Crystal and Molecular Structure of Tricarbonyl-π-[1,1,1-tricarbonyl-2-methyl-3-diphenylmethylene-6-methoxyferra-2-oxacyclohexenyl]iron-(*Fe–Fe*), a Product from the Reaction between Diphenyldiazomethane and Tricarbonyl-π-[1,1,1-tricarbonyl-2,5-dimethoxyferracyclopentadiene]iron

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The crystal and the molecular structure of the title compound (2) have been determined by *X*-ray diffraction methods from photographic data. Crystals are monoclinic prisms, space group $P2_1/c$, with $Z = 4$ in a cell with $a = 11{\cdot}76$, $b = 17{\cdot}60$, $c = 13{\cdot}66$ Å, $\beta = 119{\cdot}2°$. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to R 0·138 for 1527 reflections. Both iron atoms have distorted octahedral co-ordination. The C–C bond lengths in the π-allyl system are 1·38 and 1·44 Å, and the mean C–Fe distance to this system is 2·08 Å. Fe–Fe distance is 2·62 Å. The structure possesses a dative bond from oxygen to iron of 2·07 Å.

IRRADIATION of a mixture of diphenyldiazomethane and tricarbonyl-π-[1,1,1-tricarbonyl-2,5-dimethoxyferracyclopentadiene]iron (1) produces a complex mixture of compounds. The crystal structure determination of one of these, tricarbonyl-π-[1,1,1-tricarbonyl-2-methyl-3-diphenylmethylene-6-methoxyferra-2-oxacyclohexenyl]-iron(*Fe–Fe*) (2), is described here. The results have been summarized in an earlier publication.[1]

EXPERIMENTAL

The compound separated from light petroleum as brown prisms, m.p. 157°, elongated along *c* with {100} prominent.

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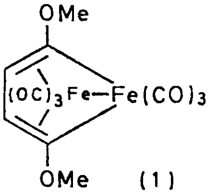
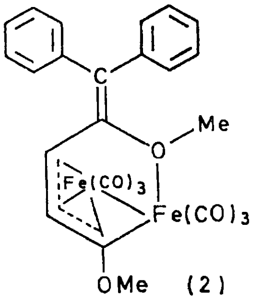
[1] M. M. Bagga, G. Ferguson, J. A. D. Jeffreys, (Miss) C. M. Mansell, P. L. Pauson, I. C. Robertson, and J. G. Sime, *Chem. Comm.*, 1970, 672.

Crystal Data.—$C_{25}H_{18}Fe_2O_8$, $M = 558$, Monoclinic, $a = 11{\cdot}76$, $b = 17{\cdot}60$, $c = 13{\cdot}66$ Å, $\beta = 119{\cdot}2°$, $U = 2466$ Å^3, $D_m = 1{\cdot}47 \pm 0{\cdot}01$, $Z = 4$, $D_c = 1{\cdot}509$, $F(000) = 1136$.



(1)



(2)

Space group $P2_1/c$ (No. 14) from systematic absences. Cu-K_α radiation, $\lambda = 1{\cdot}542$ Å; μ(Cu-K_α) = 107·5 cm^{-1}. Crystal dimensions, 0·04 × 0·14 × 0·9 mm.

Crystallographic Measurements.—The symmetry and cell dimensions were obtained from rotation, and Weissenberg photographs about *c*, with Cu-K_α radiation, and from precession photographs with Mo-K_α radiation. The intensity data for the layers *hk*0—9 were collected as equi-inclination multiple-film Weissenberg photographs and estimated visually. Accidentally absent reflections were assessed at one third of the locally observable minimum.[2] The intensities were corrected for time of exposure, polarization, and Lorentz factors, but not for absorption, and 1527 independent structure factors evaluated, of which 326 were unobserved.

Structure Determination.—A three-dimensional Patterson map yielded co-ordinates for the two iron atoms, and successive rounds of structure-factor calculations and Fourier syntheses revealed the remaining carbon and oxygen atom positions. In every round the data were rescaled so that for each layer $\Sigma(\text{scaled}|F_o|) = \Sigma|F_c|$. Positions and isotropic temperature factors were initially refined by an automated correction based on difference syntheses,[3] *R* being reduced from 0·214 to 0·173 in four rounds. Refinement subsequently converged after six rounds of block diagonal least-squares refinement. Each last-squares round refined an overall scale factor, and the last three rounds included anisotropic temperature parameters for the iron atoms, and a correction for the real part of the anomalous dispersion of these atoms. The final *R* was 0·138. The weighting scheme used in the refinement was $\sqrt{w} = 1{\cdot}0$ if $|F_o| \leqslant F^*$; $\sqrt{w} = F^*/|F_o|$ if $|F_o| > F^*$. The value of F^* was adjusted during the refinement, and for the last three rounds was 35·0. After refinement had converged, a Fourier map based on $|F_o| - |F_c|$ was computed and searched for peaks of height 0·5 eÅ^{-3}. Six such peaks were found; two, of height 0·6 eÅ^{-3} are in the positions expected for hydrogen atoms attached to C(20), and C(32), and of the remaining four, one is at Fe(1) and another at Fe(2). In the structure-factor calculations the atomic scattering factors were taken from ref. 4. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20573 (8 pp., 1 microfiche).*

Table 1 shows the final weighting scheme analysis and the convergence of the refinement. Table 2 gives the final co-ordinates of the atoms, their temperature factors, and standard deviations derived from the final least-squares matrix. Figure 1 shows the molecule in projection on the *ac* plane, together with the crystallographic numbering system used. Table 3 lists interatomic distances, valency

TABLE 1

Convergence of the refinement

Least-squares round no.	*R* overall	*R′* *
5	0·1381	0·0290
6	0·1378	0·0289

Average values of $w\Delta^2$ in round (6)

Range of $\lvert F_o \rvert$	0	10	20	30	40	50	60	70	80	90	100	>100
$w\Delta^2$		14·76	16·11	15·99	17·43	20·20	19·71	16·93	16·22	29·31	14·41	12·24
No. of values		375	415	258	171	91	72	48	37	16	16	28

Final structure-factor calculation with output from round (6)

Layer *l* =	0	1	2	3	4	5	6	7	8	9
R	0·145	0·128	0·132	0·139	0·121	0·113	0·134	0·146	0·179	0·234
No. of data	142	168	196	167	173	154	181	146	111	89

* $R' = \Sigma w\Delta^2/\Sigma w(aF_o^2)$.

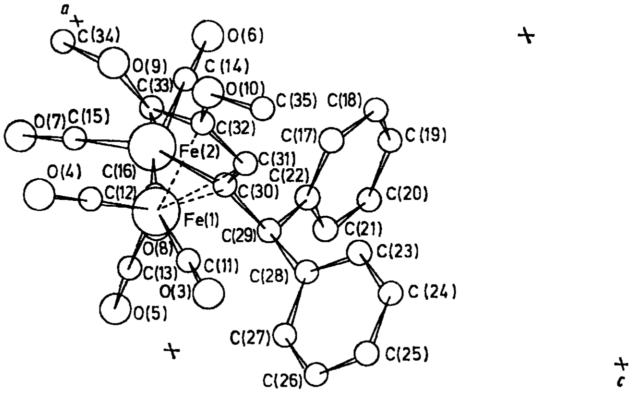


FIGURE 1 The molecule projected on the *ac* plane, showing the crystallographic numbering system

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[2] W. C. Hamilton, *Acta Cryst.*, 1955, **8**, 185.

[3] J. A. D. Jeffreys and Mrs. C. M. Willis *née* Mansell, *J.C.S. Dalton*, 1972, 2169.

[4] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.

angles, and some non-bonded interactions. Table 4 gives the mean values for the lengths and angles for selected types of bond, together with the means of some previously measured values, and the mean estimated standard deviations for bond lengths and angles.

TABLE 2

Final co-ordinates and isotropic temperature parameters with standard deviations in parentheses

Atom	$10^4\ X/A$	$10^4\ Y/B$	$10^4\ Z/C$	$10^3\ U_{iso}$
Fe(1)	2494(3)	795(1)	2207(2)	*
Fe(2)	653(3)	1823(1)	1379(2)	*
O(3)	3540(15)	404(8)	720(13)	110(5)
O(4)	3857(14)	−317(8)	4006(12)	100(5)
O(5)	483(13)	−305(8)	1185(11)	93(4)
O(6)	−915(17)	3172(9)	471(15)	125(6)
O(7)	1420(14)	1707(8)	−352(12)	101(5)
O(8)	−1713(16)	956(9)	523(14)	117(5)
O(9)	1079(12)	750(7)	3378(11)	78(4)
O(10)	3846(10)	1667(5)	2824(9)	58(3)
C(11)	3116(23)	580(13)	1237(20)	102(8)
C(12)	3405(19)	115(11)	3336(17)	80(6)
C(13)	1253(21)	178(12)	1575(18)	89(7)
C(14)	−293(22)	2635(12)	869(19)	94(7)
C(15)	1115(20)	1750(11)	288(18)	83(6)
C(16)	−758(21)	1274(12)	888(19)	93(7)
C(17)	6358(22)	3157(12)	2810(19)	93(7)
C(18)	7450(21)	2988(12)	2690(19)	91(7)
C(19)	7300(21)	2451(13)	1917(20)	97(7)
C(20)	6181(23)	2077(13)	1310(20)	99(7)
C(21)	5061(19)	2216(11)	1446(17)	78(6)
C(22)	5180(18)	2758(10)	2226(16)	69(6)
C(23)	3598(18)	4120(10)	3158(16)	66(6)
C(24)	3239(20)	4923(11)	2981(17)	83(6)
C(25)	2994(20)	5274(11)	2044(18)	83(6)
C(26)	3024(19)	4904(11)	1186(17)	83(6)
C(27)	3366(19)	4116(10)	1296(16)	72(6)
C(28)	3663(18)	3746(10)	2275(16)	68(6)
C(29)	4022(18)	2966(10)	2359(16)	69(6)
C(30)	3359(18)	2400(10)	2594(16)	71(6)
C(31)	2136(17)	2516(10)	2554(15)	66(5)
C(32)	1597(21)	2040(11)	3084(18)	86(7)
C(33)	1599(19)	1264(10)	2927(17)	75(6)
C(34)	307(23)	1047(13)	3870(20)	102(8)
C(35)	4959(20)	1575(11)	3932(18)	85(7)

* An anisotropic temperature factor (T) was used given by $T = \exp[-2\pi^2(U_{11}h^2a^* + U_{22}k^2b^* + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{13}klb^*c^*)]$.

Final values for the components of the tensor ×10^3

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
Fe(1)	77(2)	59(2)	74(2)	−9(3)	94(4)	−11(3)
Fe(2)	72(2)	63(2)	87(3)	0(3)	93(4)	3(3)

TABLE 3

Selected valency parameters

(*a*) Bond lengths (Å)

Fe(1)–Fe(2)	2·62	C(18)–C(19)	1·36
Fe(1)–C(11)	1·84	C(19)–C(20)	1·34
Fe(1)–C(12)	1·83	C(20)–C(21)	1·44
Fe(1)–C(13)	1·68	C(21)–C(22)	1·39
Fe(1)–O(10)	2·07	C(23)–C(24)	1·46
Fe(1)–C(33)	1·94	C(23)–C(28)	1·41
Fe(2)–C(14)	1·73	C(24)–C(25)	1·32
Fe(2)–C(15)	1·82	C(25)–C(26)	1·36
Fe(2)–C(16)	1·75	C(26)–C(27)	1·43
Fe(2)–C(31)	2·09	C(27)–C(28)	1·37
Fe(2)–C(32)	2·07		
Fe(2)–C(33)	2·09	C(22)–C(29)	1·50
C(11)–O(3)	1·09	C(28)–C(29)	1·42
C(12)–O(4)	1·10	C(29)–C(30)	1·40
C(13)–O(5)	1·16	C(30)–C(31)	1·43
C(14)–O(6)	1·16	C(31)–C(32)	1·44
C(15)–O(7)	1·10	C(32)–C(33)	1·38
C(16)–O(8)	1·13	C(30)–O(10)	1·38
		O(10)–C(35)	1·45
C(17)–C(18)	1·40	C(33)–O(9)	1·39
C(17)–C(22)	1·40	O(9)–C(34)	1·47

TABLE 3 (*Continued*)

(*b*) Valency angles (°)

(i) Round Fe(1)

Fe(2)–Fe(1)–O(10)	88	O(10)–Fe(1)–C(33)	89
Fe(2)–Fe(1)–C(11)	112	C(11)–Fe(1)–C(12)	101
Fe(2)–Fe(1)–C(12)	147	C(11)–Fe(1)–C(13)	93
Fe(2)–Fe(1)–C(13)	84	C(11)–Fe(1)–C(33)	163
Fe(2)–Fe(1)–C(33)	52	C(12)–Fe(1)–C(13)	91
O(10)–Fe(1)–C(11)	87	C(12)–Fe(1)–C(33)	95
O(10)–Fe(1)–C(12)	97	C(13)–Fe(1)–C(33)	89
O(10)–Fe(1)–C(13)	172		

(ii) Carbonyl groups

Fe(1)–C(11)–O(3)	174	Fe(2)–C(14)–O(6)	176
Fe(1)–C(12)–O(4)	174	Fe(2)–C(15)–O(7)	179
Fe(1)–C(13)–O(5)	173	Fe(2)–C(16)–O(8)	176

(iii) Round Fe(2)

Fe(1)–Fe(2)–C(14)	167	C(15)–Fe(2)–C(16)	105
Fe(1)–F3(2)–C(15)	78	C(15)–Fe(2)–C(31)	101
Fe(1)–Fe(2)–C(16)	102	C(15)–Fe(2)–C(32)	136
Fe(1)–Fe(2)–C(31)	82	C(15)–Fe(2)–C(33)	125
Fe(1)–Fe(2)–C(32)	76	C(16)–Fe(2)–C(31)	154
Fe(1)–Fe(2)–C(33)	47	C(16)–Fe(2)–C(32)	115
C(14)–Fe(2)–C(15)	97	C(16)–Fe(2)–C(33)	94
C(14)–Fe(2)–C(16)	90	C(31)–Fe(2)–C(32)	41
C(14)–Fe(2)–C(31)	88	C(31)–Fe(2)–C(33)	71
C(14)–Fe(2)–C(32)	101	C(32)–Fe(2)–C(33)	39
C(14)–Fe(2)–C(33)	135		

(iv) Internal angles in the benzene rings

C(17)	123	C(23)	116
C(18)	117	C(24)	121
C(19)	123	C(25)	122
C(20)	122	C(26)	120
C(21)	117	C(27)	119
C(22)	120	C(28)	121

(v) Internal bond angles in the heterocyclic ring

O(10)	117	C(32)	118
C(30)	116	C(33)	123
C(31)	125		

(vi) Other angles

C(17)–C(22)–C(29)	121	C(32)–C(33)–O(9)	123
C(21)–C(22)–C(29)	120	C(33)–O(9)–C(34)	118
C(23)–C(28)–C(29)	121	Fe(2)–C(31)–C(30)	113
C(27)–C(28)–C(29)	121	Fe(2)–C(31)–C(32)	69
C(22)–C(29)–C(28)	118	Fe(2)–C(32)–C(31)	71
C(22)–C(29)–C(30)	120	Fe(2)–C(32)–C(33)	72
C(28)–C(29)–C(20)	122	Fe(2)–C(33)–C(32)	70
C(29)–C(30)–C(31)	123	Fe(2)–C(33)–Fe(1)	81
C(29)–C(30)–O(10)	120		
C(30)–O(10)–C(35)	114	C(19)–C(22)–C(29)	180
Fe(1)–O(10)–C(35)	118	C(25)–C(28)–C(29)	178
Fe(1)–C(33)–O(9)	114		

(*c*) Intermolecular contacts <3·6 Å

O(4) ··· O(4^{II})	2·95	C(34) ··· O(6^{III})	3·44
O(5) ··· O(5^{I})	3·06	O(5) ··· C(16^{I})	3·45
O(3) ··· O(8^{I})	3·11	O(8) ··· C(11^{I})	3·45
O(5) ··· O(7^{I})	3·15	O(5) ··· O(8^{I})	3·49
C(32) ··· O(7^{III})	3·15	O(4) ··· C(12^{II})	3·50
O(5) ··· C(15^{I})	3·22	C(34) ··· C(27^{II})	3·51
O(5) ··· C(13^{I})	3·30	O(9) ··· C(26^{III})	3·56
O(4) ··· C(35^{II})	3·31	C(17) ··· O(4^{IV})	3·58
C(24) ··· O(3^{IV})	3·41		

The Roman numerals as superscripts refer to the following equivalent positions:

I $\bar{x}, \bar{y}, \bar{z}$ III $x, \frac{1}{2} - y, \frac{1}{2} + z$
II $1 - x, \bar{y}, 1 - z$ IV $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$

TABLE 4

Means of selected valency parameters. Values in parentheses are the means of previously published values from ref. 10, unless otherwise stated

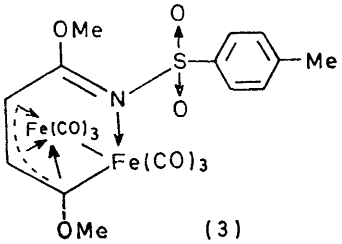
Bond lengths	Å	
C(ar)–C(ar)	1·39	(1·39)
Fe–C(carbonyl)	1·78	
C–O(carbonyl)	1·12	
Bond angle at carbonyl carbon	175°	

Mean estimated standard deviations over all values

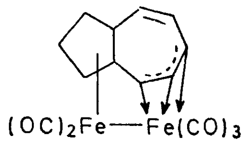
Bond lengths (Å)	Fe–C	0·024
	C–O	0·029
	C–C	0·031
Bond angles (°)	Fe–C–O	3·1
All types (C–C–C, C–C–O, and C–O–C)		2·7

DISCUSSION

The structure is analogous to that of the compound (3) formed when (1) is made to react with dichloramine-T.[5] The Fe–Fe separation, 2·62 Å is similar to that (2·64 Å) found in (3). The co-ordination about Fe(1) is that of a distorted octahedron (Figure 2a). If the centre carbon atom, C(32), of the π bonded allyl system is ignored, the co-ordination about Fe(2) approximates to octahedral, and the additional atom, C(32), lies near the centre of one of the edges of the co-ordination polyhedron. The other vertices of the polyhedron are displaced towards the intruder (Figure 2b). Similar co-ordination is found in (3) (Figure 2c), and in the azulene derivative (4) (Figure 2d),[6] and has been reported for another π allyl system bonded to iron.[7]



(3)



(4)

The Fe–C–O systems show apparent small departures from linearity.[8] The nearest approaches between a carbonyl carbon and an iron atom to which it is not formally bonded are Fe(1)···C(15) 2·86 Å, and Fe(2)···C(13) 2·96 Å. A similar approach, 2·80 Å, occurs in (3), and weak interaction was inferred, as the bond angle at the carbonyl carbon was 172°, differing from the mean value by 3σ.[5] In the compound we describe, the angle at C(15) is 179°, and we consider that there is no interaction. The mean Fe–C bond length is unexceptional, but the mean C–O bond length is shorter than usual (Table 4).

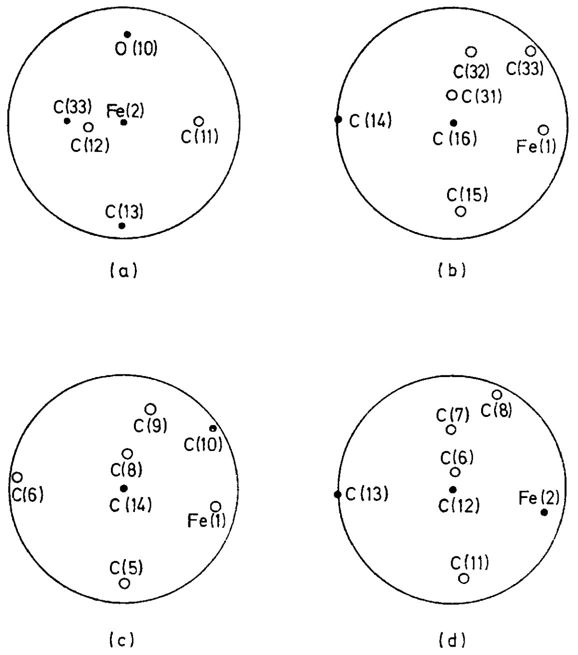


FIGURE 2 The co-ordination about (a) Fe(1), (b) Fe(2), (c) Fe(2) in compound (3) (numbered according to ref. 5), and (d) Fe(1) in compound (4) (numbered according to ref. 6)

Of the other bonds round Fe(1), the Fe(1)–C(33) bond has nearly the same length (1·94 Å) as the corresponding bond (1·91 Å) in compound (3), and is relatively short for this type of bond.[3,5] The Fe(1)–O(10) bond length

TABLE 5

Deviations (Å) of atoms from planes

Plane (1): C(17)—(22)
C(17) 0·03, C(18) −0·02, C(19) 0·00, C(20) 0·01, C(21) 0·00, C(22) −0·02, C(29) 0·06

Plane (2): Fe(1), O(10), C(30), C(35)
Fe(1) −0·06, O(10) 0·24, C(30) −0·09, C(35) −0·09

Plane (3): C(22), C(28)—(30)
C(22) 0·00, C(28) 0·00, C(29) 0·01, C(30) 0·00, O(10) −0·18, C(31) 0·23

Plane (4): C(23)—(28)
C(23) 0·01, C(24) 0·01, C(25) −0·01, C(26) 0·01, C(27) 0·01, C(28) −0·01, C(29) −0·04

Plane (5): C(31)—(33)
Fe(1) −0·24, O(9) 0·03, C(30) −0·87

Plane (6): O(10), C(29)—(31)
O(10) 0·01, C(31) 0·01, C(30) −0·02, C(29) 0·01, C(28) −0·21 C(22) 0·22

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[5] L. Rodrique, M. van Meersche, and P. Piret, *Acta Cryst.*, 1969, **B25**, 519.

[6] M. R. Churchill, *Inorg. Chem.*, 1967, **6**, 190.

[7] J. Weaver and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 3521.

[8] S. F. A. Kettle, *Inorg. Chem.*, 1965, **4**, 1661.

(2·07 Å) is very similar to that (2·09 Å) between the iron atom and the closer water molecules in $FeCl_2,4H_2O$.[9] The oxygen atom bears a formal positive charge, but this has not affected the bonding to carbon. The O(10)–C(35) distance (1·45 Å) is not significantly different from a normal C(tetrahedral)–O bond (1·43 Å),[10] and the value for bond O(10)–C(30), 1·38 Å, is close to that (1·37 Å) of the similar bond in furan.[10] Analogously, conversion of an amine into a salt has little effect on the C–N bond length.[10]

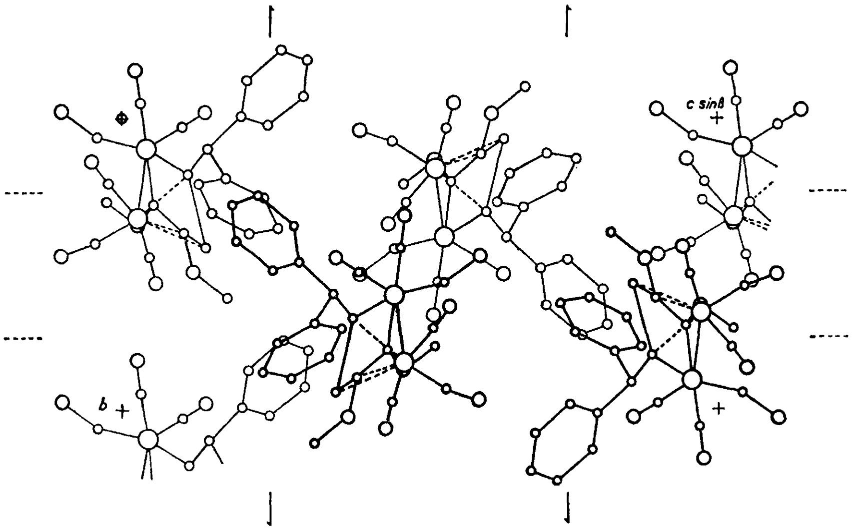

FIGURE 3 The packing of the molecules, viewed down the *a* axis. Those in heavy outline are closest to the observer

The two phenyl rings are planar (Table 5), but C(29) departs from the plane of either, and the π bond C(29)–C(30) is twisted by 9·8°. The distortions may be due to forces involved in crystal packing, though Table 3 shows no unusually close contacts.

Carbon–carbon bond lengths in the heterocyclic ring are different from those in compound (3), but are similar to the corresponding lengths in the azulene derivative described in ref. 6. The lengths of the corresponding bonds are as follows, the values for compounds (3) and (4) being given, where possible, in square brackets: C(30)–C(31) 1·43 [1·41 compound (3)], C(31)–C(32) 1·44 [1·45 and 1·43], C(32)–C(33) 1·38 [1·47 and 1·39 Å]. The bond angle at C(32), 118°, is similar to that in other π allyl systems, [*e.g.* 116°, compound (3),[5] and 122·8, compound (4) [6]], and the lengths of the bonds from Fe(2) to C(31), C(32), and C(33) are unexceptional.

The closest intermolecular contacts are of the –C–O · · · O–C– type, and are of the order of the sum of the van der Walls radii of the atoms concerned.

Figure 3 shows the packing in projection down *a*. The molecules are packed with polar carbonyl groups facing each other, and with phenyl groups toward each other. For the latter groups the packing is open; and overall the atoms have relatively large temperature factors.

[2/1591 *Received, 6th July,* 1972]

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[9] B. R. Penfold and J. A. Grigor, *Acta Cryst.*, 1959, **12**, 850.

[10] Chem. Soc. Special Publ., No. 18, 1965.