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The Crystal and Molecular Structure of Bisindenylruthenium*

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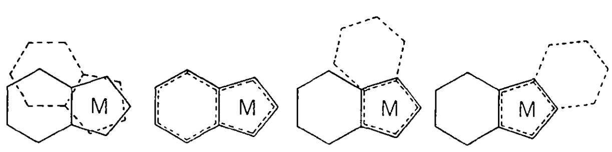
The crystal structure of bisindenylruthenium, $(C_9H_7)_2Ru$, has been determined and refined by three-dimensional X-ray diffraction techniques. The crystals are monoclinic, space group $P2_1/a$, with $a=14\cdot51$, $b=14\cdot05$, $c=6\cdot23$ Å, $\beta=94\cdot10°$; there are four molecules in the cell. 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, $\beta=90°$; 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).



(I) (II) (III) (IV)

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, $\beta=90°$. The space group is $P2_1/a$ ($h0l$ 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 $P2_1/a$
	$a=14\cdot514\pm0\cdot005$ Å	
	$b=14\cdot052\pm0\cdot005$	
	$c=6\cdot229\pm0\cdot004$	
	$\beta=94\cdot10°\pm0\cdot08°$	
	(Cu $K\alpha=1\cdot5418$ Å)	
$Z=4$		$F(000)=664$
$D_x=1\cdot737$ g.cm^{-3}		$D_m=1\cdot723$ g.cm^{-3}

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Intensities were estimated visually from multiple-film 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 ($\mu r \simeq 1 \cdot 0$).

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 β, 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 $hk3$ intensities 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. Three-dimensional 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

$$\sqrt{w}=1/F_o^2 \text{ if } F_o \geq 24;$$
$$\sqrt{w}=1/24F_o \text{ if } F_o \leq 24\,.$$

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.

	Indenyl group I			Indenyl group II		
	x	y	z	x	y	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 parentheses*)

Values for the ruthenium atom have been multiplied by 10^5, the coordinates of the carbon atoms by 10^4. The anisotropic temperature factor of the ruthenium atom is in the form $\exp\,[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ru	16520 (3)	03460 (3)	26372 (8)	244 (3)	272 (3)	1800 (15)	11 (4)	72 (8)	−10 (9)

		x	y	z	B
Indenyl 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)
	C(6)	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)	2·84 (11)
Indenyl group II	C(1)	1171 (6)	−0637 (6)	0094 (13)	3·49 (13)
	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.

[illegible]	[illegible]	[illegible]

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 elements 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.

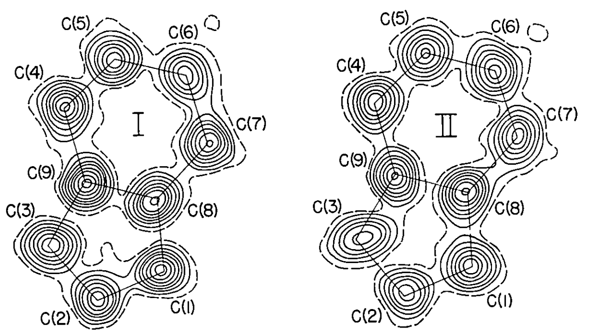

Fig. 1. The electron density in the planes of the two indenyl groups, calculated at the end of the refinement. Contours are at intervals of 1·0 e.Å^{-3} beginning at 1·0 e.Å^{-3} (dashed). The trace of the bc plane is horizontal.

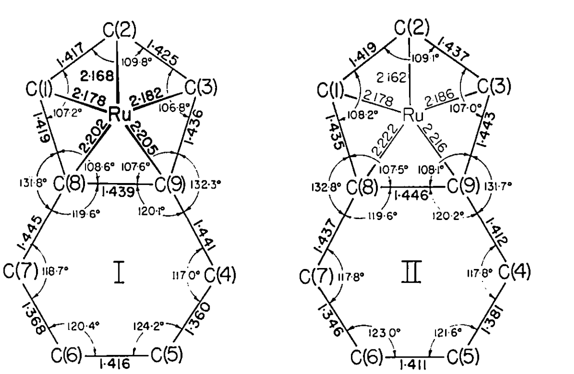

Fig. 2. The final bond distances and the angles at the carbon atoms.

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

$$0{\cdot}0104\,X'+0{\cdot}9506\,Y+0{\cdot}3101\,Z'=2{\cdot}812\text{ Å}$$

nor any of group II farther than 0·015 Å from the plane

$$0{\cdot}0251\,X'+0{\cdot}9503\,Y+0{\cdot}3102\,Z'=-0{\cdot}793\text{ Å}.$$

(The coefficients are direction cosines relative to **a**, **b**, and **c***.) These planes are tilted with respect to one another by about 0·8° 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 $D(n)=D(1)-0\cdot60 \log n$, 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 approaches are: Ru···H, 3·3 Å and 3·6 Å (twice); C···C, 3·3 Å and 3·5 Å; H···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

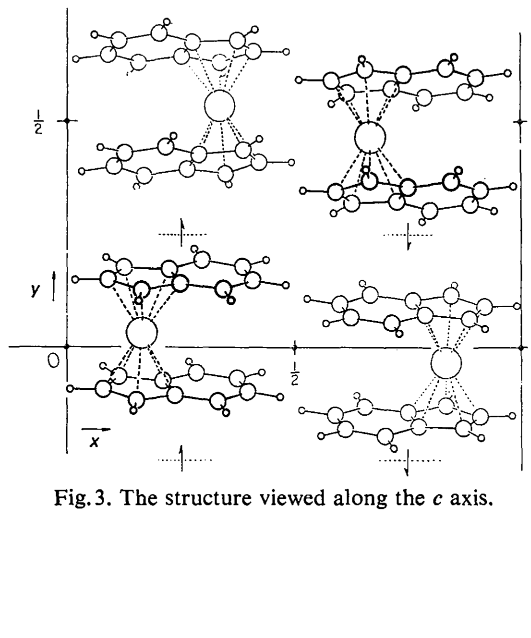

Fig. 3. The structure viewed along the c axis.

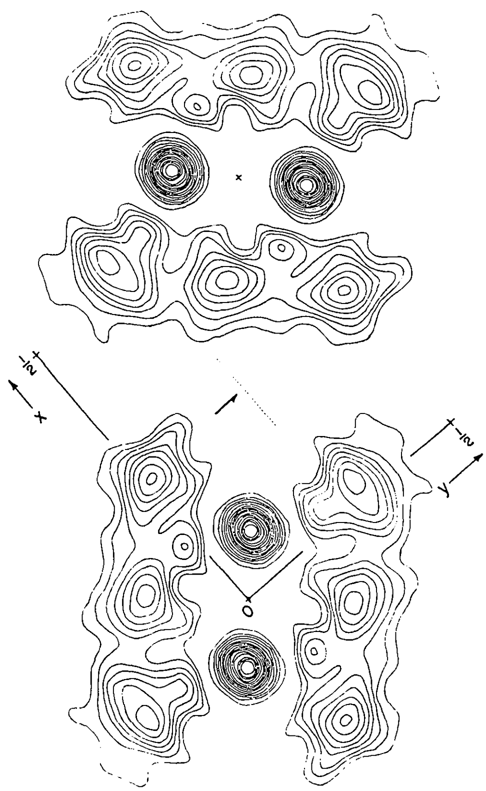

Fig. 4. An electron density projection, onto (001), of the disordered modification. The contours are at equal but arbitrary intervals (no structure factors were calculated, and hence the scale factor was not determined).

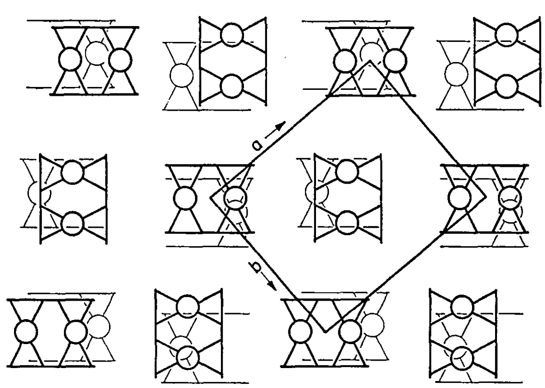

Fig. 5. The disordered structure (heavy lines) superposed on the ordered structure (lighter lines). The view is along **c**, and the molecules are represented schematically; for comparison, see Fig. 3.

C(5) and C(6) relatively large ones. The anisotropic parameters of the ruthenium atom correspond to values of B ranging from 2·8 (in a direction approximately parallel to **c**) to 2·0 (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.

We are grateful to Dr D. Hall for providing us with a sample of the compound. One of us (N.C.W.) is grateful to the U.S. Rubber Company and to the National Science Foundation for providing financial support.

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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