Crystal and Molecular Structure of α,α,γ-Trimethyl-γ-ferrocenyl-1,2-trimethyleneferrocene

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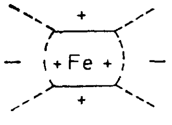
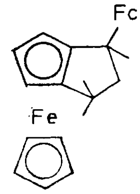
An X-ray crystallographic study has shown that in the title compound the second ferrocenyl group is *exo*- and is aligned as indicated in Figure 1 (a). It is confirmed that deformation of the molecular structure is necessary to accommodate the two *endo*-methyl groups. The unit cell of the crystals is orthorhombic with $a = 14{\cdot}719 \pm 0{\cdot}007$, $b = 24{\cdot}630 \pm 0{\cdot}112$, $c = 11{\cdot}354 \pm 0{\cdot}005$ Å, space group $Pbca$, $Z = 8$. The structure was solved by direct methods from diffractometer data, and refined to R 0·117 for the 4075 observed structure factors. Mean Fe–C is 2·045 Å.

Interest has been focused recently on the synthesis and stereochemistry of the ferrocenophanes.[1] In particular an n.m.r. study of [3](1,2)ferrocenophanes has examined the shielding and deshielding of the substituents in the trimethylene ring.[2] This work has substantiated the Mulay and Fox model [3] (1) which is based upon magnetic susceptibility measurements for shielding around the ferrocenyl nucleus. Only a few proton n.m.r. studies have been reported on ferrocenophanes which have been interpreted in support of this model.

Our own interest in this problem arose from the observation that 2-ferrocenylpropene gave a [3](1,2)-ferrocenophane (2) in addition to a [3](1,1′)ferrocenophane (3) when treated with 90% formic acid.[4] Indeed these two compounds have been isolated along with other products in the reaction of acetylferrocene with methylmagnesium iodide [5] and on dilution of concentrated sulphuric acid solutions of 2-ferrocenylpropene.[6] The structural proof for (2) relied heavily upon n.m.r.



(1)



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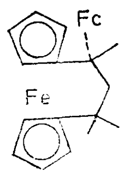

(3)

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evidence[4] and although there is little doubt that the structure is as shown, the actual assignments for the methyl and hydrogen atoms have been questioned.[2] In terms of the Mulay and Fox model the assignments given by us should probably be reversed.

However, the problem of assignment of nuclear magnetic resonances observed in the spectra of the ferrocenophanes is not a matter of black or white, particularly when the influence of the second ferrocenyl group is not known. Indeed the actual assignment of the second ferrocenyl group as *exo* was made on chemical intuition and the use of molecular models rather than by rigorous chemical proof. It is conceivable that the second ferrocenyl group could either enhance or diminish the shielding experienced by the *exo*-methyl and hydrogen. This of course will depend on which conformation is adopted by the ferrocenyl group in question. Two extremes are possible with the more likely *exo*-ferrocenyl arrangement, in Figure 1. In view of the foregoing considerations an *X*-ray crystallographic study was undertaken in an effort to clarify the situation.

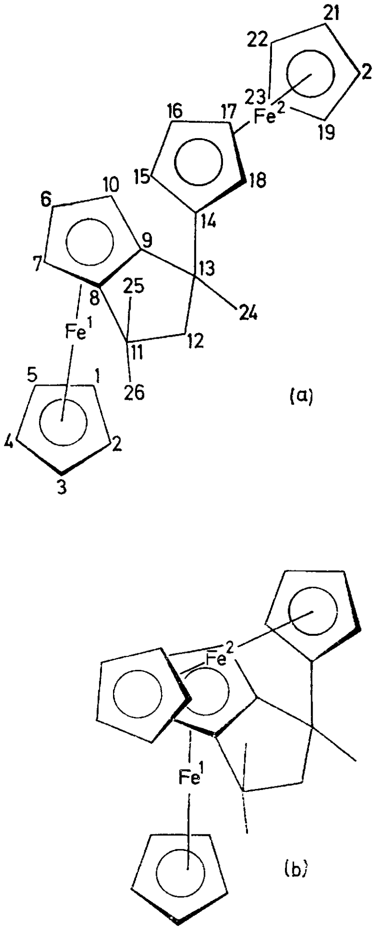

FIGURE 1 Two possible extremes of the *exo*-ferrocenyl arrangement

EXPERIMENTAL AND RESULTS

The title compound was obtained from the reaction of methylmagnesium iodide with acetyl ferrocene,[5] and was purified by column chromatography and crystallised from light petroleum (b.p. 40—60 °C). Spectroscopic data were identical to those previously reported.

Crystallographic Measurements.—Crystals (m.p. 186 °C) were clear orange pyramids which had parallelogram-shaped bases with the apex of the pyramid slightly offset from the midpoint of the base. Preliminary unit-cell dimensions were determined from oscillation, rotation, and Weissenberg photographs, and were confirmed from diffractometer settings for a number of reflexions.

Crystal Data.—$Fe_2C_{26}H_{28}$, $M = 452{\cdot}1$, $a = 14{\cdot}719 \pm 0{\cdot}007$, $b = 24{\cdot}630 \pm 0{\cdot}112$, $c = 11{\cdot}354 \pm 0{\cdot}005$ Å, $U = 4116$ Å^3, $D_m = 1{\cdot}448$, $Z = 8$, $D_c = 1{\cdot}459$, $F(000) = 1888$. Space group *Pbca*, No. 61, from systematic absences: $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd. Cu-K_α radiation, $\lambda = 1{\cdot}5918$ Å; μ(Cu-K_α) = 115·8 cm^{-1}. The intensities of 4075 independent reflexions, measured on a Wooster four-circle diffractometer (Cu-K_α, Ni filter), were corrected for Lorentz and polarisation effects and converted to structure factors in the usual way. Absorption corrections were neglected. A scale factor and an overall temperature factor were then obtained from a Wilson plot and the F_o values converted to E values (normalized structure factors). Comparison of the intensity statistics with theoretical values did not give a clear indication of whether the structure was centrosymmetric or non-centrosymmetric possibly due to the presence of the iron atoms.

Structure Analysis.—The structure was determined by a direct method using computer programs supplied by Dr. P. Main, University of York.

392 E Values $> 1{\cdot}60$ were used to set up a maximum of 2000 phase relationships. The reflexions chosen to define the origin were: 2,2,1, 4,7,12, and 1,11,6. These were assigned phases of 0°. Eight phases determined by the Σ_1 formula were, along with three other reflexions which were assigned values of 0, 180°, as follows:

h k l	Phase	*h k l*	Phase	*h k l*	Phase
0,0,2	180	0,10,0	0	2,10,12	(0, 180)
2,0,8	180	2,0,10	0	9,15,5	(0, 180)
0,4,0	180	0,16,2	0	6,5,13	(0, 180)
0,10,2	180	2,0,12	180		

The eight sets of phases were assessed for reliability and the figures of merit output with each set. For the set with the highest figures of merit an E map was computed, and this revealed part of the structure. The positions of seven atoms, two iron atoms and five carbon atoms of one cyclopentadienyl ring, were located. A structure-factor calculation, with seven out of twenty-eight atoms, had R 0·34. The other remaining atoms were located on a F_o Fourier map. With the co-ordinates of all twenty-eight peaks included in a structure-factor calculation R was 0·20.

Refinement.—Initially, refinement was by block-diagonal least-squares analysis with isotopic temperature factors. During five cycles of refinement R fell from 0·209 to 0·145. At this point the positions of nineteen hydrogen atoms (not belonging to methyl groups) were calculated and included in further cycles of refinement with a temperature factor (B) of 4·5. The hydrogen atom parameters were not refined. The scattering factor curve for iron was corrected for anomalous scattering using the relation: $f = [(f_o + \Delta f')^2 + (\Delta f'')^2]$ as defined in ref. 12. A further six cycles of refinement were computed with anisotropic temperature factors for the iron atoms, isotropic temperature factors for carbon and hydrogen atoms, and with the weighting scheme: $w = 1/\{1 + [(F_o - F^*)/G^*]^2\}$, where F^* and G^* were each 35.

The final R was 0·117. As the data had been collected from only one crystal and the problem was one of stereochemistry rather than the determination of accurate atomic parameters further refinement was not justified. Observed and calculated structure factors are given in Supplementary Publication No. SUP 20887 (7 pp., 1 microfiche).‡ Only those reflexions included in the refinement are given.

TABLE 1

(*a*) Atomic parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
C(1)	0·3333(33)	0·1491(17)	0·1242(41)	7·00(20)
C(2)	0·2475(27)	0·1340(15)	0·0920(32)	5·21(17)
C(3)	0·2436(23)	0·0769(13)	0·0802(27)	4·19(16
C(4)	0·3299(28)	0·0563(15)	0·1078(34)	5·73(18)
C(5)	0·3827(28)	0·1003(16)	0·1338(37)	6·37(19)
C(6)	0·1694(18)	0·0869(10)	0·3571(22)	2·98(14)
C(7)	0·2284(19)	0·0408(11)	0·3608(24)	3·42(15)
C(8)	0·3132(16)	0·0578(9)	0·4044(20)	2·28(14)
C(9)	0·3091(15)	0·1167(9)	0·4196(20)	2·15(14)
C(10)	0·2201(16)	0·1343(9)	0·3915(20)	2·24(13)
C(11)	0·2037(17)	0·1923(10)	0·4194(23)	2·97(14)
C(12)	0·3031(19)	0·2128(12)	0·4416(25)	3·63(15)
C(13)	0·3647(17)	0·1614(10)	0·4737(22)	2·83(15)
C(14)	0·3704(17)	0·1548(10)	0·6087(22)	2·76(15)
C(15)	0·3106(17)	0·1209(11)	0·6777(23)	2·94(15)
C(16)	0·3321(24)	0·1331(13)	0·7990(29)	4·59(15)
C(17)	0·4005(22)	0·1711(13)	0·8015(29)	4·34(16)
C(18)	0·4253(18)	0·1852(11)	0·6866(23)	3·27(15)
C(19)	0·5205(22)	0·0517(12)	0·6151(28)	4·12(16)
C(20)	0·4626(23)	0·0248(13)	0·6914(30)	4·87(18)
C(21)	0·4825(23)	0·0361(13)	0·8084(28)	4·40(17)
C(22)	0·5533(21)	0·0748(12)	0·8069(26)	3·87(16)
C(23)	0·5876(21)	0·0836(12)	0·6857(26)	3·80(16)
C(24)	0·4590(22)	0·1677(13)	0·4174(28)	4·32(16)
C(25)	0·1598(22)	0·2244(12)	0·3191(27)	4·08(16)
C(26)	0·1464(20)	0·1989(12)	0·5301(26)	3·67(15)
H(17) *	0·429	0·189	0·878	
H(16)	0·299	0·116	0·872	
H(15)	0·262	0·092	0·648	
H(18)	0·476	0·214	0·663	
H(22)	0·583	0·092	0·881	
H(21)	0·448	0·019	0·882	
H(20)	0·409	−0·003	0·668	
H(19)	0·519	0·049	0·519	
H(23)	0·632	0·108	0·657	
H(1)	0·354	0·190	0·135	
H(2)	0·192	0·159	0·074	
H(3)	0·185	0·053	0·050	
H(4)	0·350	0·012	0·103	
H(5)	0·452	0·095	0·159	
H(8)	0·370	0·032	0·424	
H(7)	0·209	−0·001	0·336	
H(6)	0·099	0·086	0·331	
H(12)	0·304	0·241	0·514	
H(12′)	0·328	0·232	0·365	
Fe(1)	0·2788(3)	0·0969(2)	0·2483(3)	
Fe(2)	0·4448(3)	0·1044(2)	0·7147(3)	

* A fixed isotropic temperature parameter (B) of 4·5 was used for the hydrogen atoms.

(*b*) Anistropic temperature factors† × 10^5) for the iron atoms, with estimated standard deviations in parentheses

Atom	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Fe(1)	385(16)	34(18)	−13(40)	110(5)	18(23)	392(21)
Fe(2)	299(14)	47(17)	−57(35)	106(6)	−135(21)	540(24)

† In the form: $T = \exp[-(h^2b_{11} + k^2b_{12} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$.

Co-ordinates and Molecular Dimensions.—Final positional and thermal parameters, together with their estimated standard deviations, are in Table 1. Fe–C bond lengths are in Table 2; C–C bond lengths and bond angles are in Figure 2. The standard deviations of bond lengths are 0·023—0·045 Å for Fe(1)–C, 0·025—0·034 Å for Fe(2)–C, and 0·023—0·060 Å for C–C bonds.

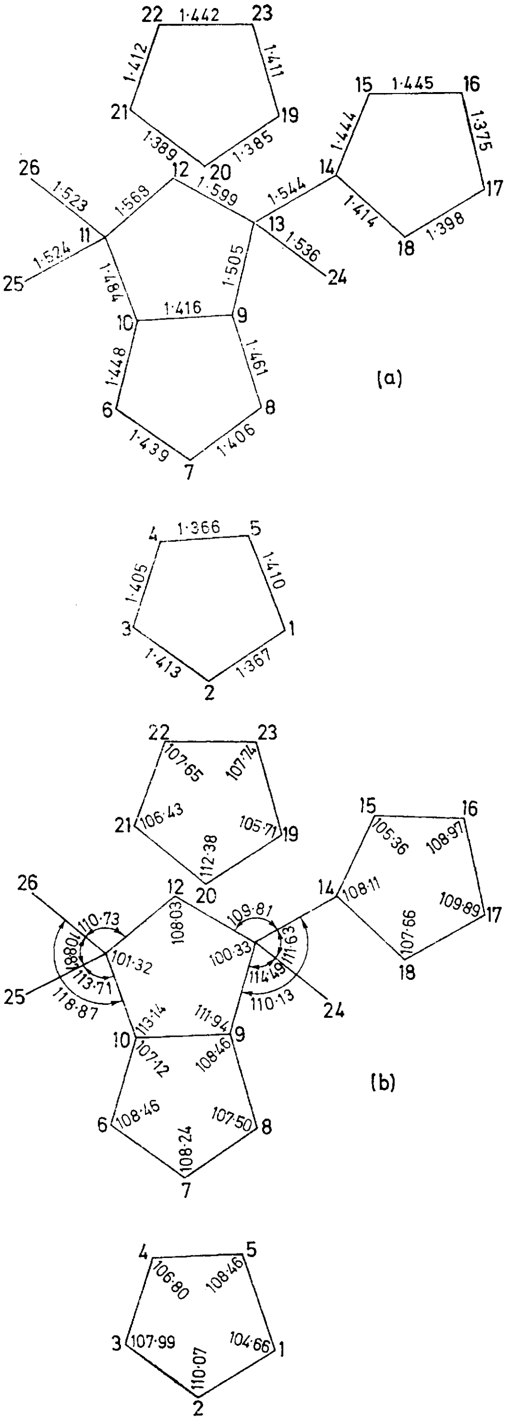

FIGURE 2 (a) Bond lengths (Å) and (b) angles (deg.)

The mean planes of the cyclopentadienyl rings, the saturated ring and of the fused cyclopentadienyl, and saturated ring system are given in Table 3, with reference to the numbering scheme shown in Figures 1 and 3.

Within each ferrocene group the cyclopentadienyl rings

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‡ See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

are planar and almost parallel with a separation of 3·30 Å. The mean Fe–C distance in the molecule is 2·045 Å and the mean C–C distance in the cyclopentadienyl rings is 1·412 Å. In the saturated ring the mean C–C distance is 1·514 Å, with exocyclic C–C bonds 1·531 Å. If the ferrocene groups are viewed along the normals to the planes of the rings then in group one the rings are almost fully staggered, the mean rotation from the fully eclipsed position being 34°, and in group two the rings are nearly eclipsed: the mean rotation from the fully eclipsed position is 8° (Figures 3). Two views of the complete molecule are shown in Figure 4.

TABLE 2

Individual Fe–C bond lengths (Å)

Fe(1)–C(8)	2·080(23)	Fe(2)–C(17)	2·025(31)
Fe(1)–C(9)	2·054(23)	Fe(2)–C(16)	2·042(34)
Fe(1)–C(6)	2·056(26)	Fe(2)–C(22)	2·044(30)
Fe(1)–C(10)	2·059(23)	Fe(2)–C(15)	2·062(26)
Fe(1)–C(7)	2·022(27)	Fe(2)–C(21)	2·066(32)
Fe(1)–C(3)	3·039(31)	Fe(2)–C(14)	2·048(25)
Fe(1)–C(1)	2·071(45)	Fe(2)–C(19)	2·050(32)
Fe(1)–C(2)	2·049(36)	Fe(2)–C(18)	2·037(27)
Fe(1)–C(4)	2·028(39)	Fe(2)–C(23)	2·062(31)
Fe(1)–C(5)	2·010(41)	Fe(2)–C(20)	1·996(33)

Mean Fe–C 2·045

TABLE 3

Mean planes of several groups of atoms

Plane	Atoms	Equation *
(1):	(6)—(13)	$-0{\cdot}2933X - 0{\cdot}1592Y + 0{\cdot}9427Z = 2{\cdot}7416$
(2):	(6)—(10)	$-0{\cdot}2863X - 0{\cdot}1493Y + 0{\cdot}9464Z = 2{\cdot}7891$
(3):	(6), (8)—(10)	$-0{\cdot}2811X - 0{\cdot}1304Y + 0{\cdot}9508Z = 2{\cdot}8802$
(4):	(9)—(11), (13)	$-0{\cdot}3189X - 0{\cdot}2630Y + 0{\cdot}9105Z = 2{\cdot}1376$
(5):	(1)—(5)	$0{\cdot}2621X + 0{\cdot}0754Y - 0{\cdot}9621Z = 0{\cdot}2021$
(6):	(19)—(23)	$0{\cdot}6548X - 0{\cdot}7547Y + 0{\cdot}0424Z = 4{\cdot}3455$
(8):	(14)—(18)	$0{\cdot}6838X - 0{\cdot}7297Y - 0{\cdot}0040Z = 0{\cdot}9190$

* X, Y, Z are the unit-cell axes.

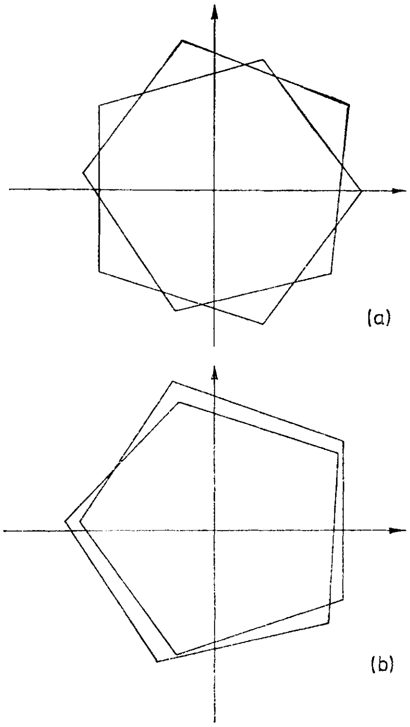

FIGURE 3 View of each ferrocene group along the normal to the planes of the five-membered rings

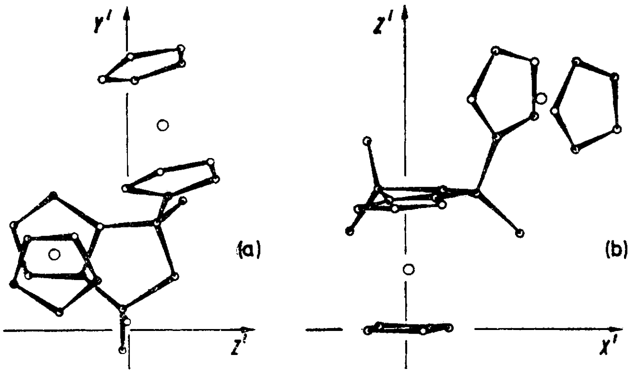

FIGURE 4 (a) A general view of the molecules [Z' is perpendicular to the mean plane of atoms (11), (24), (25)]. (b) A view of the molecule from the mean plane of atoms (1)—(5) (Z' is perpendicular to this plane)

DISCUSSION

The results obtained clearly show, that at least in the crystal, the second ferrocenyl group is *exo*- and is aligned as in Figure 1(a) (see also Figure 4). If this arrangement also obtains in solution then it is likely that the second ferrocenyl group will enhance the shielding of the groups on the *exo*-face of the trimethylene ring. Consequently a reassignment of the resonances (see Figure 5) already reported[4] is required.

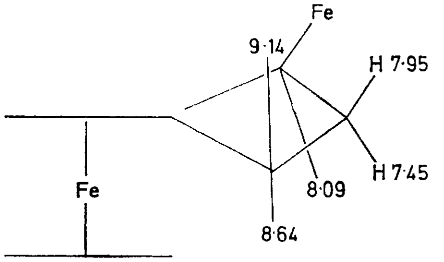

FIGURE 5 A reassignment of the n.m.r. resonances (τ values)

Several other features are worthy of attention. Molecular models show that even although the second ferrocenyl group is in the *exo*-position deformations of the structure are necessary to accommodate the two *endo*-methyl groups. This is confirmed by the X-ray analysis. First some relief is obtained by non-parallel rings in the first ferrocenyl unit. This angle of tilt (6·4°) moves the hydrogens on the unsubstituted cyclopentadienyl ring away from the hydrogens on the *endo*-methyl groups. The angle of tilt is fairly large and is to be compared with that in 2-biphenylferrocene (8°).[7] Larger angles of tilt have been measured for ferrocenyl systems where the rings are linked by carbon chains: in α-keto-1,1′-trimethyleneferrocene[8] it is 8·8° and in α,α,β,β-tetramethyl-1,1′-dimethyleneferrocene[9] 23·2°, the largest

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[7] J. Trotter and C. S. Williston, *J. Chem. Soc.* (*A*), 1967, 1379.

[8] N. D. Jones, R. E. Marsh, and J. H. Richards, *Acta Cryst.*, 1965, **19**, 330.

[9] M. B. Laing and K. N. Trueblood, *Acta Cryst.*, 1965, **19**, 373.

recorded. In the latter molecule the exocyclic C–C bonds are displaced by 11° below the plane of the cyclopentadienyl rings. A displacement of the exocyclic C–C bonds is also found in the ferrocenophane (2) but the dihedral angle of 8·4° is in the *exo*-direction further relieving the methyl-hydrogen interaction. The final deformation of the structure results in the relief of unfavourable *trans*-annular 1,3-methyl interactions. This is achieved by the displacement of 0·37 Å of the methylene group at C(12) below the plane of the remainder of the trimethylene ring [C(9)—(11),C(13)]. The puckering of the trimethylene ring in the relief of unfavourable eclipsing interactions between the substituents on the trimethylene ring of [3](1,2)ferrocenophanes had already been suggested.[2]

Finally in the molecule (2) the angular rotation of the cyclopentadienyl rings in the two ferrocenyl units is different. In the first ferrocenyl unit the angle is 34° and is thus almost in the completely staggered position. Ferrocene itself has an angle of rotation of 36°.[10] In the second ferrocenyl unit the angle is only 8°. The angle of rotation has been shown to vary from structure to structure and it has been suggested [11] that the conformation adopted by a particular ferrocene molecule is a balance between the intramolecular repulsions and the crystal packing forces.

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[3/1672 *Received, 7th August,* 1973]

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[10] J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Cryst.*, 1956, **9**, 373; E. O. Fischer and W. Pfab, *Z. Naturforsch.*, 1952, **7b**, 377; P. F. Eiland and R. Pepinsky, *J. Amer. Chem. Soc.*, 1952, 74, 4971; J. D. Dunitz and L. E. Orgel, *Nature*, 1953, **171**, 121.

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[12] International Tables for *X*-Ray Crystallography, Vol. III, Kynoch Press, 1962, 213.