Crystal and Molecular Structure of Tricarbonyl(*exo*-7-phenylcyclohepta-1,3,5-triene)iron†

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The crystal and the molecular structure of the title compound have been determined by *X*-ray diffraction methods from photographic data assessed by a film-scanner. Crystals are orthorhombic, space group $Pca2_1$, with $Z = 4$ in a cell with $a = 12.48(1)$, $b = 14.90(2)$, $c = 7.53(1)$ Å. The structure was solved by Patterson and Fourier methods, and refined by least-squares techniques to R 0.081 2 for 406 reflections. The geometries of the (formal) butadiene–iron systems in derivatives of cycloheptatriene and azepine are compared and analysed.

THE compound was prepared by stirring 7-phenylcycloheptatriene with enneacarbonyldi-iron in benzene.[1] This study was undertaken to determine the configuration of the phenyl group, which was not revealed by spectroscopic methods.

EXPERIMENTAL

The compound separated from light petroleum as yellow blades, m.p. 69.5—71.5 °C, elongated along *c* with (010) prominent, and (101) present. Crystal dimensions 0.4 × 0.1 × 0.9 mm.

Crystal Data.—$C_{16}H_{12}FeO_3$, $M = 308$, Orthorhombic, $a = 12.48(1)$, $b = 14.90(2)$, $c = 7.53(1)$ Å, $U = 1\,400$ Å^3, $D_m = 1.42$, $Z = 4$, $D_c = 1.46$, $F(000) = 632$. Space group $Pca2_1$ (No. 29). Cu-K_α radiation, $\lambda = 1.542$ Å; μ(Cu-K_α) 91.1 cm^{-1}. The diffraction symmetry, *mmm Pca* –, showed the space group as either $Pca2_1$ (No. 29) or *Pcam* (≡*Pbcm*, No. 57). The structure of the molecule prevents it having any one of the symmetry elements needed for *Pbcm* with $Z = 4$, whence the true space group followed. D_m was determined by flotation in aqueous potassium iodide solution to which a little detergent had been added.

Crystallographic Measurements.—The symmetry and cell dimensions were obtained from rotation and Weissenberg photographs about *c*, with Cu-K_α radiation. Intensity data for the layers *hk*0—6 were collected as equi-inclination Weissenberg photographs. Initially, these (789, including 117 unobserved ones assessed at one half the locally observable minimum [2]) were estimated visually and used, uncorrected for absorption, to determine the structure. Subsequently intensities were measured and corrected for absorption at the S.R.C. Microdensitometer Laboratory; data for 406 reflections were provided. In each case these were corrected for time of exposure, polarization, and Lorentz factors.

Structure Determination.—A three-dimensional Patterson map yielded co-ordinates for the iron atom, and a Fourier map phased on this revealed one carbonyl group. These two new atoms sufficed to resolve the false symmetry. Successive rounds of structure-factor calculations and Fourier syntheses followed, in the early stages, by least-squares refinement of occupation numbers, revealed the sites of the remaining oxygen and carbon atoms. The structure-factor program automatically scales the data so that for each layer $\Sigma(\text{scaled}|F_o|) = \Sigma(|F_c|)$. Throughout these calculations and the later ones, scattering factors were corrected for the real component of anomalous dispersion. When all the atoms had been located, their positions and temperature factors were adjusted by block-diagonal least-squares refinement. Each such round included an overall

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† No reprints available.

[1] P. L. Pauson, personal communication.

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

scale factor, an overall temperature parameter, and the later rounds included an anisotropic temperature factor for the iron atom. When the data from the film-scanner were available, atom sites previously determined using only the real component of the anomalous dispersion were entered for a structure-factor calculation using the imaginary component of the anomalous dispersion. The indexing in use gave R 0.096 5, reduced to 0.086 5 by two rounds of least-squares refinement; mirror-image indexing gave R 0.103 3, falling to 0.090 2. The original indexing was retained, and refinement converged at R 0.081 2. Final layer scaling was achieved by calling the structure-factor program after convergence of least-squares refinement using both components of anomalous dispersion, and isotropic temperature parameters. Initially in the least-squares refinement all data had $\sqrt{w} = 1.0$. Later the weighting scheme used gave $\sqrt{w} = 1.0$ if $|F_o| \leqslant F^*$; $\sqrt{w} = F^*/|F_o|$ if $|F_o| > F^*$; the value for F^* was set automatically by the least-squares program, being 17.9 for three rounds, and 18.0 for the final two rounds. After refinement had converged a difference-Fourier map was computed but no peaks >0.5 eÅ^{-3} were found. In the structure-factor calculations the atomic scattering factors, and the components of anomalous dispersion were taken from ref. 3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21889 (4 pp., 1 microfiche).*

TABLE 1

Convergence of the refinement

Least-squares round no. with non-unitary weights *	R overall	R'
(4)	0.081 3	0.112 6
(5)	0.081 2	0.112 5

Mean $w\Delta^2$ in round (5)

Range of F_0	0		10		20		30		40		50		60		70		80		90		100	>100
$\langle w\Delta^2\rangle$		0.33		3.9		5.0		2.6		3.3		2.4		3.5		2.9		9.4		0.2		2.6
No. of values		1		101		150		78		42		17		12		1		2		1		1

Final structure-factor calculation with output from round (5)

Layer l =	0	1	2	3	4	5	6
R	0.094	0.073	0.078	0.083	0.071	0.086	0.087
No. of data	73	78	64	64	52	41	34

* $R = \Sigma|\Delta|/\Sigma K|F_o|$, $R' = [\Sigma w\Delta^2/\Sigma(K|F_o|)^2]^{\frac{1}{2}}$.

TABLE 2

Final co-ordinates ($\times$ 10^4) and isotropic temperature parameters ($U_{\text{iso}} \times 10^3$) and, in parentheses, their standard deviations

	x/a	y/b	z/c	U_{iso}
Fe(1)	5 551(3)	8 174(3)	5 000(0)	*
O(2)	6 563(22)	9 369(17)	2 518(38)	105(9)
O(3)	5 608(22)	9 240(18)	8 355(39)	105(9)
O(4)	7 446(21)	7 096(14)	5 980(33)	90(7)
C(5)	6 141(30)	8 942(22)	3 649(51)	73(10)
C(6)	5 561(29)	8 822(25)	7 037(49)	77(10)
C(7)	6 809(28)	7 558(21)	5 626(49)	83(11)
C(8)	5 188(23)	7 189(20)	3 061(35)	40(7)
C(9)	4 655(23)	7 046(18)	4 643(39)	58(10)
C(10)	4 025(18)	7 766(17)	5 377(34)	37(6)
C(11)	3 981(25)	8 615(20)	4 488(33)	44(8)
C(12)	3 608(28)	8 738(25)	2 771(44)	72(10)
C(13)	3 949(26)	8 271(20)	1 326(40)	58(8)
C(14)	4 780(19)	7 550(16)	1 282(29)	27(6)
C(15)	4 382(22)	6 662(16)	414(39)	49(8)
C(16)	3 297(25)	6 370(17)	677(32)	47(8)
C(17)	2 848(25)	5 550(19)	−262(44)	67(10)
C(18)	3 665(28)	5 133(21)	−1 381(44)	67(10)
C(19)	4 697(20)	5 361(16)	−1 647(33)	34(7)
C(20)	5 061(22)	6 206(16)	−788(33)	29(7)

* An anisotropic temperature factor (T) was used given by $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]$ with parameters:

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
Fe(1)	38(2)	38(2)	44(2)	−19(6)	0(7)	0(0)

TABLE 3

Selected valency parameters

(*a*) Bond lengths (Å)

Fe(1)–C(5)	1.70	C(9)–C(10)	1.44
Fe(1)–C(6)	1.81	C(10)–C(11)	1.43
Fe(1)–C(7)	1.88	C(11)–C(12)	1.39
Fe(1)–C(8)	2.12	C(12)–C(13)	1.36
Fe(1)–C(9)	2.04	C(13)–C(14)	1.49
Fe(1)–C(10)	2.02	C(14)–C(15)	1.56
Fe(1)–C(11)	2.10	C(15)–C(16)	1.44
O(2)–C(5)	1.19	C(15)–C(20)	1.41
O(3)–C(6)	1.17	C(16)–C(17)	1.52
O(4)–C(7)	1.08	C(17)–C(18)	1.46
C(8)–C(9)	1.38	C(18)–C(19)	1.35
C(8)–C(14)	1.53	C(19)–C(20)	1.49

(*b*) Valency angles (°)

(i) Around Fe(1)

C(5)–Fe(1)–C(6)	98	C(7)–Fe(1)–C(8)	91
C(5)–Fe(1)–C(7)	97	C(7)–Fe(1)–C(9)	95
C(5)–Fe(1)–C(8)	98	C(7)–Fe(1)–C(10)	127
C(5)–Fe(1)–C(9)	136	C(7)–Fe(1)–C(11)	168
C(5)–Fe(1)–C(10)	134	C(8)–Fe(1)–C(9)	39
C(5)–Fe(1)–C(11)	95	C(8)–Fe(1)–C(10)	72
C(6)–Fe(1)–C(7)	92	C(8)–Fe(1)–C(11)	84
C(6)–Fe(1)–C(8)	163	C(9)–Fe(1)–C(10)	42
C(6)–Fe(1)–C(9)	124	C(9)–Fe(1)–C(11)	74
C(6)–Fe(1)–C(10)	93	C(10)–Fe(1)–C(11)	41
C(6)–Fe(1)–C(11)	90		

(ii) Carbonyl groups

Fe(1)–C(5)–O(2)	170	Fe(1)–C(7)–O(4)	170
Fe(1)–C(6)–O(3)	178		

(iii) Internal angles in the carbocyclic rings

C(8)	131	C(15)	121
C(9)	119	C(16)	122
C(10)	120	C(17)	111
C(11)	124	C(18)	130
C(12)	125	C(19)	116
C(13)	127	C(20)	120
C(14)	118		

(iv) Other angles

C(8)–C(14)–C(15)	100	C(14)–C(15)–C(16)	120
C(13)–C(14)–C(15)	114	C(14)–C(15)–C(20)	119
C(14)–C(15)–C(18)	176		

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[3] 'International Tables for X-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974, p. 71.

TABLE 3 (*Continued*)

(*c*) Intermolecular contacts <3.5 Å

$\mathrm{O(2)\cdots O(3^{I})}$	3.36	$\mathrm{O(3)\cdots O(5^{IV})}$	3.49
$\mathrm{O(2)\cdots O(3^{II})}$	3.47	$\mathrm{O(4)\cdots C(8^{V})}$	3.35
$\mathrm{O(3)\cdots C(12^{IV})}$	3.20	$\mathrm{C(5)\cdots O(3^{II})}$	3.49
$\mathrm{O(3)\cdots C(11^{IV})}$	3.35	$\mathrm{C(8)\cdots O(4^{III})}$	3.35
$\mathrm{O(3)\cdots C(2^{II})}$	3.36	$\mathrm{C(11)\cdots O(3^{II})}$	3.35
$\mathrm{O(3)\cdots C(13^{VI})}$	3.37	$\mathrm{C(12)\cdots O(3^{II})}$	3.20
$\mathrm{O(3)\cdots O(2^{IV})}$	3.47	$\mathrm{C(13)\cdots O(3^{I})}$	3.37

Roman numerals as superscripts refer to the following equivalent positions:

I	$x, y, -1 + z$	IV	$1 - x, 2 - y, \frac{1}{2} + z$
II	$1 - x, 2 - y, -\frac{1}{2} + z$	V	$\frac{3}{2} - x, y, \frac{1}{2} + z$
III	$\frac{3}{2} - x, y, -\frac{1}{2} + z$	VI	$x, y, 1 + z$

(*d*) Mean estimated standard deviations

Bond lengths (Å)	C–O	0.04
	Fe–C, C–C	0.03
Bond Angles (°)	Fe–C–O	4.0
	C–Fe–C	2.4
	C–C–C	3.2

TABLE 4

(*a*) Departures (Å) of atoms from planes

Plane (1): C(8)—(11)

[C(8) 0.00, C(9) −0.01, C(10) 0.01, C(11) 0.00, Fe(1) −1.56, C(12) 0.97, C(14) 0.93]

Plane (2): C(11)—(14)

[C(11) 0.00, C(12) 0.00, C(13) 0.00, C(14) 0.00, C(8) 0.22, C(10) 0.94]

Plane (3): C(5)—(7)

[Fe(1) 0.92]

Plane (4): C(15)—(20)

[C(15) −0.02, C(16) −0.01, C(17) 0.01, C(18) 0.01, C(19) −0.03, C(20) 0.04, C(14) 0.07]

(*b*) Interplanar angles (°): (1)–(2) 46, (1)–(3) 18, (4)–(5) * 80

* Plane (5): C(8), C(14), C(13).

Table 1 shows the final weighting-scheme analysis and the convergence of the refinement. Table 2 gives final atomic co-ordinates, temperature factors, and standard deviations derived from the final least-squares matrix. Figure 1 shows the molecule displayed and the crystallographic numbering system used; Figure 2 is a stereopair of drawings showing the molecule viewed down the *a* axis. Table 3 lists interatomic distances, valency angles, and some non-bonded interactions, and Table 4 departures of atoms from some planes fitted by least squares to groups of atoms.

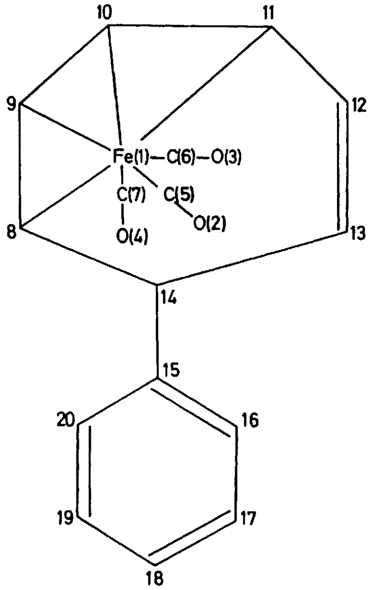

FIGURE 1 The molecule displayed showing the crystallographic numbering system

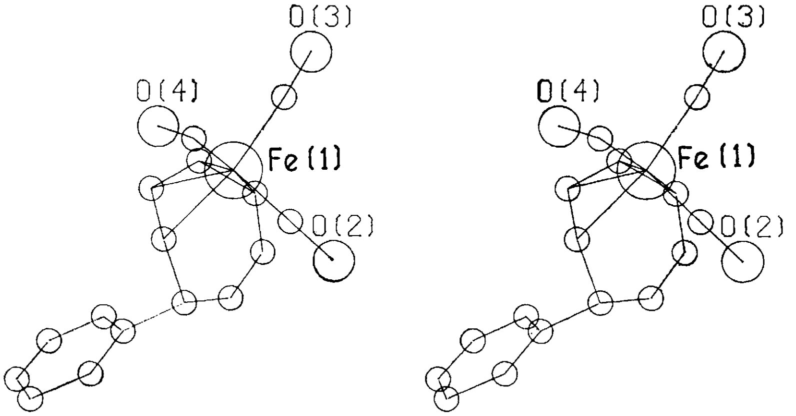

FIGURE 2 A stereopair showing the molecule viewed down *a*

DISCUSSION

This is the first report on the structure of a simple cycloheptatriene–tricarbonyliron complex. The structure of the chromium analogue of the title compound has been described,[4] but the bonding requirements of chromium differ from those of iron. Structures have been reported for a number of compounds containing tricarbonyliron linked with a (formal) cycloheptatriene system, namely diazulenedecacarbonyltetrairon,[5a] tricarbonyltroponeiron,[5b] in summary tricarbonyl-(2,4,6-triphenyltropone)iron,[5c] azepinetricarbonyliron,[5d] (3-acetylazepine)tricarbonyliron,[5e] 1-methoxycarbonylazepinetricarbonyliron,[5f] and tricarbonyl[1-(ethoxycarbonyl)-3-formylazepine]iron.[5g] It is convenient to

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[4] P. E. Baikie and O. S. Mills, *J. Chem. Soc.* (*A*), 1968, 2704.

[5] (*a*) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, 1969, **8**, 1941; (*b*) R. P. Dodge, *J. Amer. Chem. Soc.*, 1964, **86**, 5429; (*c*) D. L. Smith and L. F. Dahl, *ibid.*, 1962, **84**, 1743; (*d*) A. Gieren and W. Hoppe, *Acta Cryst.*, 1972, **B28**, 2766; (*e*) M. G. Waite and G. A. Sim, *J. Chem. Soc.* (*A*), 1971, 1009; (*f*) S. M. Johnson and I. C. Paul, *J. Chem. Soc.* (*B*), 1970, 1783; (*g*) D. I. Woodhouse, G. A. Sim, and J. G. Sime, *J.C.S. Dalton*, 1974, 1331.

summarize these structures and to designate the bonds as in Figure 3, where X = C(sp^3) in the present study

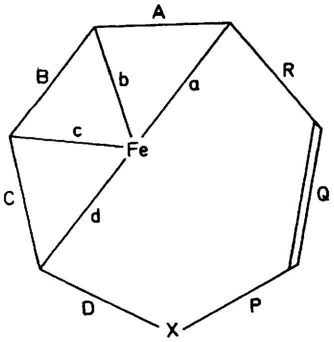


FIGURE 3 The designations of the bonds in derivatives of tricarbonyl(cyclohepta-1,3,5-triene)iron

and in the diazulene derivative, CO in the tropone derivatives, and N(substituent) in the azepine derivatives.

In the present structure the Fe–C(carbonyl) bonds have different lengths, but the mean value is unexceptional. The shortest bond, Fe(1)–C(5), is that *trans* to the C_4-ligand, a situation observed before,[5f] though tricarbonyltroponeiron and tricarbonyl-[1-(ethoxycarbonyl)-3-formylazepine]iron do not show this arrangement. As usual,[5f,6] the two C(carbonyl)–Fe–C(carbonyl) bond angles involving the group C(5)–O(2) *trans* to the C_4-ligand are larger (98 and 97°) than the third such angle (92°); again, tricarbonyltroponeiron [5b] departs from this pattern. The lengths of the bonds Fe–C(C_4-ligand) [(a)—(d) in Figure 3] are unexceptional and, as usual, the inner ones are shorter than the outer. If the centre of the bond C(9)–C(10) is taken as one site [7,5c] then the co-ordination about iron is approximately octahedral (Table 5); however, the sites of the C_4-ligand occupy less than one octant, and the other bond vectors are displaced from their idealized directions toward this octant. Table 6(*a*) tabulates the difference between the lengths of the a and d bonds (Figure 3) according to X for a series of structures. It is clear that, while the individual lengths show no clear trend, as the inductive (−*I*) effect of X rises, so the difference [(a) − (d)] between these distances to the ligand increases. This difference is thus a sensitive indicator of the structural *trans*-effect.[8]

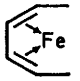
TABLE 5

Stereographic representation of the co-ordination round Fe(1); limiting radius 100

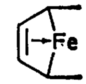
Atom	Radius	Azimuth
C(5) *	0	0
C(6)	86	0
C(7)	89	93
C(8)	86	−175
C(9)	41	−162
C(10)	42	−102
C(11)	92	−90
M(9,10) †	37	−132

* Vectors ending in the upper hemisphere or on the equator; all others end in the lower hemisphere. † M(9,10) is the mid-point of the bond C(9)–C(10).

The C_4-ligand is planar, and the iron atom 1.56 Å out of this plane. The bonding within this ligand is considered to be intermediate between the ground state and the first excited state, implying linkage to the iron respectively as (1) and (2), the latter implying octahedral co-ordination to the iron atom. One can, in principle, denumerate the departure of the bonding in the butadienoid system from its ground state by a bond-alternation index defined as $100[1-(l_A + l_C)/2l_B]$, where l_A, l_B, l_C are the lengths of the corresponding bonds in Figure 3. For a ligand with the three bonds of equal length the index is zero: positive values would imply electron localization toward the ground state, negative values toward the first excited state. Hückel calculations [6] give for the ground state $l_A = l_C = 1.36$, $l_B =$



(1)



(2)

TABLE 6

Bond lengths (Å) in various compounds containing the unit shown in Figure 3

(*a*) Bonds (a) and (d)

Compound	(a)	(d)	(a) − (d) × 10^3	X
(1)	2.10	2.12	−20	C(sp^3)
(2)	2.134	2.138	−4	C(sp^3)
(3) [a]	2.203	2.193	10	NH
(4)	2.182	2.168	14	NH
			23 [b]	NH
			28 [c]	NH
(5)	2.149	2.114	30	CO
(6)	2.17	2.13	40	CO
(7) [a]	2.209	2.155	45	NH
(8)	2.145	2.091	54	N·CO_2Me
(9)	2.151	2.096	55	N·CO_2Et

(b) Bonds A, B, C, Q, and R

Compound	Bond alternation index	A	B	C	Q	R	(B+R)
(1)	2.4	1.38	1.44	1.43	1.36	1.39	2.83
(3)	0.9	1.404	1.418	1.406	1.325	1.454	2.872
(8)	−0.7	1.398	1.409	1.440	1.334	1.439	2.848
(7)	−1.6	1.424	1.395	1.412	1.318	1.448	2.843
(9)	−1.8	1.431	1.406	1.431	1.343	1.465	2.871
(5)	−3.0	1.435	1.396	1.442	1.343	1.463	2.859
(4)	−4.9	1.457	1.392	1.464	1.364	1.458	2.850
(2)	−5.0	1.434	1.371	1.444	1.427 [d]	1.473	2.844
(6)	−6.5	1.45	1.38	1.49	Not available		

All compounds except (2) contain the tricarbonyliron group, joined with: (1) *exo*-7-phenylcyclohepta-1,3,5-triene, present work; (2) diazulenedecacarbonyltetrairon;[5a] (3) azepine;[5d] (4) 3-acetylazepine;[5e] (5) tropone;[5b] (6) 2,4,6-triphenyltropone;[5c] (7) azepine;[5d] (8) 1-methoxycarbonylazepine;[5f] (9) 1-ethoxycarbonyl-3-formylazepine [5g].

[a] The asymmetric unit contained two molecules of azepine. [b] Mean for (3), (4), and (7), the (1-*H*)-azepines. [c] Mean for azepine. [d] Not comparable with the other entries, as this bond is part of a cyclopentadienyl system π-bonded to iron.

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[6] M. R. Churchill and R. Mason, *Proc. Roy. Soc.*, 1967, **A301**, 433.

[7] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3753.

[8] M. R. Churchill, *Perspectives in Structural Chem.*, 1970, **3**, 91.

1.46 Å, and for the first excited state, $l_A = l_C = 1.45$, $l_B = 1.39$ Å. These values imply a bond alternation index of 7 for the ground state, and of −4 for the first excited state. Table 6(*b*) gives the values for this index for compounds of the type shown in Figure 3. The results show that this index shows no clear dependence on the length of bond C, and a stronger dependence on the length of bond B than of bond A. Within this series of compounds the length of bond B is strongly correlated with that of bond R (empirically, their sum is practically constant). In other words, bond lengths within the butadienoid ligand are strongly influenced by participation from the π-electrons of the (formally) isolated double-bond. We have not found any correlation between variations in the geometries of the C_4-ligand and the tricarbonyliron moiety.

As is usual for analogously-complexed tropones and azepines,[5g] the atoms of the seven-membered ring form two planar systems; those [C(8)—(11)] of the C_4-ligand, and the four atoms [C(11)—(14)] that symmetrically contain the uncomplexed double bond. The dihedral angle (46°) between these planes is unexceptional. At the convergence of least-squares refinement, the bond lengths in the phenyl group, revealed as *exo*, were abnormal, the ring seeming stretched along the vector C(15) ··· C(18). These sites (Table 2) represent a true least-squares minimum. Atoms C(17)—(19) were reset to more conventional sites, and least-squares refinement re-started. The three atoms returned to the sites given by the original refinement. The unusual geometry shown for the benzenoid ring may be a consequence of slight disorder in the crystal. The six sites are not quite coplanar, and C(14) lies well out of this plane. The mean plane of the phenyl group makes an angle of 80° with the plane through C(8), C(14), and C(13). There are no unusually close contacts between the molecules which pack, as is usual, with the carbonyl groups of one molecule facing those of another. Figure 4 is a stereopair showing this packing viewed down *c*.

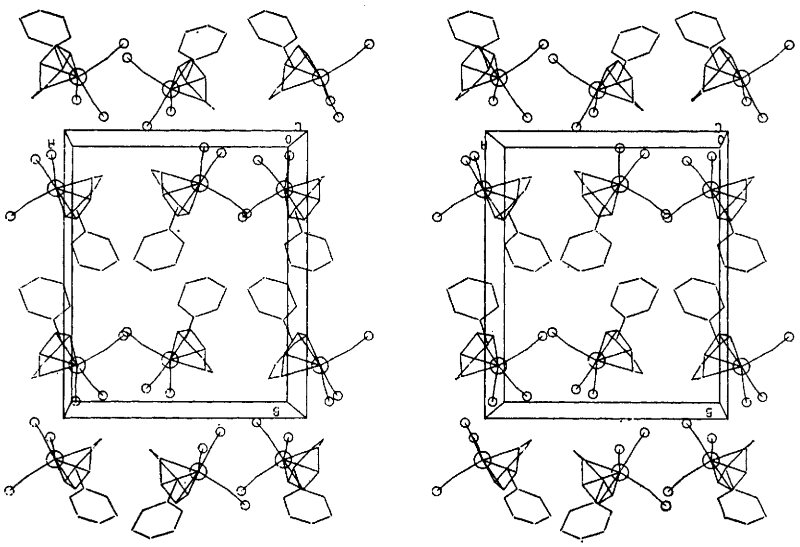

FIGURE 4 A stereopair showing the molecular packing viewed down *c*

We thank Professor Pauson for suggesting the problem and for supplying the sample, and Dr. Elder and his staff of the S.R.C. Microdensitometer Service for scanning the films and supplying a list of indexed reflections corrected for absorption. Subsequent computing was carried out using programs of the SCXR series written by one of us (J. A. D. J.) run on the ICL 1904 computer at the University of Strathclyde.

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