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The Crystal and Molecular Structure of 2,3-*exo*-Ferroco-4,4-dimethylbicyclo[3,2,1]octa-2,6-diene, a Product of the Reaction of Cyclopentadiene with the 2-Ferrocenyl-2-propyl Cation

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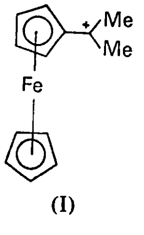
(π-C_5H_5)Fe(π-$C_{13}H_{15}$) crystallizes in space group $P2_1/c$, $a = 10{\cdot}733$, $b = 8{\cdot}122$, $c = 16{\cdot}873$ Å, $\beta = 110{\cdot}95°$, with four formula units in the unit cell. The crystals are reflexion twins about the (001) face and the structure was determined with X-ray data from one half of the twin and refined by the least-squares method to $R = 0{\cdot}091$ for 842 independent reflexions. The substituted cyclopentadienyl moiety had the predicted tricyclic configuration formed with a bridging ethylene group. The cyclopentadienyl rings are in the eclipsed conformation and inclined at an angle of 7°.

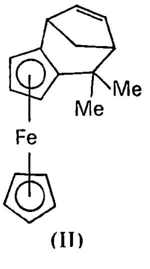
Introduction

Turbitt & Watts (1974) reported that the ferrocenyl carbonium ion (I) reacts stereospecifically with cyclopentadiene to give a single product for which the structure (II) was proposed from ^{1}H n.m.r. evidence.

The crystal structure of this product has been determined in order to confirm the proposed structure and to establish its stereochemical features. The results have been reported in a preliminary communication (Cameron, Maguire, Turbitt & Watts 1973).



(I)



(II)

Experimental

The crystals were prepared by Turbitt & Watts (1974).

Crystal data

$C_{18}H_{20}Fe$, M.W. 519·14, $F(000) = 616$.

Monoclinic: $a = 10{\cdot}733 \pm 0{\cdot}003$, $b = 8{\cdot}122 \pm 0{\cdot}001$, $c = 16{\cdot}873 \pm 0{\cdot}005$ Å, $\beta = 110{\cdot}95 \pm 0{\cdot}01°$.

$D_m = 1{\cdot}414$, $D_c = 1{\cdot}412$ g cm^{-3}, Mo $K\alpha$ $\lambda = 0{\cdot}7107$ Å, $\mu = 10{\cdot}15$ cm^{-1}.

Systematic extinctions $h0l$: $l = 2n+1$, $0k0$: $k = 2n+1$; space group $P2_1/c(C_{2h}^5$, No. 14).

The crystals are thin orange plates and all appear to be reflexion twins about the (001) face which is parallel to the face of the plates. It was not possible to bisect any crystal and retain a single crystal large enough for X-ray intensity measurements. A twinned crystal was mounted about the unique axis and the intensities of 924 independent reflexions (with $I > 2\sigma$)

from one half of the twin only were measured on a Hilger and Watts† linear diffractometer (*h*0*l*–*h*5*l*).

Fig. 1 shows the interpenetrating reciprocal lattices for the twin, and it can be seen that there is some coincidental overlap from both halves for reflexions with *h* equal to 8 or 9. In the final structure the cumulative *R* index for each set of reflexions with *h* equal to 7, 8, 9, 10 is 0·095, 0·110, 0·115 and 0·089 respectively.

The reflexions with $2\sigma > I > 3\sigma$ were removed leaving 842 reflexions, and in the final two refinement cycles contributions to the normal equations were not included for the 109 reflexions with *h* equal to 8 or 9. The intensities of the 20*l*–50*l* reflexions were measured for the other half of the twin to determine the contribution this half makes to the 00*l* reflexions and the intensities of these axial reflexions were adjusted accordingly. The data were corrected for Lorentz and polarization effects but not for absorption.

Solution and refinement of structure

From an unsharpened Patterson synthesis a tentative position was assigned to the iron atom in spacegroup $P2_1/c$. A Fourier synthesis, phased on this iron atom position clearly showed the location of the light atoms, and these were confirmed by a Fourier synthesis phased on all the light atoms.

The positions of the atoms were determined from the Fourier syntheses by a 19-point Gaussian interpolation peak-search routine (Dawson 1961), and refined by the method of least squares with the block-diagonal approximation to the normal matrix.

After three cycles of refinement with isotropic temperature factors and a weighting scheme $W = \{1 + [(|F_o| - 40)/34]^2\}^{-1}$ the *R* value was 16%. The individual layer scale factors $\sum F_o/\sum F_c$ for *h*0*l*–*h*5*l* were calculated and none deviated significantly from the mean. Positions were calculated for the hydrogen atoms with locations defined by the molecular structure and they were allocated the temperature factors of the atoms to which they are bonded. Refinement of all but the hydrogen atoms was continued with the weighting scheme un-

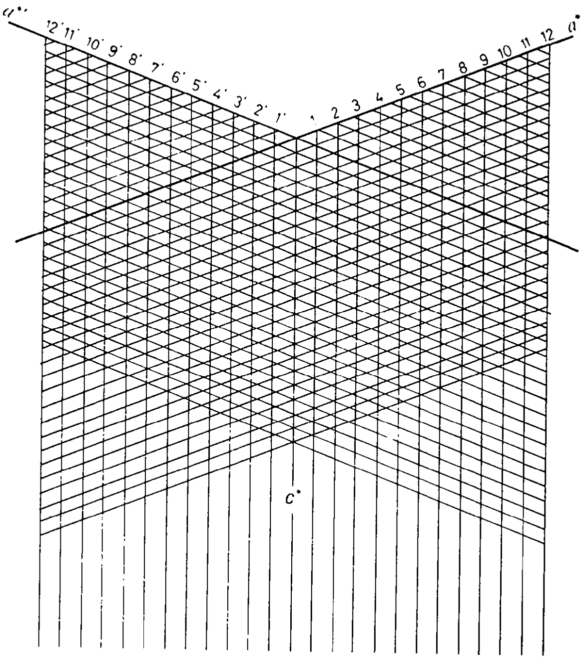


Fig. 1. Interpenetrating reciprocal lattices of the twinned crystal.

Table 2. *Atomic parameters* × 10^4 ($B \times 10^2$)

The temperature factor $T = \exp\,[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})$ for the light atoms and $T = \exp\,(-\frac{1}{4}B)$ for the hydrogen atoms.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	7258 (2)	879 (1)	2323 (1)	93	73	30	−4	36	−45
C(1)	8346 (17)	1975 (11)	1659 (11)	87	194	38	−1	57	−83
C(2)	7538 (17)	3106 (10)	1829 (10)	94	66	32	−5	64	−46
C(3)	7904 (17)	3140 (10)	2720 (10)	81	127	27	−59	10	−173
C(4)	8896 (21)	1982 (13)	3090 (13)	124	22	67	−61	57	−105
C(5)	9170 (22)	1126 (11)	2425 (11)	196	216	31	157	106	274
C(6)	8464 (15)	1638 (9)	803 (9)	89	22	22	−4	32	21
C(7)	9863 (19)	1900 (12)	850 (12)	125	92	54	2	103	67
C(8)	8037 (24)	−95 (11)	431 (11)	179	199	31	−75	54	−16
C(9)	7438 (17)	2804 (10)	158 (10)	85	145	32	107	11	−33
C(10)	6169 (18)	3001 (10)	319 (10)	102	80	32	60	8	23
C(11)	6614 (18)	4060 (10)	1128 (10)	120	69	41	17	39	23
C(12)	7950 (22)	4545 (13)	355 (13)	143	379	50	166	95	96
C(13)	7488 (22)	5268 (11)	896 (11)	161	6	41	17	29	25
C(21)	6763 (20)	−548 (11)	3091 (11)	170	14	51	56	125	71
C(22)	6860 (21)	−1519 (17)	2407 (17)	136	48	116	−66	104	−89
C(23)	5944 (19)	−866 (11)	1631 (11)	114	239	39	−65	19	−221
C(24)	5255 (22)	472 (18)	1900 (18)	69	655	102	160	88	22
C(25)	5750 (23)	437 (13)	2776 (13)	185	75	64	−112	111	−56

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† The authors thank Dr C. K. Prout, Chemical Crystallography Laboratory, Oxford, for allowing them the use of this diffractometer.

Table 2 (*cont.*)

	x	y	z	B
H(3)	7526	3895	3026	249
H(4)	9299	1387	3123	581
H(5)	9757	351	2465	425
H(9)	7272	2418	−438	432
H(101)	5783	1963	399	368
H(102)	5506	3629	−166	368
H(11)	5840	4616	1253	407
H(12)	8522	4903	42	780
H(13)	7739	6437	1070	439
H(21)	7247	−837	3724	420
H(22)	7501	−2406	2452	663
H(23)	5832	−1194	1118	500
H(24)	4471	1151	1476	744
H(25)	5405	1288	3091	750

changed and anisotropic temperature factors on all atoms. It converged after three cycles at $R=0·091$. Table 1* lists the observed structure amplitudes and structure factors calculated from the atomic parameters in Table 2. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1969) and the curve for neutral iron was corrected for the real part of the anomalous dispersion effect. The interatomic distances and interbond angles are given in Table 3. Fig. 2 shows the projection of the structure down **b** and Fig. 3 shows the projection parallel and perpendicular to the plane of the cyclopentadienyl ring C(1)–C(5). All calculations were performed on the New University of Ulster 1903A Computer with the Cameron (1973) *CRYSTAL* system.

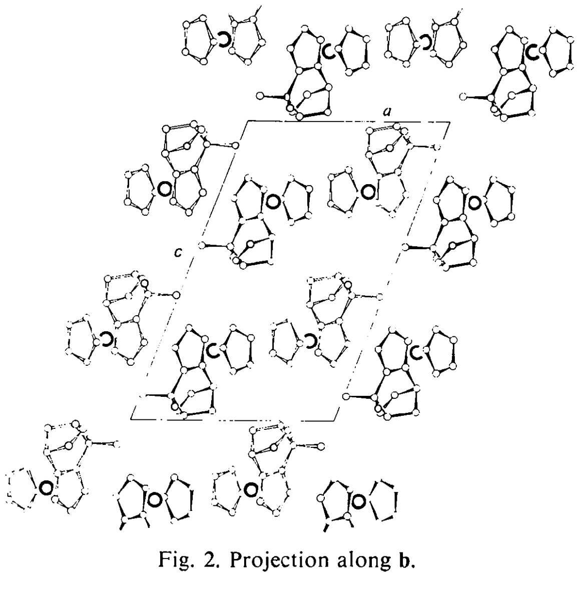

Fig. 2. Projection along **b**.

Table 3. *Interatomic distances and interbond angles*

C(1)–C(2)	1·36 (3) Å	C(9)—C(10)	1·49 (2) Å
C(1)–C(5)	1·45 (3)	C(9)—C(12)	1·51 (4)
C(1)–C(6)	1·51 (2)	C(10)–C(11)	1·54 (2)
C(2)–C(3)	1·41 (2)	C(11)–C(13)	1·50 (3)
C(2)–C(11)	1·47 (3)	C(12)–C(13)	1·32 (3)
C(3)–C(4)	1·39 (3)	C(21)–C(22)	1·43 (3)
C(4)–C(5)	1·44 (3)	C(21)–C(25)	1·30 (3)
C(6)–C(7)	1·50 (3)	C(22)–C(23)	1·43 (3)
C(6)–C(8)	1·55 (3)	C(23)–C(24)	1·48 (4)
C(6)–C(9)	1·56 (2)	C(24)–C(25)	1·38 (3)

C(2)–C(1)–C(5)	111 (2)°	C(6)—C(9)—C(10)	113 (2)°
C(2)–C(1)–C(6)	127 (2)	C(6)—C(9)—C(12)	108 (2)
C(5)–C(1)–C(6)	122 (2)	C(10)–C(9)—C(12)	98 (2)
C(1)–C(2)–C(3)	106 (2)	C(9)—C(10)–C(11)	102 (2)
C(1)–C(2)–C(11)	119 (2)	C(2)—C(11)–C(10)	109 (2)
C(3)–C(2)–C(11)	135 (2)	C(2)—C(11)–C(13)	105 (2)
C(2)–C(3)–C(4)	110 (2)	C(10)–C(11)–C(13)	99 (2)
C(3)–C(4)–C(5)	108 (2)	C(9)—C(12)–C(13)	112 (2)
C(1)–C(5)–C(4)	104 (2)	C(11)–C(13)–C(12)	108 (2)
C(1)–C(6)–C(7)	111 (2)	C(22)–C(21)–C(25)	108 (2)
C(1)–C(6)–C(8)	116 (2)	C(21)–C(22)–C(23)	108 (2)
C(1)–C(6)–C(9)	106 (1)	C(22)–C(23)–C(24)	104 (2)
C(7)–C(6)–C(8)	107 (2)	C(23)–C(24)–C(25)	106 (3)
C(7)–C(6)–C(9)	113 (2)	C(21)–C(25)–C(24)	113 (2)
C(8)–C(6)–C(9)	103 (2)		

Results and discussion

The crystal is constructed from isolated molecules of the form (II). The atoms of each of the cyclopentadienyl groups are coplanar [mean deviation from the least-squares] best plane 0·03 Å for C(1)–C(5), 0·04 Å for C(21)–C(25) and the rings are in the eclipsed conformation, inclined at an angle of 7°, with mean carbon-to-carbon bond lengths of 1·410(14) [C(1)–C(5)] and 1·405(19) [C(21)–C(25)]. The carbon atoms of the unsubstituted cyclopentadienyl ring are less well resolved: a difference Fourier synthesis indicates no alternative positions for the atoms of this ring but suggests that it is librating, and this uncertainty is also reflected in the temperature factors. The iron atom is 1·64(1) Å from the least-squares best planes through each of these rings which compares with 1·66 Å for ferrocene where the mean C–C bond length is 1·419 Å (Dunitz & Ibers, 1967).

Carbon atoms C(6) and C(11) are 0·19 and 0·06 Å respectively from the plane of the ring C(1)–C(5) and C(9), although not required to be near this plane, is only 0·21 Å from it. Carbon atom C(10) is 0·70 Å from the plane and, as predicted (Turbitt & Watts, 1971), on the same side as the iron atom while C(12) and C(13) are 1·45 and 1·41 Å from the plane on the opposite side. The bond length C(12)–C(13) is 1·32 Å and represents a double bond; the other carbon-to-carbon bonds in the substituent rings are single bonds (*International Tables for X-ray Crystallography*, 1968). The bridge formed by carbon atoms C(12) and C(13) between carbon atoms C(9) and C(11) is strained. Within the five-membered ring formed by the bridge, the nominal sp^3 angles formed at carbon atoms C(9), C(10) and C(11) are reduced to 98, 102 and 99°, and

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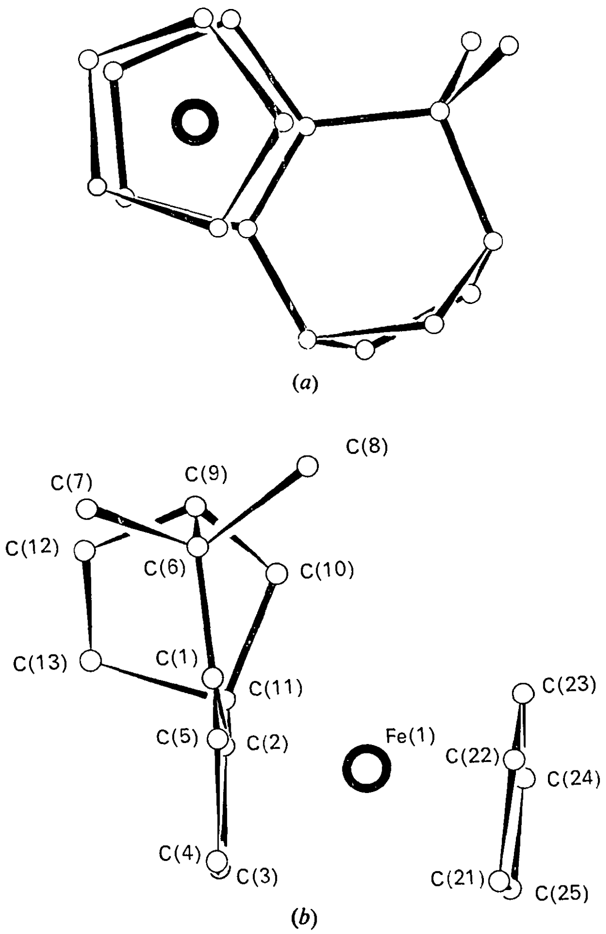
* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30340 (9pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.



(*a*)

(*b*)

Fig. 3. Projection of the molecule: perpendicular (*a*) and parallel (*b*) to the least-squares best plane through atoms C(1)–C(5). The equation of this plane is $7·892x+5·461y-3·098z=7·129$.

the sp^2 bond angles formed at carbon atoms C(12) and C(13) are reduced to 112 and 108° respectively. The torsional angle of the C(11)–C(13) and C(12)–C(9) bonds about the C(12)–C(13) bond is 0·1°. Clearly it is energetically more favourable to distort the angles in the ring rather than to reduce the π-orbital overlap by a twist in the C(12)–C(13) double bond. The five-membered ring is not planar: C(10) is 0·69 Å from the least-squares best plane through the other four atoms.

Hydrogen atom H(101) bonded to carbon atom C(10) is 3·19 Å from the iron atom. The hydrogen atoms bonded to carbon atom C(8) could not be located reliably from a difference Fourier synthesis calculated for the final structure, but their position must be somewhere between the two extremes of one hydrogen atom 3·0 Å from the iron atom or two hydrogen atoms an equal distance of 3·4 Å away. The steric repulsion between these hydrogen atoms and the iron atom is relieved by an inclination of 7° between the planes through the two cyclopentadienyl rings.

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