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X-RAY COMPARISON OF THE MOLECULAR STRUCTURES OF 4*a*-METHYL-1,3,9-TRIPHENYL-4*a*-*H*-FLUORENE AND ITS $Fe(CO)_3$ COMPLEX

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Summary

4*a*-Methyl-1,3,9-triphenyl-4*a*-*H*-fluorene, which is a tetrameric product formed on vigorous dehydration of acetophenone, has structure **1**, in which rings A and B form an indene fragment, the diene ring C approximates to half-chair configuration, and the three phenyl rings, D, E, and F, are considerably rotated relative to rings B,C about their connecting bonds. In the $Fe(CO)_3$ complex, **3**, a marked change has occurred in the conformation of ring C to allow Fe coordination on the side opposite to the methyl group. The complexed Fe–C distances are 2.117, 2.049, 2.067, 2.220 Å, and there are marked changes in the bond lengths in the complexed diene, but all other bond lengths correspond closely in the two molecules. **1** ($C_{32}H_{24}$) is triclinic, a 12.506, b 10.237, c 10.121 Å, α 108.53, β 84.93, γ 112.32°; space group $P\bar{1}$, $Z = 2$. The complex, $C_{32}H_{24}Fe(CO)_3$, is monoclinic, a 30.283, b 12.709, c 14.514 Å, β 92.73°; space group $B2_1/c$, $Z = 8$.

Introduction

Vigorous dehydration of acetophenone using polyphosphoric acid yields a tetrameric product, $C_{32}H_{24}$, which was assigned formula **1** by the original investigators [1–5]. They considered formula **2** and adduced evidence against it [1], but it was not rigorously excluded. As knowledge of the stereochemistry of the compound was important to the researches of Professor C.W. Rees and his colleagues of this Department, and, as all spectroscopic and other studies had failed to distinguish between **1** and **2** or other less likely postulates, an X-ray study was undertaken with crystals supplied by Professor Rees' coworkers. This has established **1** as the correct structure.

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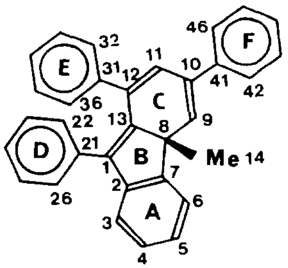

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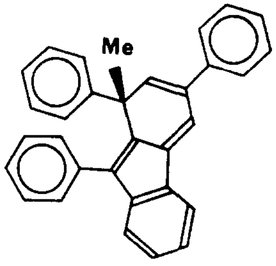

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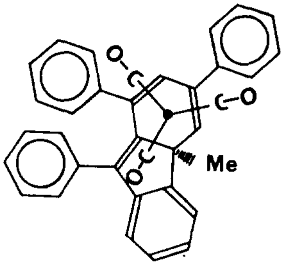

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Before the X-ray results on **1** were complete, crystals of its $Fe(CO)_3$ complex (**3**) became available, also from Professor Rees' coworkers. Consideration of models showed that access to the diene ring in **1** is very hindered, by the methyl group on one side and by the phenyl groups, especially ring F, on the other. Complexation with the diene could, therefore, occur only if the molecule underwent a major conformational change. Alternatively, complexation might occur so as to involve one of the double bonds of the diene and part of an adjoining phenyl ring. As the complex appeared to be quite stable, and in view of the general stabilizing effects of $Fe(CO)_3$ complexation, it was thought worthwhile to extend the X-ray work to this too. This has shown, see Fig. 3 and 4, that the complexation involves the four atoms of the diene and that the diene ring changes to a deformed boat conformation with consequential changes in the relative dispositions of the phenyl groups. For convenience the tetramer **1** will be termed T and its $Fe(CO)_3$ complex FeT.

Experimental

Accurate unit-cell parameters were obtained by least-squares refinement of 29 (T), 21 (FeT), high-angle α_1 reflexions measured at ca. 10°C on a diffractometer using Cu-K_α radiation. The cell chosen for FeT and used throughout was morphologically convenient but non-standard.

Crystal data

T: $C_{32}H_{24}$, $M = 408.5$; yellow blocky crystals from petroleum + ca. 5% benzene; triclinic, a 12.506(3), b 10.237(3), c 10.121(2) Å, α 108.53(3), β 84.93(3), γ 112.32(3)°;

U 1135.6 Å^3; D_c 1.19 g cm^{-3}; $Z = 2$; $F = 432$. Space group $P\bar{1}$ (No.2) from intensity statistics and later confirmed by structure solution. Cu-K_α radiation, λ 1.5418 Å, μ(Cu-K_α) 6.18 cm^{-1}.

FeT: $C_{32}H_{24}Fe(CO)_3$, $M = 548.4$; red prisms from (40–60°) petroleum ether; monoclinic, a 30.283(2), b 12.709(1), c 14.514(1) Å, β 92.73(1)°; U 5579.6 Å^3; D_c 1.31 g cm^{-3}; $Z = 8$; $F = 2272$. Space group $B2_1/c$, uniquely from absences. (The Delaunay reduced cell is a 16.476, b 12.709, c 14.514 Å, β 133.37°; $P2_1/c$.) μ(Cu-K_α) 50.2 cm^{-1}.

The reflexion intensities were measured on a Siemens automatic four-circle diffractometer. A crystal of approximate dimensions (T: 0.40 × 0.25 × 0.15 mm^3; FeT: 1.0 × 0.5 × 0.35 mm^3) was mounted with c (for both T and FeT) parallel to the ϕ axis. Filtered Cu-K_α radiation was used with Na(Tl)I scintillation counter. 3384 (T), 4152 (FeT) independent reflexions were measured to θ 60° (for T and FeT) using the θ–2θ scan technique and the "five-value" measuring procedure. Of these

TABLE 1

FRACTIONAL COORDINATES (×10^4) FOR THE NON-HYDROGEN ATOMS, IN COMPOUND T, WITH ESTIMATED STANDARD DEVIATIONS

Atom	*x*	*y*	*z*
C(1)	7033(2)	2316(2)	836(2)
C(2)	6652(2)	1095(2)	1448(2)
C(3)	6550(2)	−380(3)	876(3)
C(4)	6237(2)	−1276(3)	1735(3)
C(5)	6021(2)	−724(3)	3131(3)
C(6)	6118(2)	746(3)	3700(3)
C(7)	6437(2)	1641(2)	2861(2)
C(8)	6592(2)	3253(2)	3192(2)
C(9)	7463(2)	4373(3)	4353(2)
C(10)	8058(2)	5749(2)	4287(2)
C(11)	7901(2)	6138(3)	3059(2)
C(12)	7419(2)	5101(2)	1839(2)
C(13)	7006(2)	3555(2)	1827(2)
C(14)	5402(2)	3408(3)	3550(3)
C(21)	7459(2)	2167(2)	−595(2)
C(22)	8526(2)	3145(3)	−841(3)
C(23)	8916(2)	3012(3)	−2186(3)
C(24)	8246(3)	1884(4)	−3299(3)
C(25)	7197(3)	896(3)	−3068(3)
C(26)	6793(2)	1028(3)	−1731(2)
C(31)	7311(2)	5489(2)	579(2)
C(32)	8138(2)	6723(3)	289(3)
C(33)	7996(3)	7094(3)	−868(3)
C(34)	7039(3)	6245(3)	−1751(3)
C(35)	6223(3)	5018(3)	−1487(3)
C(36)	6353(2)	4637(3)	−330(3)
C(41)	8904(2)	6908(3)	5409(2)
C(42)	9599(2)	6534(3)	6107(3)
C(43)	10428(2)	7614(3)	7109(3)
C(44)	10556(2)	9076(3)	7444(3)
C(45)	9854(3)	9467(3)	6800(3)
C(46)	9040(3)	8390(3)	5778(3)

367 (T) and 882 (FeT) reflexions had $I < 2.58\sigma(I)$ and were classed as unobserved [6]. The $6\bar{1}0$ (T) and 840 (FeT) reflexions were monitored as a reference every 50 reflexions and in neither case was any significant deterioration observed over some 5 days for each specimen. The intensities were scaled by use of the reference reflexions and corrections were applied only to the data for FeT, a $12 \times 12 \times 12$ grid being used with Gaussian integration [7] and crystal path lengths determined by the vector-analysis procedure [8].

TABLE 2

FRACTIONAL COORDINATES ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS IN COMPOUND FeT WITH ESTIMATED DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*
Fe	3019(0)	2522(0)	2997(0)
O(1)	3490(1)	1878(3)	4710(2)
O(2)	2780(1)	4695(2)	3426(2)
O(3)	2136(1)	1701(3)	3296(2)
C(51)	3301(1)	2134(3)	4053(2)
C(52)	2873(1)	3849(3)	3261(2)
C(53)	2479(1)	2045(3)	3196(2)
C(1)	4249(1)	1819(3)	3095(2)
C(2)	4254(1)	695(3)	3340(2)
C(3)	4547(1)	131(3)	3921(2)
C(4)	4458(1)	−923(3)	4078(3)
C(5)	4093(1)	−1405(3)	3667(3)
C(6)	3803(1)	−854(3)	3062(3)
C(7)	3886(1)	198(2)	2915(2)
C(8)	3663(1)	972(2)	2252(2)
C(9)	3168(1)	1134(2)	2270(2)
C(10)	2986(1)	1945(2)	1678(2)
C(11)	3240(1)	2885(2)	1710(2)
C(12)	3631(1)	2947(2)	2301(2)
C(13)	3889(1)	1997(2)	2520(2)
C(14)	3783(1)	646(3)	1253(2)
C(21)	4576(1)	2561(2)	3514(2)
C(22)	4622(1)	2659(3)	4471(2)
C(23)	4932(1)	3344(3)	4868(3)
C(24)	5200(1)	3923(3)	4325(3)
C(25)	5163(1)	3828(3)	3378(3)
C(26)	4850(1)	3154(3)	2977(2)
C(31)	3844(1)	4013(2)	2401(2)
C(32)	3908(1)	4510(3)	3260(2)
C(33)	4116(1)	5478(3)	3313(3)
C(34)	4257(2)	5969(3)	2531(3)
C(35)	4193(1)	5487(3)	1692(3)
C(36)	3986(1)	4516(3)	1625(2)
C(41)	2573(1)	1835(3)	1090(2)
C(42)	2290(1)	2677(3)	915(3)
C(43)	1913(1)	2568(4)	345(3)
C(44)	1812(1)	1612(5)	−49(3)
C(45)	2083(2)	772(4)	126(3)
C(46)	2467(1)	869(3)	694(3)

Solution and refinement

Both structures were solved by direct methods, applying the MULTAN program [9] to 250 reflexions in each case, $E < 1.84$ for T and 1.815 for FeT. In each case the E map for the phase solution with the highest combined figure of merit revealed all 32 (T) or 39 (FeT) non-hydrogen atoms in the molecules. Isotropic refinement gave $R = 0.136$ (T), 0.133 (FeT), which for the latter fell to 0.114 after the absorption correction. Anisotropic refinement with allowance for the anomalous dispersion of iron gave $R = 0.113$ (T) and 0.089 (FeT). A number of strong low-angle reflexions were judged to be affected by extinction and were excluded from subsequent refinement; they were: T $1\bar{2}0$, $2\bar{1}0$, $\bar{3}11$, 201: FeT, 1000, $\bar{6}02$, $\bar{2}02$, 002, 210, 412, 020, 220, 620. The 24 hydrogen atoms in each molecule were located either from a $\Delta\rho$ map or by calculation. They were isotropically refined in T, but in FeT they were included as fixed-atom contributions with isotropic temperature factors equivalent to those of the carbon atoms to which each was attached. For T the final R factor was 0.043, for which the maximum shift/error ratios for carbon and hydrogen were 0.074 and 0.091 respectively. The final difference Fourier synthesis was featureless, with a maximum residual electron density of 0.14 e Å^{-3}. Unit weights were used for T: nothing more elaborate seemed to be called for. For FeT, however, a Hughes-type

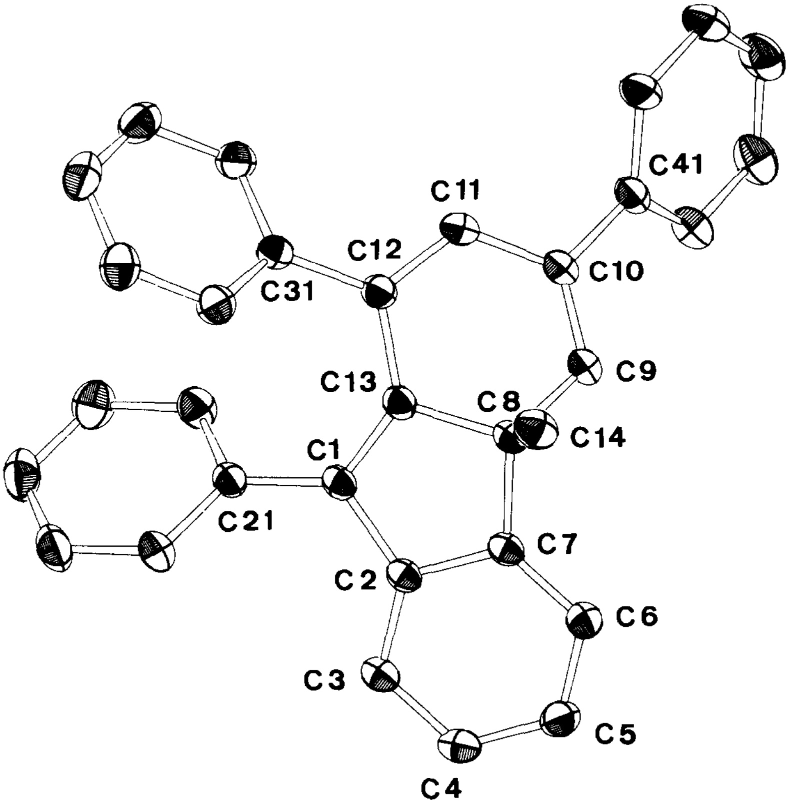

Fig. 1. Plan view of a molecule of T. The numbering scheme is the same as that shown in the diagram 1.

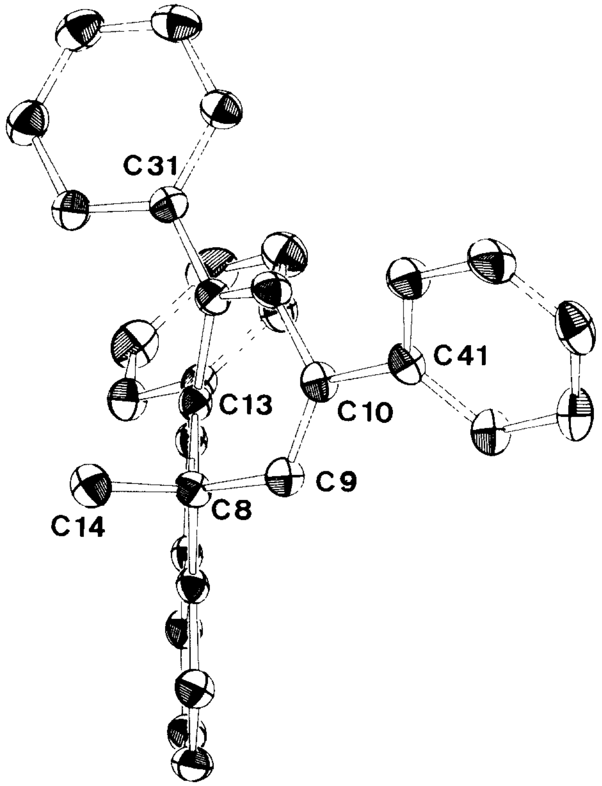

Fig. 2. Edge view of a molecule of T.

weighting scheme [10] was used: $w = 1$ for $F < F^\star$, $w = F^\star/F$ for $F \geqslant F^\star$, with $F^\star = 70$. The final R was 0.045. The maximum shift/error ratios were 0.55 for two U values for the iron atom, but all others were much smaller. Here the final difference synthesis contained no regions in excess of 0.26 e Å^{-3}. The atomic scattering factors used were those given by Doyle and Turner [11], except in the case of hydrogen for which the values were those given by Stewart et al. [12].

An up-dated version (April, 1974) of XRAY72 was used for the refinement [13]. The calculations were carried out on the University of London's CDC 7600 computer. Structural illustrations were drawn with the aid of the Imperial College CDC Cyber 174 computer using the program ORTEP [14].

The coordinates of T are given in Tables 1a, 2a and those for FeT in Tables 1b, 2b. Tables of hydrogen coordinates, thermal parameters and structure factors are available from the authors upon request.

Discussion

Figures 1–4 display various aspects of these two molecules. They confirm the structure of T as **1**, but reveal considerable conformational differences between T and FeT. Nevertheless, comparison of bond lengths and angles shows that the effects

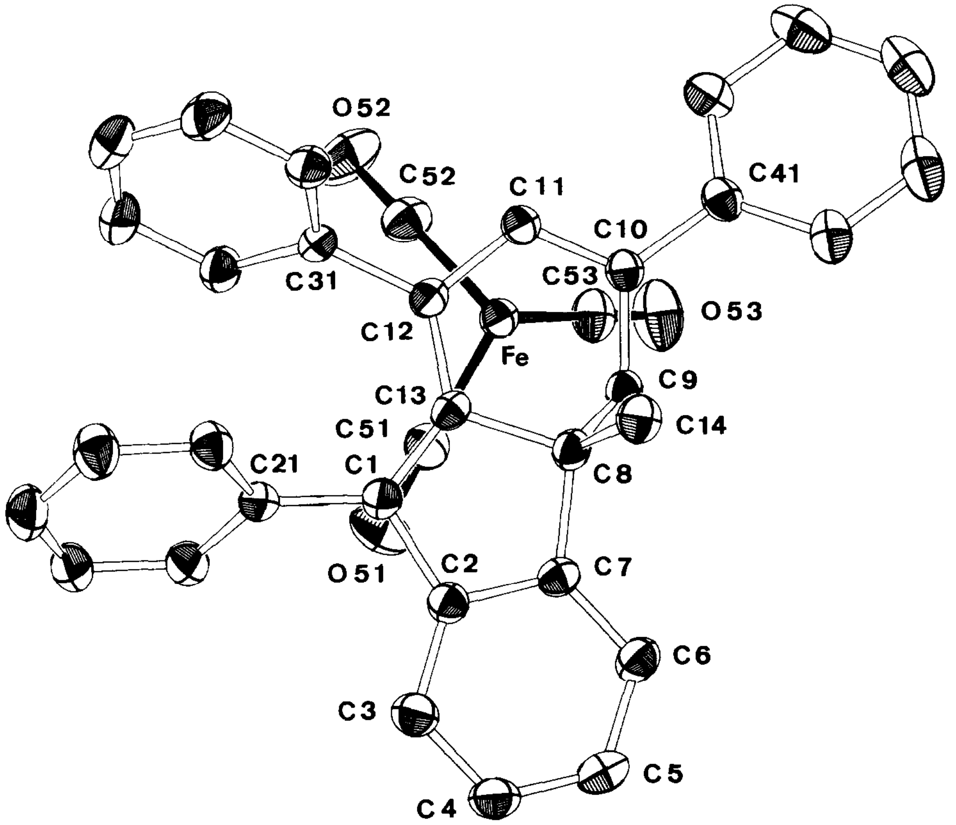

Fig. 3. Plan view of a molecule of FeT, with the same numbering scheme as for T.

of complexation on these quantities are quite localised, and that elsewhere there is a high degree of concordance.

Table 3 compares the bond lengths. In T they fall into distinct categories with good internal consistency, as shown by the averages and standard error of the means given in Table 3. This means that the bond pattern depicted in **1** is a faithful representation of T. The uniformity of bond lengths in the aromatic rings is good internal evidence for accuracy. In FeT, it is noteworthy that the changes of bond length due to complexation are apparently confined to four bonds. Elsewhere none of the discrepancies between the molecules is statistically significant, and the last two lines of Table 3 show that the discrepancies are essentially random. The four starred entries in Table 3, together with the third line from the bottom in Table 3, however, show how large are the alterations due to complexing, and that even the bond linking the diene to ring E is significantly affected. If one compares the averages and their standard errors for FeT with those of T (see Table 3) it is evident that the sharply defined distinctions in T are blurred in FeT. Indeed, the three bonds constituting the diene are statistically hardly distinguishable in the complex despite the somewhat lop-sided coordination. Moreover, although C(10) remains accurately flat (sum of the angles 360.0°), C(12) becomes appreciably pyramidal (angle-sum

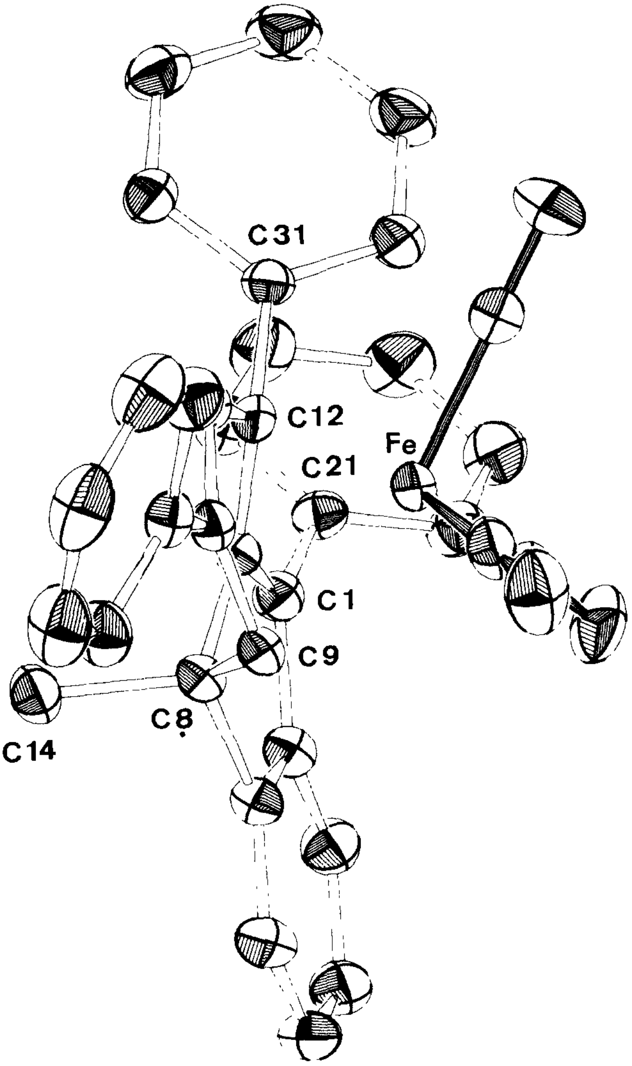

Fig. 4. Edge view of a molecule of FeT.

356.7°) to an extent which is visible in some of the Figures. The C(12)–C(31) bond increases from 1.482 Å (typical of $C_{sp^2,\mathrm{arom}}-C_{sp^2,\mathrm{non\text{-}arom}}$) to 1.505 Å, which approaches the $C_{sp^2}-C_{sp^3}$ length. This may be due partly to a steeper tilt of ring E (vide infra) with consequent weaker conjugation, as well as to the partial sp^3 hybridization at C(12).

Table 4 compares the valence angles, and the footnote gives averages for various groups. Here again the discrepancies at all atoms except C(9), C(10), C(11), C(12) suggest a low level of near-random fluctuations, but at these four atoms much larger changes are evident. The effect is not as marked as with the bond lengths, but is just as localised.

TABLE 3

BOND LENGTHS (Å)

	T	FeT		T	FeT
Fe–C(9)		2.117(3)	Fe–C(51)		1.789(3)
Fe–C(10)		2.049(3)	Fe–C(52)		1.788(4)
Fe–C(11)		2.067(3)	Fe–C(53)		1.780(4)
Fe–C(12)		2.220(3)	C(51)–O(1)		1.137(4)
C(1)–C(2)	1.470(4)	1.473(5)	C(52)–O(2)		1.141(5)
C(2)–C(3)	1.393(3)	1.394(5)	C(53)–O(3)		1.142(5)
C(3)–C(4)	1.388(4)	1.387(5)	C(21)–C(22)	1.389(3)	1.395(5)
C(4)–C(5)	1.389(4)	1.375(5)	C(22)–C(23)	1.388(4)	1.385(5)
C(5)–C(6)	1.391(4)	1.400(5)	C(23)–C(24)	1.382(4)	1.372(6)
C(6)–C(7)	1.370(4)	1.378(5)	C(24)–C(25)	1.374(4)	1.379(6)
C(7)–C(8)	1.514(3)	1.513(4)	C(25)–C(26)	1.385(4)	1.384(5)
C(7)–C(2)	1.403(3)	1.396(4)	C(26)–C(21)	1.398(3)	1.388(5)
C(8)–C(9)	1.518(3)	1.515(4)	C(31)–C(32)	1.394(3)	1.403(5)
C(8)–C(13)	1.515(3)	1.514(4)	C(32)–C(33)	1.384(5)	1.382(5)
C(8)–C(14)	1.555(4)	1.566(5)	C(33)–C(34)	1.376(4)	1.380(6)
C(9)–C(10)*	1.340(3)	1.435(4)	C(34)–C(35)	1.372(4)	1.369(6)
C(10)–C(11)*	1.469(4)	1.421(4)	C(35)–C(36)	1.386(5)	1.385(5)
C(11)–C(12)*	1.352(3)	1.430(4)	C(36)–C(31)	1.391(3)	1.383(5)
C(12)–C(13)	1.462(3)	1.464(4)	C(41)–C(42)	1.390(5)	1.387(5)
C(13)–C(1)	1.355(3)	1.360(4)	C(42)–C(43)	1.389(3)	1.385(5)
C(1)–C(21)	1.480(3)	1.477(4)	C(43)–C(44)	1.374(5)	1.370(8)
C(12)–C(31)*	1.482(4)	1.505(4)	C(44)–C(45)	1.374(5)	1.362(7)
C(10)–C(41)	1.490(3)	1.487(4)	C(45)–C(46)	1.390(3)	1.399(6)
			C(46)–C(41)	1.388(4)	1.388(5)

Average values of C–C bond lengths and standard errors of the means

		T	FeT	Lit. values
$C_{sp^2,arom}-C_{sp^2,nonarom}$	(4)	1.481(4)	1.486(7)	
$C_{sp^2,nonarom}-C_{sp^2,nonarom}$	(2)	1.466(2)	1.443(22)	1.49
$C_{sp^2,nonarom}=C_{sp^2,nonarom}$	(3)	1.349(5)	1.408(24)	1.337
$C_{sp^2}-C_{sp^3}$	(3)	1.516(1)	1.514(1)	1.516
$C_{sp^2,arom}-C_{sp^2,arom}$	(24)	1.386(2)	1.385(2)	
Ring D	(6)	1.386(3)	1.384(3)	
Ring E	(6)	1.384(3)	1.384(4)	1.395
Ring F	(6)	1.384(3)	1.382(5)	

For the four starred C–C bonds in col. 1	$\lvert\langle\Delta\rangle\rvert = 0.037$;	$\langle\lvert\Delta\rvert\rangle = 0.061$
For the remaining 15 C–C bonds in col. 1	$= 0.0005$;	$= 0.005$
For the 18 aromatic C–C bonds in col. 2	$= 0.0016$;	$= 0.005$
	$(\ \Delta = l(\mathrm{T}) - l(\mathrm{FeT}))$	

The aromatic rings A, D, E and F are flat with r.m.s. deviations (in mÅ) of

	A	D	E	F
T	2.5	4.5	3.0	8.9
FeT	7.6	3.6	2.2	4.4

TABLE 4

BOND ANGLES (degrees)

	T	FeT		T	FeT
C(2)–C(1)–C(13)	108.5(2)	107.9(3)	C(1)–C(21)–C(22)	121.0(2)	120.1(3)
C(2)–C(1)–C(21)	123.2(2)	121.4(3)	C(1)–C(21)–C(26)	120.4(2)	121.5(3)
C(13)–C(1)–C(21)	128.2(2)	130.5(3)	C(22)–C(21)–C(26)	118.6(2)	118.5(3)
C(1)–C(2)–C(3)	130.9(2)	130.1(3)	C(21)–C(22)–C(23)	120.8(2)	120.3(3)
C(1)–C(2)–C(7)	109.0(2)	109.5(3)	C(22)–C(23)–C(24)	119.9(2)	120.4(3)
C(3)–C(2)–C(7)	120.0(2)	120.4(3)	C(23)–C(24)–C(25)	119.8(3)	120.2(3)
C(2)–C(3)–C(4)	118.5(2)	118.3(3)	C(24)–C(25)–C(26)	120.8(2)	119.7(4)
C(3)–C(4)–C(5)	121.0(2)	121.1(3)	C(25)–C(26)–C(21)	120.1(2)	121.0(3)
C(4)–C(5)–C(6)	120.6(3)	121.1(3)	C(12)–C(31)–C(32)	121.5(2)	122.2(3)
C(5)–C(6)–C(7)	118.8(2)	117.9(3)	C(12)–C(31)–C(36)	120.1(2)	119.1(3)
C(6)–C(7)–C(8)	130.0(2)	130.5(3)	C(36)–C(31)–C(32)	118.3(3)	118.7(3)
C(6)–C(7)–C(2)	121.2(2)	121.2(3)	C(31)–C(32)–C(33)	120.4(2)	119.6(3)
C(2)–C(7)–C(8)	108.8(2)	108.0(3)	C(32)–C(33)–C(34)	120.5(3)	121.0(4)
C(7)–C(8)–C(9)	117.0(2)	119.4(3)	C(33)–C(34)–C(35)	119.8(3)	119.5(4)
C(7)–C(8)–C(13)	102.2(2)	102.3(2)	C(34)–C(35)–C(36)	120.4(3)	120.4(4)
C(9)–C(8)–C(13)	109.0(2)	108.3(2)	C(35)–C(36)–C(31)	120.6(2)	120.8(3)
C(7)–C(8)–C(14)	109.1(2)	107.5(3)	C(10)–C(41)–C(42)	120.6(2)	122.0(3)
C(9)–C(8)–C(14)	108.3(2)	109.0(2)	C(10)–C(41)–C(46)	121.5(3)	119.5(3)
C(13)–C(8)–C(14)	111.0(2)	110.1(3)	C(46)–C(41)–C(42)	117.9(2)	118.5(3)
C(8)–C(9)–C(10)*	119.7(2)	116.0(3)	C(41)–C(42)–C(43)	121.1(3)	121.2(4)
C(9)–C(10)–C(11)*	119.7(2)	113.2(3)	C(42)–C(43)–C(44)	119.9(3)	119.9(4)
C(9)–C(10)–C(41)*	122.3(2)	124.4(3)	C(43)–C(44)–C(45)	120.0(2)	119.8(4)
C(11)–C(10)–C(41)*	118.1(2)	122.5(3)	C(44)–C(45)–C(46)	120.0(3)	121.1(4)
C(10)–C(11)–C(12)*	122.5(2)	119.8(3)	C(45)–C(46)–C(41)	121.0(3)	119.5(4)
C(11)–C(12)–C(13)*	116.0(2)	120.2(3)	C(51)–Fe–C(52)		100.9(2)
C(11)–C(12)–C(31)*	122.6(2)	116.5(3)	C(52)–Fe–C(53)		92.8(2)
C(13)–C(12)–C(31)*	121.4(2)	120.0(3)	C(53)–Fe–C(51)		99.9(2)
C(12)–C(13)–C(1)	131.4(2)	132.3(3)	Fe–C(51)–O(1)		178.0(3)
C(12)–C(13)–C(8)	116.8(2)	115.1(3)	Fe–C(52)–O(2)		179.8(3)
C(1)–C(13)–C(8)	111.4(2)	110.7(3)	Fe–C(53)–O(3)		176.8(3)

Averages of C–C–C angles	$\lvert\langle\Delta\rangle\rvert$	$\langle\lvert\Delta\rvert\rangle$
For the eight starred angles	1.2	3.8
For the remaining 22 non-aromatic angles	0.1	0.9
For the 24 aromatic angles	0.1	0.7
	($\Delta = \theta(\mathrm{T}) - \theta(\mathrm{FeT})$)	

Ring B is a very shallow envelope in both molecules but with different atoms as the flap. In T it is C(7) which deviates by only 64 mÅ from the plane of the other four atoms (r.m.s. deviation 1.7 mÅ). In FeT it is C(8), 193 mÅ from the rest (r.m.s. 4.0 mÅ). There is a slight but significant departure from planarity at both C(2) and C(7): on complexing the former does not change but the latter does. Thus, the deviations in mÅ from ring A are

	C(1)	C(8)
T	+79	−16
FeT	+85	−134

The diene ring C undergoes a marked change as shown by the torsion angles in Table 5. Thus, in T ring C has an approximate C_2 symmetry axis through the midpoints of the C(10)–C(11) and C(8)–C(13) bonds, the diene torsion angle is −17.4°, and C(8) and C(13) diverge from the plane through the other four atoms (r.m.s. 56 mÅ) by −364 and +237 mÅ respectively. In FeT, however, C(9), C(10), C(11) and C(12) are accurately coplanar (r.m.s. 2.1 mÅ) with C(8) and C(13) deviating to the same side of this plane by −956 and −612 mÅ respectively, so that ring C approximates to a boat. The changes in ring C induce a marked flattening into the ABC ring system in FeT and appear to be responsible for the switch in the conformation of ring B: they are best appreciated by comparing Fig. 2 and 4. The changes in ring C also cause large shifts in the major axes of rings D, E and F, thus exposing the face of the diene to allow complexation. Furthermore, to avoid collision with the CO groups, rings D, E and F all rotate clockwise around their major axes (i.e., the bonds attaching them to rings B, C). As a result, the lack-of-conjugation tilt for each of these rings changes as follows:

D 51 → 120°
E 36 → 110°
F 36 → 146°

In accord with these changes, C(1) is apparently non-planar in both molecules C(12) is flat in T but appreciably pyramidal in FeT as described above; and C(10) is closely flat in both molecules. Thus, the tendency toward sp^3 hybridization increases directly with decreasing conjugation.

Table 6 compares the complexes Fe–C distances and the Fe–C≡O average geometries in FeT with those in some other diene-iron complexes. In all the complexes except IV, the middle two Fe–C bonds are shorter than the other two. In compound IV the π-bonding effect is extended to a further carbon atom. The geometry of the three Fe–C≡O groups is similar to that in the quoted examples and

TABLE 5

TORSION ANGLES IN T AND FeT (degrees)

	T	FeT
C(13)–C(1)–C(2)–C(7)	−2.4	−1.0
C(1)–C(2)–C(7)–C(8)	4.2	8.5
C(2)–C(7)–C(8)–C(13)	−4.2	−11.9
C(7)–C(8)–C(13)–C(1)	2.8	11.7
C(2)–C(1)–C(13)–C(8)	0	−7.1
C(9)–C(8)–C(13)–C(12)	−46.2	−28.0
C(13)–C(8)–C(9)–C(10)	32.4	58.4
C(8)–C(9)–C(10)–C(11)	−2.9	−44.2
C(9)–C(10)–C(11)–C(12)	−17.3	0
C(10)–C(11)–C(12)–C(13)	2.9	29.4
C(11)–C(12)–C(13)–C(8)	30.0	−12.3
C(7)–C(2)–C(3)–C(4)	0	−1.3
C(2)–C(3)–C(4)–C(5)	0	0
C(3)–C(4)–C(5)–C(6)	0	1.2
C(4)–C(5)–C(6)–C(7)	0	−2.2
C(5)–C(6)–C(7)–C(2)	0	1.4
C(3)–C(2)–C(7)–C(6)	0	0

TABLE 6

COMPARISON OF THE LENGTHS OF THE FOUR COMPLEXED Fe–C BONDS, AND THE Fe–C≡O AVERAGE GEOMETRY IN FeT (in Å and degrees) WITH VALUES FOUND IN SOME OTHER DIENE-IRON COMPLEXES

		Fe–C^1	Fe–C^2	Fe–C^3	Fe–C^4	Fe–C_c [a]	Fe–C≡O [b]	C≡O [c]	Ref.
FeT	$[Fe(CO)_3(C_{32}H_{24})]$	2.117	2.049	2.067	2.220	1.786	178.2	1.140	This work
I	$[Fe(CO)_3(C_{11}H_{16}O_4)]$	2.112	2.070	2.092	2.087	1.788	178.4	1.137	15
II	$[Fe(CO)_3(C_{10}H_{12}O_4)]$	2.095	2.049	2.058	2.092	1.793	176.5	1.130	16
III	$[Fe(CO)_3(C_{16}H_{16})]$	2.117	2.065	2.076	2.153	1.794	178.2	1.147	17
IV	$[Fe(CO)_3(C_{10}H_{15})](PF_6)$	2.191	2.088	2.199	2.098	1.824	178.6	1.120	18

[a] Average Fe–C_c (carbonyl) bond length. [b] Average Fe–C≡O bond angle. [c] Average C≡O bond length.

in many other tricarbonyliron complexes [19]. The observed differences in IV for Fe–C_c and C≡O were thought probably to be caused by increased back-donation of electron density from Fe^0 compared to Fe^{II} in this compound [18].

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