were those of Berghuis *et al.*,[10] for chromium those of Thomas and Umeda,[11] and for hydrogen those of McWeeny.[12] For Fourier syntheses Mills's general Fourier series programme [9] was used, and for interatomic distances and angles Sparks's programme.[9]

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[7] Whiting, personal communication.

[8] Rollett and Sparks, *Acta Cryst.*, 1960, **13**, 273.

[9] Mills and Rollett, " Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis," Pergamon, London, 1961, p. 107.

[10] Berghuis, Haanapel, Potters, Loopstra, MacGillavry, and Veenendal, *Acta Cryst.*, 1955, **8**, 478.

[11] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

[12] McWeeny, *Acta Cryst.*, 1951, **4**, 513.