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The Crystal and Molecular Structure of Diindenyl Iron

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The structure of diindenyl iron has been determined from projections down two crystal axes, and the 'sandwich' nature of the molecule is well illustrated in these projections. The aromatic rings are probably rotating freely in solution and in the vapour state, but fixed in the crystal, and the present analysis shows that the molecular configuration is not *trans*, as originally postulated, but *gauche*. Disorder in the crystal reduces the accuracy with which the molecular dimensions have been determined.

1. Introduction

Diindenyl cobalt, $Co(C_9H_7)_2$, the first member of a new type of complex of indene with the transition metals, analogous to but rather less stable than the cyclopentadienyl derivatives, was obtained by Fischer, Seus & Jira (1953). Diindenyl iron, $Fe(C_9H_7)_2$, was prepared by Fischer & Seus (1953) and by Pauson & Wilkinson (1954), and powder photographs indicated that the iron and cobalt compounds have similar structures.

The properties of the molecules indicate that they have structures similar to the *cyclo*pentadienyl complexes, with the central metal atom situated between the five-membered rings, which are parallel. A three-dimensional X-ray investigation of ferrocene (Dunitz, Orgel & Rich, 1956) shows that in the solid state the five-membered rings are fixed in the staggered configuration, but in the vapour phase and in solution the rings are rotating freely (Pauson, 1955). It is probable that the aromatic rings in the indenyl analogues are also rotating in solution, but that the molecules have a fixed configuration in the solid, and it was postulated that the six-membered rings are probably in the *trans* configuration.

The present investigation, which was undertaken to obtain an accurate account of the geometry and dimensions of the diindenyl iron and diindenyl cobalt molecules, using X-ray diffraction methods, has been confined to the iron analogue, which is more stable in air than the cobalt compound.

2. Experimental

Crystals of diindenyl iron are deep-purple in colour, reasonably stable in air, and consist of thin plates elongated along the b axis with {001} developed. The density was determined by flotation in potassium iodide solution.

The data required for the X-ray investigation were collected using Co $K\alpha$ radiation ($\lambda = 1{\cdot}790$ Å), and the unit-cell dimensions were obtained by use of single-crystal rotation, oscillation and moving-film photographs about the a, b, c and $[10\bar{1}]$ axes.

Crystal data.—Diindenyl iron, $C_{18}H_{14}Fe$; $M = 286{\cdot}1$; m. 184–185° C. (in an evacuated tube). Monoclinic $a = 11{\cdot}32 \pm 0{\cdot}03$, $b = 7{\cdot}85 \pm 0{\cdot}02$, $c = 8{\cdot}09 \pm 0{\cdot}02$ Å, $\beta = 115{\cdot}3° \pm 0{\cdot}5°$. Volume of the unit cell = 650·0 Å^3. Density, calculated (assuming two molecules per unit cell) = 1·462 g.cm.$^{-3}$, found 1·457 g.cm.$^{-3}$. Absorption coefficients for X-rays: $\lambda = 1{\cdot}790$ Å, $\mu = 26{\cdot}4$ cm.$^{-1}$. Total number of electrons per unit cell = 296. Absent spectra: $(h0l)$ when h is odd; possibly $(0k0)$ when k is odd. Space group is either C_s^2–Pa, C_{2h}^4–$P2/a$, or C_{2h}^5–$P2_1/a$.

The intensities were measured on moving-film exposures of the equatorial layers for crystals rotating about the b and c axes, the multiple-film technique (Robertson, 1943) being used to correlate strong and weak reflexions. The range of intensities measured was about 1600 to 1, the estimates being made visually. The cross-sections of the crystals, normal to the rotation axes, were $0{\cdot}20 \times 0{\cdot}06$ mm. and $0{\cdot}40 \times 0{\cdot}20$ mm. for the $(h0l)$ and $(hk0)$ zones respectively, and approximate absorption corrections were applied by considering the path length in the crystals of rays reflected from their centres (Albrecht, 1939). The values of the structure factors were derived by the usual formulae for a mosaic crystal, and are listed in Table 3. The absolute scale was derived by correlation with the F values calculated from the final coordinates.

3. Structure analysis

Space group

Of the $(h0l)$ reflexions with h even, 56 independent reflexions were observed of a possible 81 observable with Co $K\alpha$ radiation, and no reflexions with h odd were recorded, so that the presence of a glide plane a is established. Only (040) of the $(0k0)$ reflexions was observed with cobalt radiation (a weak (020) spot was recorded when Cu $K\alpha$ was used) and no reflexions

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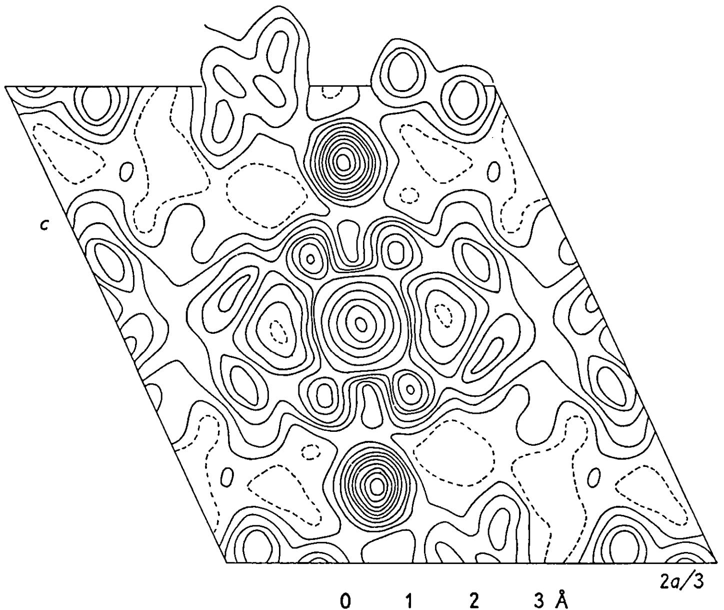


Fig. 1. Electron-density projection on (010); all phase angles zero. Contours at intervals of 1 e.Å^{-2}, one-electron line broken, except on the iron atom, where contours are 6, 10, 15, 20, ... e.Å^{-2}.

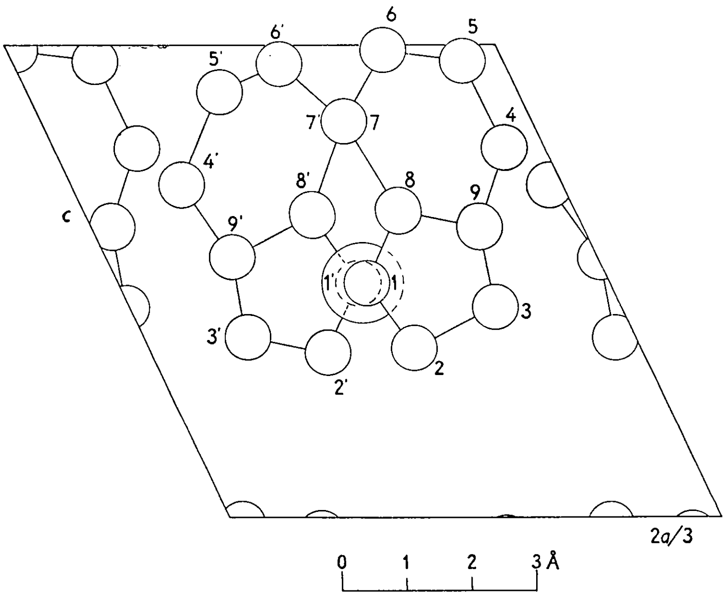


Fig. 2. First trial structure; space group *Pa*.

with *k* odd. These absences indicate the presence of a screw axis 2_1, but the evidence is rather doubtful since the number of (0*k*0) planes observed is small.

The $N(z)$ test for centrosymmetry was applied to the (*h*0*l*) and (*hk*0) zone intensities, and in each case the intensity distribution corresponded to a centrosymmetric projection.

Both these lines suggested that the space group is $P2_1/a$, and structure analysis proceeded on this basis. However, the screw axis is not definitely established and the $N(z)$ test might not be reliable in the presence of the heavy iron atom, so that it was borne in mind that the space group might still be *Pa* or *P*2/*a*.

The (010) *projection*

The space group $P2_1/a$ requires four asymmetric units per unit cell, and since the unit cell contains only two molecules, each molecule has a centre of symmetry at the iron atom, and the two iron atoms in the unit cell are at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0). The molecular centre of symmetry defines the configuration of the molecule; the six-membered rings must be *trans*, as postulated.

The iron atoms contribute $2f_{\text{Fe}}$ or 0 towards the structure factors according as $(h+k)$ is even or odd, and, using the heavy-atom method, preliminary analysis was carried out in a direct manner. The function $\varrho(x, z)$ was computed using positive signs (zero phase angle) for all $F(h0l)$; this function is shown in Fig. 1. The iron atom and the carbon atoms of the five-membered ring are clearly resolved, but the positions of the six-membered rings are less certain. If the iron atom and five-membered rings are fixed, positions have to be chosen for eight more carbon atoms; there are, however, fourteen available peaks, two of these being much heavier than the rest and probably corresponding to two overlapping carbon atoms. There are then sixteen available sites (two sets of eight, related by a centre of symmetry at the iron atom) and only eight atoms. Some of these sixteen peaks are very low, with peak height 2–4 e.Å^{-2} compared with 6–8 e.Å^{-2} for the atoms of the five-membered rings.

It seems likely then that this electron-density map contains a false centre of symmetry. The origin of the projection has been chosen at one of the iron atoms, so that the phase angles of the contributions of the iron atoms to the structure factors are zero. Since these phase angles have been used to compute the electron density, they must inevitably give a centrosymmetrical structure, and, if the true structure is not centrosymmetrical, the electron-density map represents a superposition of two structures—the correct one, and another related to it by centres of symmetry at the iron atoms, and midway between the iron atoms. So that of each pair of centrosymmetrically related peaks only one is correct, and when only one peak of each pair was chosen, the structure shown in Fig. 2 was obtained. The space group is now *Pa*, and the molecular configuration is not *trans*, but *gauche*.

Structure factors were calculated from these iron and carbon positions. In the calculation, the scattering factor used for iron was that given in the *International Tables*, corrected for the anomalous dispersion of the Co $K\alpha$ radiation, and for thermal vibration, taking $B = 3{\cdot}5$ Å^2. McWeeny's scattering curve was used for the carbon atoms, with $B = 4{\cdot}4$ Å^2. In general the agreement between measured and calculated values was quite good, with $R = 29\%$ over all the $(h0l)$ planes. There were, however, a few exceedingly poor agreements (especially 201, $20\bar{2}$, 600, $60\bar{3}$) and some of these were planes of small sin θ, so that this structure did not seem to be the correct one, although it might be close to the true structure.

In Fig. 1 the height of the peak where atoms 7 and 7′ overlap is $11\frac{1}{2}$ e.Å^{-2}, so that there is associated with atoms 7 and 7′, and the false atoms related to these by a centre of symmetry at the iron, a total peak height of 23 e.Å^{-2}, which is much too great for only two carbon atoms. There is also a deficiency of density at atoms 4 and 4′, with peak heights just over 2 e.Å^{-2}. The agreement between measured and calculated structure factors would be improved if a structure which explained these excesses and deficiencies of electron density could be chosen.

However, no perfectly-ordered structure would resolve these difficulties. The agreement could be improved and peak height anomalies removed only if some of the scattering matter of the present structure was transferred from the origin to the positions of atoms 7 and 7′. Since chemical evidence definitely suggests that the iron atom is sandwiched between the five-membered rings, the structure which resulted from this transfer is that shown in Fig. 3. It is the structure of Fig. 2, plus another related to it by a centre of symmetry midway between the origin and the position of atoms 7, 7′. This centre of symmetry need be only approximate, but structure factors were calculated assuming that it was an exact centre, and also assuming that the two differently-oriented molecules occurred in equal proportions. The space group is again $P2_1/a$, and the origin was taken at the centre of symmetry. The discrepancy immediately dropped to 12·4%, and all gross anomalies were removed, so that this structure is almost certainly the correct one.

All the photographic records were carefully reexamined for evidence of weak intermediate layer lines which would indicate an ordered arrangement of the two different orientations, or of diffuse spots indicating partial ordering, but these were not present. The two orientations must therefore occur at random throughout the crystal.

A difference synthesis was computed, and some of the atoms shifted by small amounts. The final value

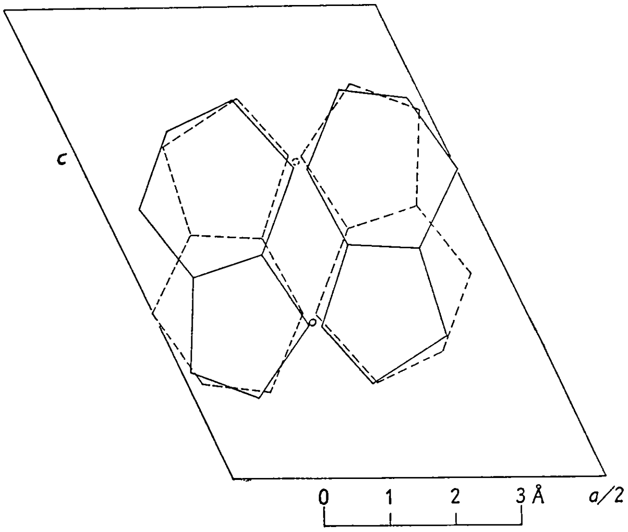


Fig. 3. Second trial structure; space group $P2_1/a$.

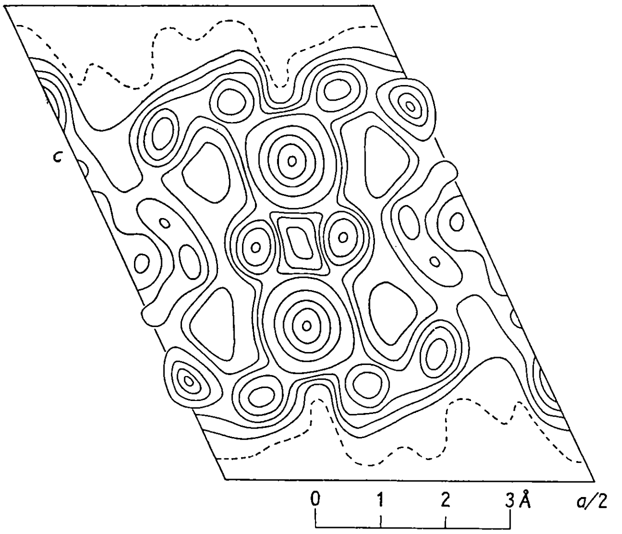


Fig. 4. Final electron-density projection on (010). Contours at intervals of 1 e.Å^{-2}, with the one-electron contour broken, except on the iron atoms where the contours are at intervals of 5 e.Å^{-2}.

of R was 11·6%; 1·3% of this is due to (001) and (20$\bar{1}$), which may be affected by extinction. Measured and calculated structure factors are listed in Table 3. The final Fourier synthesis, computed with measured F_o values and calculated signs, is shown in Fig. 4.

The (001) *projection*

In computing the initial electron-density projection down the c axis, all terms with $(h+k)$ even were included with + sign; of those with $(h+k)$ odd only $F(120)$ and $F(210)$ are of considerable magnitude, and since $F(110)$ is large and necessarily positive, it follows from the sign relation (Cochran, 1952)

$$s(h) = s(h').s(h+h')$$

that these two terms have the same sign, which may be taken as either positive or negative.

Examination of the Fourier map indicated that the y coordinate of the iron atom is close to zero. The indenyl radicals are almost normal to the projection plane and none of the individual carbon atoms is resolved. Owing to the extreme overlap, the y coordinates of the carbon atoms could not be determined accurately; they were adjusted by trial on the Fourier map until satisfactory agreement between measured and calculated ($hk0$) structure factors was obtained. The final value of R was 19·2%; 8·6% of this, however, is due to (001), (110), (120) and (210), which may be affected by extinction.

Measured and calculated structure factors are listed in Table 3. The final Fourier series was computed using the signs of the final calculated structure factors (Fig. 5). The 'sandwich' nature of the molecule is well illustrated.

Coordinates and molecular dimensions

The final coordinates of the atoms in the asymmetric unit are listed in Table 1.

The indenyl radicles are approximately planar, the equations of the mean planes being:

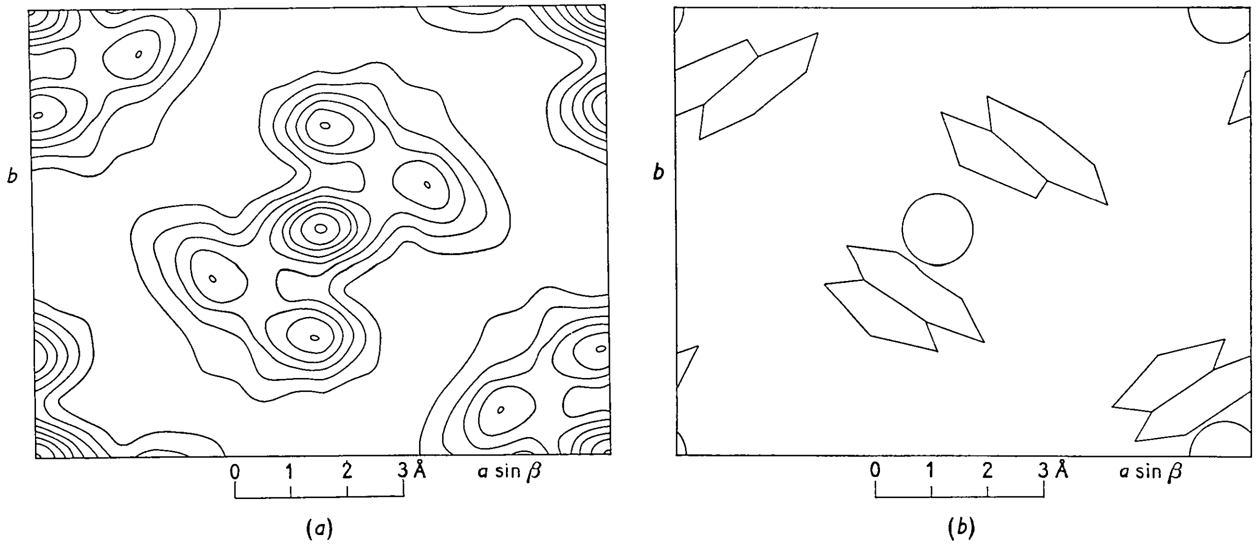
$$0{\cdot}558x'+0{\cdot}773y'-0{\cdot}302z'-1{\cdot}768 = 0$$

and

$$0{\cdot}519x'+0{\cdot}802y'-0{\cdot}295z'+1{\cdot}659 = 0\ ,$$

where x', y', z' are expressed in Ångström units, and are referred to orthogonal axes a', b and c, where a' is perpendicular to b and c.

The root-mean-square deviation of the carbon atoms from these planes is 0·06 Å. The angle between the



(a) (b)

Fig. 5. (a) Final electron-density projection on (001). Contour interval 2 e.Å^{-2}. (b) Projection on to (001) of molecules in one orientation; those in the second orientation are related to these by centres of symmetry at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0).

Table 1. *Coordinates of the atoms in the asymmetric unit*

Atom	x/a	y/b	z/c
Fe	−0·0401	0	−0·1713
C 1	−0·0311	+0·2650	−0·1817
2	−0·0021	+0·1465	−0·3038
3	+0·1307	+0·0698	−0·2030
4	+0·2484	+0·0527	+0·1518
5	+0·2290	+0·1432	+0·3021
6	+0·1456	+0·2400	+0·3229
7	+0·0512	+0·2999	+0·1540
8	+0·0562	+0·2214	−0·0067
9	+0·1512	+0·1096	−0·0190
1′	−0·0512	−0·2650	−0·1817
2′	−0·1627	−0·2273	−0·3350
3′	−0·2410	−0·1103	−0·2692
4′	−0·1945	−0·0288	+0·0737
5′	−0·1092	−0·0497	+0·2418
6′	−0·0064	−0·1491	+0·2999
7′	+0·0311	−0·2459	+0·1540
8′	−0·0670	−0·1949	−0·0299
9′	−0·1767	−0·0996	−0·0796

plane normals is 3°, so that the indenyl radicles are parallel within the limits of experimental error, and the perpendicular distance between them is about 3·43 Å.

The bond lengths and valency angles in the molecule were calculated from the coordinates of Table 1. The molecule has a twofold symmetry axis passing through the iron atom, and parallel to and midway between the planes of the indenyl rings. In addition, since it is not expected that the accuracy is very good (this point will be discussed later) it was assumed that the symmetry of the indenyl radicals is *mm*, and the bond lengths and valency angles were averaged.

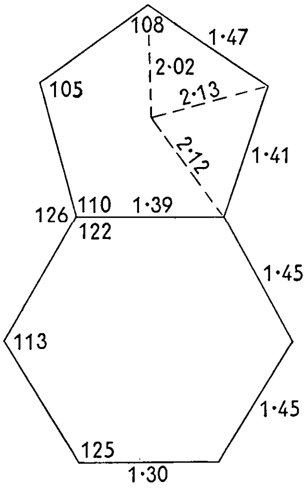


Fig. 6. Mean bond lengths and valency angles in diindenyl iron.

The mean lengths and angles are shown in Fig. 6, to 0·01 Å in bond length and 1° in valency angle.

A view of the molecule along the normal to the planes of the aromatic rings is shown in Fig. 7. and this illustrates the *gauche* configuration of the molecule. All the intermolecular contacts correspond to normal van der Waals interactions, and there appears to be no strain in building the two different orientations into the crystal.

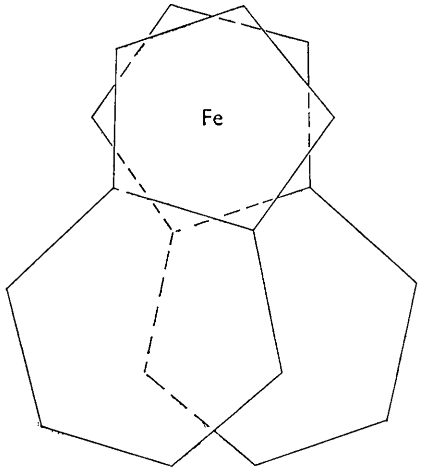


Fig. 7. View of the molecule along the normal to the planes of the aromatic rings.

4. Discussion

Since there is only a small number of observed ($0k0$) reflexions, the true space group of the crystal was rather doubtful, and during the course of the analysis, different space groups were used (Table 2). Even in the final stage, the centre of symmetry need not be exact, and the true space group might be Pa, although it would approximate very closely to $P2_1/a$.

Table 2. *Course of the analysis*

Stage	Space group used	Molecular configuration
1	$P2_1/a$	*trans*
2	Pa	*gauche*
3	$P2_1/a$	*gauche*

There is no doubt however that the molecular configuration is not *trans*, as originally postulated, but *gauche* (Fig. 7). The perpendicular distance between the planes of the rings is 3·43 Å, and the *gauche* configuration is possibly stabilized, with respect to the *trans*, by weak van der Waals forces between the atoms of the two six-membered rings.

It seems unusual that the two differently-oriented molecules should occur randomly in the crystal, but the molecule is non-polar, and the lattice energy is determined by the van der Waals forces between the carbon and hydrogen atoms of neighbouring molecules. Fig. 3 shows that the positions of the carbon and hydrogen atoms in the two orientations are not very different. The iron atoms, which have very different positions in the two orientations, are situated in the interiors of the molecules, and have little influence on the intermolecular forces.

Table 3. *Measured and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
000	—	289	$40\bar{7}$	17	+22	604	8	+10	$12\ 0\bar{4}$	< 4	− 1
001	72	+81	$\bar{6}$	16	+17	5	< 4	+ 3	$\bar{3}$	11	+13
2	58	−58	$\bar{5}$	16	−18	$80\bar{8}$	< 4	+ 3	$\bar{2}$	< 4	+ 5
3	13	−13	$\bar{4}$	49	−42	$\bar{7}$	7	+11	$\bar{1}$	< 3	− 6
4	< 5	− 2	$\bar{3}$	16	−14	$\bar{6}$	< 6	− 2			
5	6	+ 8	$\bar{2}$	26	+25	$\bar{5}$	20	−19	020	< 6	− 5
6	17	+22	$\bar{1}$	38	+35	$\bar{4}$	9	− 9	4	30	+29
7	5	+ 7	0	33	+31	$\bar{3}$	6	+ 8	110	58	+80
8	5	− 7	1	17	−15	$\bar{2}$	< 6	+ 3	2	44	−52
$20\bar{8}$	< 4	− 2	2	50	−47	$\bar{1}$	< 6	+ 6	3	11	+14
$\bar{7}$	11	+15	3	14	−14	0	< 6	− 3	4	10	−12
$\bar{6}$	15	+18	4	10	+11	1	20	−22	5	12	+13
$\bar{5}$	< 6	+ 1	5	6	+ 5	2	16	−16	210	48	−55
$\bar{4}$	11	− 8	6	< 4	+ 2	3	< 5	+ 3	2	24	−19
$\bar{3}$	31	−28	$60\bar{8}$	< 5	+ 3	$10\ 0\bar{8}$	4	+ 6	3	8	− 6
$\bar{2}$	13	−14	$\bar{7}$	< 6	+ 8	$\bar{7}$	< 5	− 1	4	28	+29
$\bar{1}$	56	+62	$\bar{6}$	7	+ 7	$\bar{6}$	17	−17	310	5	− 1
0	49	+50	$\bar{5}$	21	−21	$\bar{5}$	18	−16	2	< 6	+ 7
1	5	− 6	$\bar{4}$	39	−36	$\bar{4}$	< 6	− 3	3	13	+11
2	31	−25	$\bar{3}$	< 5	0	$\bar{3}$	< 6	+ 7	4	7	+ 2
3	34	−30	$\bar{2}$	36	+32	$\bar{2}$	< 6	+ 8	5	14	+12
4	< 6	− 1	$\bar{1}$	38	+34	$\bar{1}$	< 6	− 3	410	< 6	+ 3
5	23	+25	0	6	+ 7	0	13	−12	2	< 6	+ 4
6	10	+15	1	32	−30	1	11	− 9	3	15	+10
7	< 4	− 2	2	17	−19	$12\ 0\bar{6}$	4	− 4	4	15	+ 4
$40\bar{8}$	< 5	+ 4	3	7	+ 9	$\bar{5}$	10	− 9	510	14	+15

The accuracy with which the molecular dimensions have been determined is probably not very good for the following reasons:

(i) The presence of the iron atoms reduces the accuracy of determination of the carbon positional parameters.

(ii) Owing to the disorder, each atomic position represents only one-half of an atom, and the accuracy with which it has been determined is reduced. In addition overlap of atomic peaks (which would occur even in three dimensions) causes further difficulty.

(iii) The centre of symmetry in the space group may be only approximate.

(iv) The two orientations may not occur in equal proportions, although this seems unlikely as excess of one would probably give weak superlattice lines.

(v) The *y* coordinates have not been determined with any great accuracy, owing to the extreme overlap.

(vi) In each zone there are 38 independent positional parameters; only 56(*h*0*l*) and 24(*hk*0) reflexions have been observed.

However, the bond lengths and valency angles given in Fig. 6 are reasonable (except that bond 5–6 is rather short), but nothing can be said about bond-length variations within the molecule. The mean Fe–C distance is 2·10 Å, mean C–C distance 1·43 Å, mean valency angle in six-membered ring 120°, and mean valency angle in five-membered ring 108°.

The author wishes to thank Prof. J. M. Robertson for his interest in this work and for much helpful discussion, and Dr P. L. Pauson for suggesting the problem, supplying the crystals of diindenyl iron, and discussing various points.

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