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# The Crystal and Molecular Structure of Bisindenylruthenium\*

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The crystal structure of bisindenylruthenium,  $(C_9H_7)_2Ru$ , has been determined and refined by threedimensional X-ray diffraction techniques. The crystals are monoclinic, space group  $P_{2_1}/a$ , with a = 14.51, b = 14.05, c = 6.23 Å,  $\beta = 94.10^{\circ}$ ; there are four molecules in the cell. Intensities were estimated visually from Weissenberg photographs about **b** and **c**; the structure was derived from Patterson and electron-density maps and refined by least-squares methods. The final *R* index for 2031 observed reflections is 0.057.

The molecule is in the fully eclipsed conformation, with the ruthenium atom lying midway between the two five-membered rings and nearly on their common axis. The indenyl groups are approximately parallel, the distance between them ranging from 3.62 to 3.69 Å. A valence-bond treatment satisfactorily explains the C-C and Ru-C distances.

A second crystal modification of bisindenylruthenium has also been obtained. These crystals, too, are monoclinic, space group  $P2_1/a$ , but with approximate cell dimensions  $a=11\cdot1$ ,  $b=9\cdot3$ ,  $c=6\cdot2$  Å,  $\beta=90^\circ$ ; there are two molecules in the cell. The structure of this modification is disordered, but appears to be closely related to that of the other (ordered) form.

#### Introduction

An interesting point in regard to the structures of ferrocene-like molecules is the relative conformation of the two five-membered rings. Thus, in crystals of ferrocene itself the rings are staggered (Dunitz, Orgel & Rich, 1956) while in the congener molecule ruthenocene they are eclipsed (Hardgrove & Templeton, 1959). In bisindenyliron the five-membered rings are staggered, the molecular conformation being gauche as in (I), below (Trotter, 1958). To complete the analogy, the rings in bisindenylruthenium should be eclipsed; however, a further question arises as to which of the three eclipsed conformations, (II), (III), or (IV), might be assumed. To answer these questions, we have undertaken an X-ray diffraction study of the structure of bisindenylruthenium. We have found the conformation to be the fully eclipsed one, (II).



Experimental

A sample of bisindenylruthenium was supplied by D. Hall of this Institute. Two crystal forms were obtained, both being monoclinic needles elongated along

c. The first modification was obtained directly from the sample bottle; its approximate unit-cell dimensions are:  $a=11\cdot1$ ,  $b=9\cdot3$ ,  $c=6\cdot2$  Å,  $\beta=90^\circ$ . The space group is  $P2_1/a$  (hol absent for h=2n+1; 0k0 absent for k=2n+1), and there are two molecules in the cell. Weissenberg photographs of this modification indicate a disordered structure which will be discussed briefly at the end of this paper.

The second crystal modification, and the one on which the structure determination is based, was obtained by recrystallization from n-hexane. A long needle with rectangular cross section of dimensions 0.1 mm (along a) by 0.07 mm (along b) was selected and cut into fragments of varying lengths. Two of these fragments were used in collecting all of the X-ray data, one fragment, approximately 3 mm long, being mounted along the c (needle) axis and the second, about 0.14 mm long, being mounted along the b axis.

Unit-cell dimensions were obtained from h0l and hk0 Weissenberg photographs prepared in a special camera in which the film is held in the asymmetric position. The resulting cell dimensions and the density, measured by flotation in an aqueous zinc chloride solution, are given in Table 1. Absence of reflections h0l with h odd and 0k0 with k odd indicates the space group  $P2_1/a$ .

Table 1. Crystal data for bisindenylruthenium

$C_{18}H_{14}Ru$	M.W. 331.4
Monoclinic	Space group $P2_1/a$
$a = 14.514 \pm 0.005 \text{ Å}$	
$b = 14.052 \pm 0.005$	
$c = 6.229 \pm 0.004$	
$\beta = 94 \cdot 10^{\circ} \pm 0.08^{\circ}$	
(Cu $K\alpha = 1.5418$ Å)	
Z=4	F(000) = 664
$D_x = 1.737 \text{ g.cm}^{-3}$	$D_m = 1.723 \text{ g.cm}^{-3}$

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Intensities were estimated visually from multiplefilm Weissenberg photographs (copper radiation) of layers 0-5 about c and 0-12 about b. By this means the entire copper sphere was recorded; of 2710 independent reflections, about 670 were too weak to be observed. The intensities were corrected for Lorentz and polarization factors and scaled together in the usual manner; they were not corrected for absorption ( $\mu r \simeq 1.0$ ).

The crystal fragment mounted along c was found to be twinned, the twin plane being (100). Because of the metric relation between a, c, and  $\beta$ , the resulting obliquity is, within experimental error, 0° with a twin index of 3: a reflection of type hk3 of one crystal is exactly superimposed upon the reflection  $h+1,k,\bar{3}$  of its twin. The relative size of the two twins was estimated from the intensities of the h03 reflections for which, because of the space-group extinctions, the contributions of the two twins are separate. The resulting ratio was approximately 1:20, and the remaining hk3intensities were corrected according to a proration based on this ratio.

### Determination and refinement of the structure

The positions of the ruthenium atoms were readily derived from Patterson projections onto (001) and (010). The positions of the carbon atoms could not be deduced from electron-density projections (with signs determined by the ruthenium atoms), but were immediately apparent on a three-dimensional map. Threedimensional least-squares refinement was then initiated.

All but the last two cycles of least-squares refinement were carried out on a Burroughs 220 computer. The matrix set-up was block diagonal and the quantity minimized was  $\Sigma w(F_o^2 - F_c^2)^2$ . Various weighting schemes were used, depending upon the stage of the refinement; for the final cycles, when the discrepancies  $F_o^2 - F_c^2$  appeared to reflect the pattern of uncertainties expected for visual data, the weighting function was

$$Vw = 1/F_o^2$$
 if  $F_o \ge 24$ ;  
 $Vw = 1/24F_o$  if  $F_o \le 24$ .

Unobserved reflections were assigned zero weight unless the value of  $F_c$  was greater than the observational threshold.

The R index  $(R = \Sigma |F_o - F_c| / \Sigma F_o)$  for the first structure-factor calculation was 0.18. After four cycles of least-squares refinement with individual isotropic temperature factors, anisotropic temperature factors for the ruthenium atom were introduced; after three more cycles the R index was 0.094. Hydrogen atoms were then introduced into the structure-factor calculations, their positions assigned on the basis of C-H distances of 1.06 Å and planar indenyl groups; they were not included in the least-squares refinement. Attempts were made to refine the anisotropic temperature fac-

### Table 3. Assumed coordinates of the hydrogen atoms $(\times 10^{3})$

The atom numbers and isotropic temperature factors are the same as those of the carbon atoms to which they are bonded.

	Inde	enyl gro	oup I	In	ıp II qı		
	x	У	Ζ	x	У	Z	
H(1)	088	201	045	079	-043	-131	
H(2)	021	151	411	011	-094	233	
H(3)	160	111	701	151	-136	523	
H(4)	364	111	672	354	- 140	487	
H(5)	476	143	419	468	-103	236	
H(6)	437	198	042	427	-050	- 135	
H(7)	279	223	- 088	271	-030	- 271	

Table 2. Final parameters and their standard deviations (in parentine
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Values for the ruthenium atom have been multiplied by 10<sup>5</sup>, the coordinates of the carbon atoms by 10<sup>4</sup>. The anisotropic temperature factor of the ruthenium atom is in the form exp  $\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\right]$ .

	x	у	Z	$b_{11}$	b22	b33	<i>b</i> <sub>12</sub>	<i>b</i> <sub>13</sub>	b23
Ru	16520 (3)	03460 (3)	26372 (8)	244 (3)	272 (3)	1800 (15)	11 (4)	72 (8)	-10 (9)
				x	у	z		В	
	Indenvl group I		C(1)	1256 (6)	1810 (6)	1880	(13)	3.61 (13)	
			C(2)	0900 (6)	1541 (6)	3850	(13)	3.75 (14)	
			C(3)	1639 (5)	1306 (5)	5387	(12)	3·26 (12)	
			C(4)	3438 (6)	1339 (5)	5085	(12)	3.31 (12)	
			C(5)	4074 (6)	1528 (6)	3642	(13)	3.66 (14)	
			CÌÓ	3853 (6)	1836 (7)	1503	(14)	4.22 (15)	
			C(7)	2952 (5)	1972 (6)	0763	(12)	3.43 (13)	
			C(8)	2234 (5)	1774 (5)	2192	(11)	3.13 (12)	
			C(9)	2481 (5)	1460 (5)	4357	(11)	<b>2·</b> 84 (11)	
	Indenvl a	group H	C(1)	1171 (6)	- 0637 (6)	0094	(13)	3.49 (13)	
		устр	C(2)	0812 (6)	- 0911 (6)	2061	(13)	3.81 (14)	
			C(3)	1564 (6)	- 1146 (6)	3596	(13)	3.58 (13)	
			C(4)	3340 (6)	- 1160 (6)	3236	(13)	3.52 (13)	
			C(5)	4001 (6)	- 0959 (7)	1812	(14)	4.00 (14)	
			C(6)	3756 (6)	- 0644 (6)	-0303	(14)	3.99 (15)	
			C(7)	2874 (6)	-0522(5)	-1077	(12)	3.32 (13)	
			C(8)	2159 (5)	-0712 (5)	0345	(12)	3.17 (12)	
			C(9)	2404 (5)	- 1023 (5)	2523	(11)	3.07 (11)	

# Table 4. Observed and calculated structure factors

Within each group are listed values of h,  $10F_o$  and  $10F_c$ . Negative signs preceding observed values should be read 'less than'; asterisks denote reflections omitted from the final least-squares refinement.

2 151 4 144 4 87 8 14 10 44 12 74 14 25 16 43 18 37	74-1873 4 -1533 3 862 3 -165 3 -165 - 434 0 768 0 768 - 434 - 379 9 385 -1	2 157 3 1319 4 424 5 406 6 427 7 734 8 175 9 785 0 108	-141 11 1258 14 561 11 -366 14 -365 11 -718 -1 805 -1 88 -4	2 -124 3 -126 4 19 5 237 6 283 7 119 1 138 7 1318 3 409 4 1155	-31 -3 -26 -4 -413 -5 236 -6 287 -7 -136 -8 -972 1299 387 1 -1137 2	115 -111 126 124 -77 -15 156 154 118 111 263 -253 - 30 - 655 652 775 -834		239 -3 -299 -6 -188 -5 127 -6 239 -9 100 -10 127 -11 344 -12	291 607 607 100 127 259 351 263	275 -6 -451 -7 393 -8 193 -9 159 -10 -74 -11 L20 -12 -237 -13 -559 -14	5159 -78 259 259 259 259 -78 259 -78 259 -78 -82 -78	-246 -11 -366 -14 -227 -14 -419 -14 326 -11 -419 -14 -13 -13 -13 -13	-86 406 -78 76 270 270 4 6 141 233	-396 -396 -132 -133 -133 -113 -113	-76 305 145 997 -93 515 -99 -99 -99 -99 -99	51 278 -141 - 455 - -577 - 9 - 76 - 58 - 328	-8 138 -9 612 10 -93 11 -133 12 -98 13 403 14 -85 13 358 16 83	-155 647 -75 -75 -11 -423 11 -423 11 -425 11 -425 11 -425 11 -425 11 -425 11 -425 11 -11 -11 -11 -11 -11 -11 -11 -11 -11	7 161 8 189 9 -94 0 331 1 129 2 546 3 120 4 100 5 -52 6 216	-131 176 -31 357 121 -335 -34 112 112 112	2 -89 3 -78 4 179 5 321 6 415 7 465 8 329 9 111 0 -82 1 327	-22 -165 -351 458 457 -315 -111 -20 -355	1 184 - 2 248 - 1 495 - 3 305 - 4 05 - 5 145 - 5 145 - 1 47 -	374 -10 240 -11 108 150 334 0 288 1 401 2 140 3 86 4 122 4	243 232 135 -127 4 12 5 232 241 -66 -38 67 37 173 168 237 -267	+ 1+ 3 0 -99 1 139 - 2 335 - 3 -77 4 420 5 -70 6 202 - 7 -59 8 154 -	-44 117 298 -75 346 55 155 60
0 13 2 133 4 131 4 50 10 40 12 17		1 -96 2 106 3 400 4 118 5 303 4 1 0 73 1 1152 2 116	-61 178 -50 -129 378 -10 3 -10 3 -10 3 -10 -10 -10 -10 -10 -10 -10 -10	201 205 7 119 852 9 374 9 374 9 374 9 374 9 374 9 374	-259 3 -199 4 -157 5 874 6 372 7 -75 9 -75 9 -122 10 -205 11 459 12	1313 -1092 776 839 388 163 -65 28 529 511 596 -569 743 -756 418 639 316 339 -102 -83	* 24 5 32 6 -7 7 25 10 15 -1 31 -3 21	-237 -13 -321 -14 54 -15 -31 -16 103 217 -139 0 -342 1 -348 2 -348 2	168 -64 151 161 221 111 249	172 -14 -9 127 -173 0 5 2 -252 3 115 4 -243 5	2 4 5 3 9 5 1 7 4 3 0 5 4 3 4 5 0 5 1 3 2 - 78	-718 4 -364 9 141 6 -307 1 -413 4 535 1 130 10 -37 11	675 591 272 624 -82 145 -77 648 -78 611	442 19 -676 10 -277 -1 645 -2 -120 -4 -29 -4 -120 -4 -29 -4 -29 -4 -21 -1	-60 246 227 892 -63 673 110 249 -81	-335 -335 -432 -933 -59 842 -95 252 252 70	C 105 1 866 2 -76 3 -77 4 -81 3 539 6 170 7 307 8	2 135 934 -55 -58 -74 -571 180 575	2 284 1 111 2 475 3 362 4 535 5 -94 6 -81 7 213	244	2 200 3 274 1 234 2 153 3 120 4 146 5 413 6 398 7 379	123 1 278 1 -250 - -150 - -150 - -150 - -150 - -150 - -150 - -150 -	234 214 253 127 361 - 369 - 344 340	134 6 245 -1 253 -2 -18 -3 132 -4 366 -5 433 -6 151 -7 342 -8	62 66 143 -143 265 -287 168 174 113 138 -67 -52 118 129 133 -149 2144 -276	9 -32 -1 -81 -2 478 -3 137 -4 345 - -5 74 -6 194 - +7 -65 -8 313	-40 640 113 312 -88 178 43 323
10 11 -10 11 -10 11 -10 11 -10 11 -10 11 -10 11	5 381 1 1485 7 -1193 5 -325 8 899 8 -166 1 -699 1 -699 1 -232	3 328 4 144 5 724 6 406 7 755 8 216 9 -95 0 -98 1 463 2 -98	-307 -19 -154 -16 -550 -11 -599 -16 723 -193 -22 -1 -473 - 58	3 174 203 7 -78 5 71 4 2 1 309 1 309 2 369 3 71	172 13 -281 14 -44 15 -79 16 17 2 18 -1045 314 531 0 -52 1	212 236 256 -234 399 -351 263 215 -73 89 +60 52 -73 1 15 -136 125 -31	-4 20 -5 -8 -7 28 -7 28 -7 28 -7 28 -10 12 -11 -5 -12 10	202 4 54 5 -285 7 -258 8 272 9 103 10 58 11 40 12	154 336 -79 196 269 393 218 214 -52	344 7 -354 8 40 9 -255 10 -255 11 387 12 255 13 -256 14 -51 -1	163 483 154 484 119 -88 -65 191 221	155 12 -637 11 -159 14 -658 11 -61 -2 36 -1 -132 -4 219 -1	98 108 107 347 743 165 1362 345 168	36 -10 45 -11 -324 -14 735 -1 -151 -14 -152 -14 325 -14 139 -1	-88 237 -91 333 -85 431 -69 201 -24	43 251 41 137 -79 -499 10 234	9 -90 10 -93 11 364 12 -89 13 427 -1 743 -2 -76 -3 231 -4 -82	-46 -431 10 96 11 376 11 -765 11 -75 11 -227 -	533 9 149 0 439 1 -83 2 -86 3 -66 4 281 1 225 2 643	577 -142 -1 -448 -1 70 -1 -14 -1 30 -1 372 219 -080	- 86 1 408 2 175 3 253 4 10 0 152	-45 -1 -193 -11 300 -1 155 -11 -218 -1 -2 3 -1 -150	-18 237 - 179 - 286 72 -11 4 163 -	70 208 1 193 2 251 3 93 4 5 150 7 10 8	x 13 0 236 -255 181 -183 491 515 147 155 178 -125 178 -125 541 -315 94 -115	H 14 4 D 314 - 1 -64 2 260 3 -59 4 -55 5 -69 6 238 - -1 -80	244 15 225 12 42 11 23# -51
0 118 2 59 4 90 8 51 10 20 12 70 14 21	0 2 14 -1187 13 579 12 468 15 -923 11 539 14 539 15 273 11 -626 15 274	3 392 4 -90 5 -79 1 888 2 139 3 398 4 181 5 1354 6 381 7 621	396 -23 -48 -816 -133 -145 -145 -145 -145 -145 -145 -145 -145	385 1513 1513 153 435 -89 295 295 295 295 295 295	158 2 -344 3 -1025 4 114 5 666 6 17 7 278 8 16 9 -663 10	301 272 181 187 219 210 912 919 950 -662 1018 -1022 334 300 -91 14 186 176	0 24 1 24 2 23 3 10 4 -5 5 17 6 16 7 16	7 -2 237 -3 234 -4 -214 -5 -118 -4 -27 -7 -140 -8 166 -9 231 -10	125 135 -77 215 146 146	347 -3 210 -4 -259 -3 -72 -6 -457 -7 381 -9 377 -10 -751 -11	101 362 158 215 514 318 275	-311 -1 -347 -4 147 -4 -234 -10 252 -11 525 -12 -346 -11 -236 -14	597 289 413 78 137 151 351 -77 275	613 -259 -355 -142 -142 -142 -142 -152 -549	4 7 781 73 813 -65 207 161 535	3 -53 -547 -27 - -200 - -144 - 642 - 214 -	6 170 7 402 8 -96 9 95 10 216 11 482 12 233 13 134	-434 -12 -96 -218 -218 -10 -10 -11 -11 -11 -11	3 28 4 436 5 238 6 114 7 129 8 507 9 324 0 380 1 -88 2 93	-282 455 221 111 132 -554 -324 440 80 105 1	2 271 3 445 4 308 5 255 6 152 7 299 8 335 9 481 0 195	-288 -451 371 235 135 237 -318 -456 175	210 - 365 283 276 - -77 -81 185 - 246 146 267 -	238 9 330 13 259 11 235 1 235 1 235 1 235 1 235 1 235 1 241 2 162 1 241 2 162 1 241 2 162 1 241 2 162 1 162 1 162 1 163 1 17 17 17 17 17 17 17 17 17 17 17 17 17	-115 51 144 -130 -13 1 160 -133 620 571 -113 91 136 -123 112 117	-2 01 -3 -77 -4 165 -3 -73 -0 221 - -0 221 - -1 -39 -2 1720 -	11 162 -48 721 -17 255
-2 3 -6 55 -8 72 -10 55 -10 55 -10 -10 -10 -10 -10 -10 -10 -10 -10 -10	a 316 5 541 7 +696 - 0 233 - 15 566 - 15 566 - 15 7 143 - 13 314 - 13 -271 -	6 -85 9 193 0 242 1 572 2 -99 3 104 4 -93 5 179 6 -75	28 14 -175 15 -256 14 988 14 -312 -4 -312 -4 -175 -4 -086 -4	234 231 144 136 231 144 136 231 221 535 488	275 12 10 13 153 14 -124 15 -134 16 458 17 -197 -1 475 -2 628 -3	200 -201 354 -321 136 144 56 -5 300 245 133 144 372 321 150 -103	-2 8 -3 20 -3 28 -5 28 -6 17 -7 -3 -8 17 -7 13	10 -12 -172 -11 -213 -14 248 152 -57 0 7 1 -114 2	207	-118 -13 -235 -14 -235 -15 -357 0 397 1 291 2 -76 3	134 354 116 7 59 275 369 .79	153 362 -115 -458 -232 391	-57 543 75 136 -75 334 268	10 10 10 10 10 10 10 10 10 10	-72 -72 -72 -72 -72 -72 -72 -72 -72 -72	-07 -209 410 -10 -228 -211 -211 -211	0 63 1 235 2 89 3 653 4 113 5 445 6 -74	-135 -1 -1 -12 -32 219 -89 -672 113 455 -32	0 403 0 403 1 241 2 427 3 427	120 1 -176 1 -102 1 -102 1 -102 1 -102 1 -102 1 -172 -	1 133 2 -57 3 159 1 368 2 105 3 420 3 420 3 420 3 425 5 135 5 -85 -7 255	128 - -25 - 176 - 308 - 171 - -44 - -73 - 128 - -27 -10 253	204 277 - -91 247 - 247 - 272 295 169 -	403 5 141 6 280 7 -2 8 222 9 -55 10 751 11 277 -1 149 -2 -3	435 -435 230 -220 363 384 -99 70 93 79 -84 66 377 -310 481 -467 -139 80 -138 -40	+ 15 D 1 253 - 2 -133 3 492 4 -128 5 214 - 6 -118 7 193 - 8 -131 9 333	244 80 452 -84 214 45 178 10 337
0 22 2 4 91 8 55 10 5 12 -14	0 3 3 217 3 788 4 -967 17 278 17 503 4 -568 12 48 10 351	0 -63 1 261 2 276 3 704 6 229 5 673 6 -80	243 -10 -238 -11 -238 -11 -733 -11 -733 -11 -733 -11 -735 -11	7 324 278 278 -05 570 -105 2 544 -108 -108 -117 5 -100	-317 -5 255 -6 -14 -7 578 -8 14 -9 -671 -10 -5 -11 92 -12 5 -13	258 24 931 -955 724 -755 856 835 287 270 147 151 308 300 572 -552 289 321 289 321	0 66 1 76 2 15 3 27 6 -5 5 95 6 70 7 103 8 16	- 621 - 621 - 673 - 155 - 73 - 355 - 1 - 355 - 1 - 115 - 1 - 115 - 1 - 115 - 1 - 115 - 1 - 155 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1	275 311 241 229 101 -71 324 389 344	67 6 -277 5 -282 6 238 7 230 8 -100 9 -81 10 536 12 376 -1	145 241 377 314 154 154 255 255 255 255 255	162 1 236 8 -381 6 -381 1 226 11 157 14 78 11 101 -1 -284 -2 173 -1	404 214 167 -70 293 70 345 443 177	-772 -729 176 -729 -717 -775 -717 -176 -176 -176 -176 -176 -176 -176	414 124 532 -98 -88 -89 -89 -89 -89 -89 -89 -89 -89	-637 115 531 -07 -37 -72 -477 -13 690 70	7 114 8 115 9 440 10 -95 11 272 12 -82 13 194 -1 523 -2 151	127 -82 -87 -87 -88 -7 161 161 11 -38 143 143	5 196 5 536 7 213 8 316 9 -91 3 211 1 -81 1 -81 2 368 3 -43 4 118	184 - 573 - -215 -1 -344 -1 39 -1 -178 -1 50 -1 354 -4 -154	8 333 9 413 5 337 1 245 2 -68 3 171 4 182 9 15 0 263	-319 -319 -240 -24 163 137	- 11 9 284 - 254 - 74 - 77 - 154 - 235 - 181 - 175	-4 277 -5 248 -6 137 -7 -72 -8 76 -9 153 -10 239 -11 239 -11 239 -12	-137 122 597 575 189 -207 473 -423 124* 18 116 -87 -137 95 347 322 -78 -48	+ 15 1 + 15 1 0 102 1 517 2 -133 3 -98 4 -95 5 411 - 6 -87	-23 -28 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3
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	873       90     -755       90     -755       91     756       92     756       93     -277       93     -229       93     -229       96     -261		-912 -97 48 -139 575 12 258 11 -422 12 -123 1 -123 1	173 7 214 7 214 9 720 9 995 1 -97 2 -103 9 -93 3 -93	132 132 236 3718 -23 7 -845 8 59 9 1 10 9 11 323 12	601 74 509 -505 280 -245 332 -385 471 476 703 725 253 -245 253 -245 -88 5	0 72 1 24 2 94 3 89 4 33 5 17 7 38	1 200 -1331 9 -1331 9 -135 -1 -435 -2 177 -1	-52 183 223 162 110 276 166 230	-33 -12 69 -196 -228 0 159 1 115 2 253 1 -146 4 -219 5 -219 5	267 500 -72 153 187 159 162 162	-256 -14 -15 -15 -15 -15 -15 -15 -15 -15 -15 -15	-54 161 -72 -89 -74 461 108 337	•3 159 •65 •51 •51 157 165 165 1.57 1.5	-85 -85 -85 -82 -82 -82 -82 -82 -82 -82 -83 -83	103 - -251 - -226 -47 340 51 -17 -23 -42	13 109 14 -57 15 771 0 97 1 544 2 -85 2 91 4 -85	3+3 -1 54 -1 -748 -1 -14 -117 -627 53 311 60	1 131 2 308 3 -64 4 -34 4 -34 4 -34 1 190 2 304 3 287	-130 L 328 - -32 - -151 - -151 - -118 - 245 -	1 194 1 309 2 -82 3 330 4 359 4 359 4 527 6 400 7 259 6 -77 9 122	220 321 333 362 -532 -1 218 -1 218 -1 218 -1 218	+ 11 6 67 -51 87 173 119 - 171 -	9 101 10 -3 11 103 -1 177 -2 193 -3 113 -4 135 -5 24 -6 -7	105 -321 -62 -58 154 174 335 238 195 -149 548 -553 111 114 127 129 -87 56 364 329	+ 15 2 2 234 1 148 2 135 - 3 411 - 4 -95 5 332 6 -85 7 -72	176 133 134 333 -3 257 -40 77
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tors of the carbon atoms, but the indicated shifts were not sensible nor was their effect significant.

The last two refinement cycles were carried out under the CRYRM system (Duchamp, 1964) on an IBM 7094 computer. The form factors were from *International Tables for X-ray Crystallography* (1962), that for ruthenium having been corrected by -0.55 electron to take account of anomalous dispersion. The 82 parameters (coordinates of 19 atoms, isotropic temperature factors of 18 carbon atoms, anisotropic temperature factors of the ruthenium atom, and a scale factor) were included in a single matrix. The weighting function was that described earlier, but with weights of zero assigned to twelve reflections having anomalously large discrepancies. A check of the photographs uncovered legitimate reasons (extinction, mis-indexing, or transcription error) for rejecting all twelve.

During the last cycle the maximum shift in any parameter was less than 10% of its standard deviation. The weighted discrepancies  $\sqrt{w(F_o^2 - F_c^2)}$  were distributed uniformly, no individual value or small group of values being large enough to dominate the refinement. The final *R* index for 2031 observed reflections of non-zero weight is 0.057. The electron density in the planes of the indenyl groups, calculated at the end of the refinement, is shown in Fig. 1.

The final parameters and their standard deviations, calculated from the residuals and the diagonal ele-



Fig. 1. The electron density in the planes of the two indenyl groups, calculated at the end of the refinement. Contours are at intervals of  $1.0 \text{ e.} \text{Å}^{-3}$  beginning at  $1.0 \text{ e.} \text{Å}^{-3}$  (dashed). The trace of the *bc* plane is horizontal.



Fig. 2. The final bond distances and the angles at the carbon atoms.

ments of the inverse matrix, are given in Table 2; the standard deviations correspond to e.s.d.'s in the range 0.007-0.010 Å in the Ru-C distances and 0.010-0.014 Å in the C-C distances. The assumed coordinates of the hydrogen atoms are given in Table 3. Observed and calculated structure factors are given in Table 4.

### Discussion

# The molecular structure

The bisindenylruthenium molecule is in the fully eclipsed conformation, and has almost exact *mm* symmetry. When the two indenyl groups are projected onto the median plane passing through the ruthenium atom, all pairs of corresponding atoms from the two groups superpose within 0.04 Å. This mismatch, though very small, is probably significant; it represents not a twist of one group with respect to the other but rather a slippage of 0.025 Å in a direction approximately parallel to the C(9)–C(4) bond.

Each of the indenyl groups is planar, none of the carbon atoms in group I lying farther than 0.015 Å from the plane

0.0104 X' + 0.9506 Y + 0.3101 Z' = 2.812 Å

nor any of group II farther than 0.015 Å from the plane

0.0251 X' + 0.9503 Y + 0.3102 Z' = -0.793 Å.

(The coefficients are direction cosines relative to **a**, **b**, and **c**\*.) These planes are tilted with respect to one another by about  $0.8^{\circ}$  so as to increase very slightly the distance between the six-membered rings: the two planes are separated by 3.62 Å in the region of C(2) and by 3.69 Å in the C(5)-C(6) region.

The ruthenium atom lies midway between the two five-membered rings and almost exactly on the line joining their centers; its slight displacement (0.015 Å) from this line is in a direction towards the C(2) atoms.

The Ru–C and C–C bond distances and the C–C–C bond angles are shown in Fig.2. Corresponding dimensions in the two indenyl groups are equal within experimental error, as are the dimensions related by the mirror plane passing through the two groups. There are thus only six chemically distinct C–C distances; the average values of these distances are listed in Table 5. The scatter among the two or four independent observations of each of these distances leads to an estimated standard deviation of about 0.011 Å, in close agreement with the value 0.010–0.014 for the e.s.d. of a C–C distance as derived from the final least-squares calculation.

The bond distances can be explained quite satisfactorily on the basis of a simple valence-bond approach. Following Pauling (1960), a total of 1287 canonical structures can be drawn, each involving a formal charge of either 0 or -1 on the ruthenium atom and no more than nine Ru-C bonds. Assigning equal weight to each of these structures, the bond numbers listed in Table 5 are derived. The bond distances cor-

#### Table 5. Average C-C and Ru-C bond distances

Here, d(obs) is the average of the two or four observed distances for each chemically distinct bond, n is the bond number derived from a valence-bond calculation (see text), and d(cal)the predicted interatomic distance corresponding to that bond number.

	d(obs)	n(cal)	d(cal)
C(1)–C(2) C(2)–C(3)	1.424	1.24	1.441
C(1)–C(8) C(3)–C(9)	1.433	1.18	1.455
C(4)-C(9) C(7)-C(8)	1.434	1.24	1.441
C(4)-C(5) C(6)-C(7)	1.364	1.71	1.366
C(5)–C(6)	1.414	1.24	1.441
C(8)-C(9)	1.442	1.16	1.460
Ru-C(1) Ru-C(3)	2.181	0.53	2.159
Ru–C(2)	2.165	0.46	2.197
Ru-C(8) Ru-C(9)	2.211	0.38	2.245

responding to these bond numbers are also listed in Table 5; the C-C distances were taken from Pauling's (1960) Table 7-9 and the Ru-C distances were calculated from the expression  $D(n) = D(1) - 0.60 \log n$ , the single-bond Ru-C distance (1.994 Å) being obtained by subtracting an electronegativity-difference correction of 0.024 Å from the sum of the single-bond radii of Ru and C, 1.246 Å and 0.772 Å (Pauling, 1960, pp. 255, 229, 403).

The agreement between the observed distances and those calculated by this valence-bond method is quite good; the shortening of the C(4)-C(5) and C(6)-C(7)distances and the small displacement of the ruthenium atom toward the C(2) positions are fully explained.

# Packing of the molecules

A drawing of the structure viewed down the c axis is shown in Fig.3. The most important intermolecular



Fig.3. The structure viewed along the c axis.

approaches are:  $Ru \cdots H$ , 3.3 Å and 3.6 Å (twice);  $C \cdots C$ , 3.3 Å and 3.5 Å;  $H \cdots C$ , 2.7 Å. None of these is shorter than the sum of the normal van der Waals radii.

The pattern of temperature motions is reasonable, the central carbon atoms C(8) and C(9) having relatively small temperature factors and the peripheral atoms



Fig.4. An electron density projection, onto (001), of the disordered modification. The contours are at equal but arbitrary intervals (no structure factors were calculated, and hence the scale factor was not determined).



Fig. 5. The disordered structure (heavy lines) superposed on the ordered structure (lighter lines). The view is along c, and the molecules are represented schematically; for comparison, see Fig. 3.

C(5) and C(6) relatively large ones. The anisotropic parameters of the ruthenium atom correspond to values of *B* ranging from  $2\cdot8$  (in a direction approximately parallel to c) to  $2\cdot0$  (approximately along a).

### The disordered modification

Visual intensity data for the hk0 reflections of the disordered modification of bisindenylruthenium (see Experimental) were obtained from a set of Weissenberg photographs prepared with Cu  $K\alpha$  radiation. The Patterson projection onto (001) could be interpreted on the basis of four ruthenium atoms, each of half weight, in the unit cell; phases calculated from these ruthenium positions led to the electron-density projection shown in Fig.4. Since this projection is down a relatively short (6.2 Å) axis, separate molecules must be resolved. Accordingly, it seems quite clear that each molecule can assume either of two orientations with equal probability, one orientation being related to the other by a twofold rotation about an axis perpendicular to the rings and passing approximately through the centers of the two C(8)-C(9) bonds. A similar sort of disorder was proposed by Trotter (1958) for bisindenyliron.

In view of the near equality of the lengths of the c axes in the two modifications, there appears to be a simple relationship between the ordered and the disordered structures. This relationship is shown in Fig. 5.

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# The Crystal Structure of Terephthalic Acid

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X-ray diffraction photographs of terephthalic acid have shown the existence of two polymorphic forms which have closely related triclinic unit-cell dimensions. The crystal structures of both these forms have been determined from two-dimensional data, and a full three-dimensional analysis, including the calculation of anisotropic temperature factors, has been carried out for one of these forms. The R index over 470 F(hkl) was 7.5%. The bond lengths indicated a small amount of quinonoid character in the benzene ring, and a slight departure from planarity between the ring and the carboxyl groups. The molecules pack together in the crystal in systems of infinite chains linked together by double hydrogen bonds of length 2.608 Å.

### Introduction

In the course of examining samples of terephthalic acid, HOOC.  $C_6H_4$ . COOH, by X-ray powder photographs, two slightly different patterns were found to occur, suggesting the possibility of more than one polymorph. Single-crystal photographs showed that terephthalic acid does in fact crystallize with two different triclinic structures, both of which have been determined. In both forms, the molecules are hydrogen-bonded into infinite chains parallel to an axis of length 9.54 Å, the difference between them being in the relative longitudinal displacement of these chains, as shown in Fig. 1. Neighbouring chains in form I pack with the benzene rings of one chain adjacent to the carboxyl groups of the next chain, whereas in form II the benzene rings of adjacent chains are in line. For successive layers, however, the reverse is true; in form I layers pack with benzene rings almost in line with each other, while for form II, benzene rings pack alternately with carboxyl groups.

#### Experimental

Pure terephthalic acid was recrystallized from water in a glass tube in a Carius furnace at about 150°. The resulting crystals were mostly highly twinned, but by