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# CONFORMATIONS OF FUSED CYCLOALKANES IN ORGANOMETALLIC COMPOUNDS

## III*. THE CRYSTAL AND MOLECULAR STRUCTURES OF TRICYCLO-[6.2.0.$0^{2,7}$]DECA-3,5-DIENETRICARBONYLIRON, $(C_{10}H_{12})Fe(CO)_3$

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## Summary

The structure of tricyclo[6.2.0.$0^{2,7}$]deca-3,5-dienetricarbonyliron, $(C_{10}H_{12})Fe(CO)_3$, has been determined from X-ray counter data. The space group is $P2_12_12_1$ with cell dimensions $a$ 11.758(3), $b$ 16.987(7), $c$ 6.032(2) Å and with four molecules in the cell. The 1359 reflections, in the range $0° < 2\theta(\text{Mo-}K\alpha) \leqslant 45°$, with intensities significantly above background were included in the refinement which converged to $R_1 = 0.033$ and $R_2 = 0.029$. The molecular structure consists of an $Fe(CO)_3$ moiety bonded to the diene portion of a cyclohexadiene ring. This six-membered ring is fused to a second four-membered ring. Both four-membered rings are essentially planar.

## Introduction

A series of iron and molybdenum carbonyl derivatives (compounds I—VII, XII), of polycyclic olefins have recently been prepared and investigated by IR and NMR spectroscopy [1] and by X-ray diffraction [2—8]. Some of these structures are of particular interest because of the information they provide about the conformations of the cyclobutane ring when it is fused to other rings [9]. Compound IV, whose structure is described in this paper is a case in point. While the general structure (IV), has been deduced, correctly, from chemical and spectroscopic evidence [1], the conformational details required for a comprehensive conformational analysis of cyclobutane compounds [9] had to be obtained by X-ray crystallography. The necessary investigation of IV is described here.

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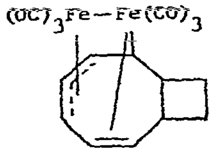

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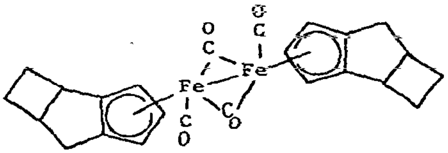

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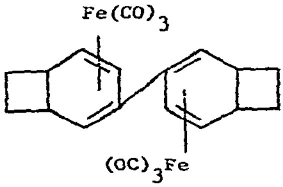

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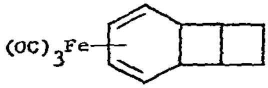

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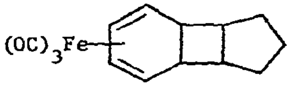

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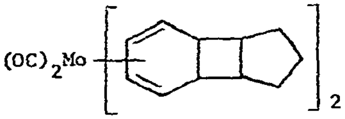

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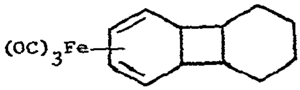

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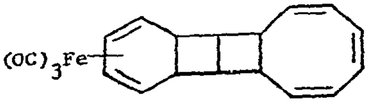

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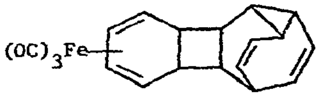

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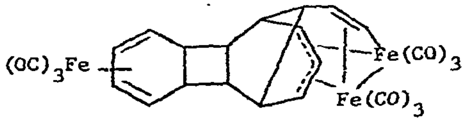

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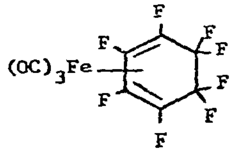

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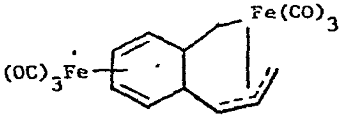

(XII)

## Experimental section

### *Collection and reduction of X-ray data*

A microcrystalline sample of the title compound was prepared by Dr. G. Deganello as previously described [1]. A single crystal suitable for data collection, measuring 0.13 × 0.20 × 0.27 mm, was obtained by recrystallization from carbon disulfide. The crystal was mounted on a thin glass fiber and from preliminary diffractometer examination shown to be orthorhombic. Systematic absences of $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; and $00l$, $l \neq 2n$, uniquely determined the space group as $P2_12_12_1$.

The unit cell dimensions at 22° and the orientation matrix for data collection were determined by least squares refinement of the setting angles for fifteen carefully centered reflections. The cell dimensions and other data are: $a$ 11.758(3), $b$ 16.987(7), $c$ 6.032(2) Å, $V$ 1204.7(7) Å$^3$, $Z = 4$, $d_{calc} = 1.50$ g cm$^{-3}$. $\omega$ scans of several intense reflections showed a width at half height of 0.25°.

The data were collected using a Syntex $P\bar{1}$ diffractometer with an incident-beam graphite-crystal monochromator and Mo-$K\alpha$ radiation. The operation of the diffractometer has been described previously [5]. Intensity measurements were taken at 22° using the $\theta$—$2\theta$ scan technique and a variable scan rate ranging from 2.0 to 24.0°/min depending on the intensity of the reflection. All data of the type $hkl$ and $\bar{h}\bar{k}\bar{l}$ with $2\theta$(Mo-$K\alpha$) values up to 45.0° were collected using a scan range from $2\theta$(Mo-$K\alpha_1$) — 0.8° to $2\theta$(Mo-$K\alpha_2$) + 0.8°. Three standard reflections, measured every 100 reflections, showed no significant change in intensity throughout the data collection. No absorption correction was made in view of the small variation in transmission factors of 81.1 ± 3.6% through the thin and thick directions of the crystal ($\mu = 12.8$ cm$^{-1}$ for Mo-$K\alpha$). Lorentz and polarization corrections were made*; no extinction correction was deemed necessary. A total of 1994 reflections were collected and only the 1359 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used for the refinement of the structure.

*Solution and refinement of the structure*

The iron atom was located using the Patterson method and its position was refined by least-squares, giving the following agreement factors: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.308$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.352$. Here $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and $w$ is the weighting factor, given by $4F_o^2/\sigma^2$, where $\sigma$ is the e.s.d. of $F_o^2$. Scattering factors were taken from the International Tables [10]. Anomalous dispersion effects were included for the iron using $\Delta f'$ and $\Delta f''$ values of Cromer and Liberman [11].

A difference Fourier map based on the phases derived from the iron atom position revealed the coordinates of all the remaining non-hydrogen atoms. Two cycles of isotropic least-squares refinement of all non-hydrogen atoms lead to the agreement indices of $R_1 = 0.059$ and $R_2 = 0.066$. A second difference Fourier map based on the above refinement showed clearly the positions of all the hydrogen atoms. Three full-matrix least-squares cycles refining non-hydrogen atoms anisotropically and hydrogen atoms isotropically converged to the final agree-

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* Computer programs used in reduction of the data and in the solution and refinement of the structure are the following: DATARED by Frenz for data reduction; JIMDAP, a Fourier program by Ibers, based on FORDAP by Zalkin; the least-squares program NUCLS by Doedens and Ibers based on Busing and Levy's ORFLS program; a local modification of Baur's SADIAN program for calculating atomic distances and angles; RSCAN by Doedens for analysing structure factors; ORTEP by Johnson for illustrations; the function and error program ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson and Thiessen; and LIST by Snyder for listing the data.

ment indices of $R_1 = 0.033$ and $R_2 = 0.029$. In the final cycle no parameter shift exceeded 0.7 times the standard deviation of the parameter. The e.s.d. in an observation of unit weight was 1.01.

To check for the correct enantiomorph the sign of the secondary anomalous dispersion factor for the iron atom was reversed in one cycle of least-squares refinement. The agreement factors of $R_1 = 0.041$ and $R_2 = 0.048$ clearly show that the original choice of enantiomorph was correct.

No systematic trends were found in the data as a function of $\lambda^{-1}\sin\theta$, $|F_o|$, indices or reflection number. A final difference Fourier map contained no peaks greater than 0.44 $e$ Å$^{-3}$, where hydrogen atoms were located on a previous map at 0.54 $e$ Å$^{-3}$. A list of observed and calculated structure factor amplitudes is available*. The atomic coordinates and their estimated standard deviations are given in Table 1. The thermal parameters are given in Table 2.

TABLE 1

ATOMIC POSITIONAL PARAMETERS[a]

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Fe | 0.2165(1) | 0.2058(1) | 0.1614(1) |
| O(1) | 0.0164(3) | 0.1978(3) | 0.4441(6) |
| O(2) | 0.3889(4) | 0.1294(2) | 0.4375(8) |
| O(3) | 0.1854(4) | 0.0662(3) | −0.1174(8) |
| C(1) | 0.0966(6) | 0.4309(4) | −0.0383(12) |
| C(2) | 0.0793(5) | 0.3478(3) | 0.0637(10) |
| C(3) | 0.1323(6) | 0.2819(4) | −0.0625(10) |
| C(4) | 0.2497(5) | 0.2783(4) | −0.1001(11) |
| C(5) | 0.3165(5) | 0.3994(4) | 0.0787(12) |
| C(6) | 0.2578(4) | 0.3201(3) | 0.2736(10) |
| C(7) | 0.1528(5) | 0.3706(3) | 0.2632(9) |
| C(8) | 0.1723(5) | 0.4537(3) | 0.1611(12) |
| C(9) | 0.0844(8) | 0.5171(5) | 0.2282(15) |
| C(10) | 0.0102(8) | 0.4913(5) | 0.0350(18) |
| C(11) | 0.0961(4) | 0.1992(3) | 0.3364(11) |
| C(12) | 0.3211(5) | 0.1582(3) | 0.3285(12) |
| C(13) | 0.1976(6) | 0.1210(3) | −0.0085(10) |
| H(1) | 0.123(4) | 0.432(3) | 0.173(8) |
| H(2) | 0.001(4) | 0.339(2) | 0.087(7) |
| H(3) | 0.095(4) | 0.260(2) | −0.167(8) |
| H(4) | 0.284(5) | 0.259(3) | −0.233(8) |
| H(5) | 0.390(4) | 0.291(3) | 0.087(7) |
| H(6) | 0.303(4) | 0.326(2) | 0.415(8) |
| H(7) | 0.111(4) | 0.379(3) | 0.388(8) |
| H(8) | 0.246(3) | 0.471(2) | 0.146(7) |
| H(9,1) | 0.059(5) | 0.506(3) | 0.363(9) |
| H(9,2) | 0.122(4) | 0.573(2) | 0.213(9) |
| H(10,1) | 0.012(4) | 0.529(2) | 0.074(8) |
| H(10,2) | −0.053(5) | 0.474(4) | 0.064(12) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digit in this and all other tables.

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* Supplementary material, which includes a list of $F_o$ and $F_c$ values has been deposited as NAPS Document No. 02387, with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th Street, New York, New York 10017. A copy may be secured by citing the document and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 2

ATOMIC THERMAL PARAMETERS[a]

| Atom | $B_{iso}$ or $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Fe | 0.0063(1) | 0.0036(1) | 0.0249(2) | −0.0002(1) | 0.0004(1) | −0.0008(1) |
| O(1) | 0.010(1) | 0.006(1) | 0.043(2) | −0.002(1) | 0.009(1) | −0.001(1) |
| O(2) | 0.012(1) | 0.007(1) | 0.057(2) | 0.002(1) | −0.008(1) | 0.001(1) |
| O(3) | 0.018(1) | 0.006(1) | 0.067(2) | −0.001(1) | −0.002(1) | −0.009(1) |
| C(1) | 0.012(1) | 0.004(1) | 0.030(3) | −0.001(1) | −0.005(1) | 0.002(1) |
| C(2) | 0.006(1) | 0.003(1) | 0.029(2) | −0.001(1) | −0.002(1) | −0.000(1) |
| C(3) | 0.010(1) | 0.004(1) | 0.021(2) | −0.001(1) | −0.003(1) | −0.002(1) |
| C(4) | 0.008(1) | 0.005(1) | 0.028(2) | 0.000(1) | 0.005(1) | −0.000(1) |
| C(5) | 0.005(1) | 0.005(1) | 0.043(3) | −0.000(1) | 0.001(1) | 0.001(1) |
| C(6) | 0.005(1) | 0.004(1) | 0.026(2) | −0.001(1) | −0.004(1) | 0.001(1) |
| C(7) | 0.007(1) | 0.003(1) | 0.019(2) | −0.000(1) | −0.001(1) | −0.001(1) |
| C(8) | 0.008(1) | 0.004(1) | 0.034(2) | −0.001(1) | −0.003(1) | −0.000(1) |
| C(9) | 0.012(1) | 0.004(1) | 0.045(4) | 0.001(1) | −0.004(2) | −0.000(1) |
| C(10) | 0.013(1) | 0.004(1) | 0.070(4) | 0.000(1) | −0.014(2) | 0.002(1) |
| C(11) | 0.008(1) | 0.003(1) | 0.027(2) | −0.001(1) | −0.002(1) | 0.000(1) |
| C(12) | 0.008(1) | 0.004(1) | 0.037(2) | −0.000(1) | 0.004(1) | −0.002(1) |
| C(13) | 0.008(1) | 0.004(1) | 0.043(2) | −0.000(1) | −0.000(1) | −0.000(1) |
| H(1) | 4.0(15) | | | | | |
| H(2) | 2.7(12) | | | | | |
| H(3) | 3.2(13) | | | | | |
| H(4) | 5.9(15) | | | | | |
| H(5) | 3.7(12) | | | | | |
| H(6) | 3.5(12) | | | | | |
| H(7) | 4.6(15) | | | | | |
| H(8) | 2.2(10) | | | | | |
| H(9,1) | 4.8(19) | | | | | |
| H(9,2) | 6.9(17) | | | | | |
| H(10,1) | 4.8(15) | | | | | |
| H(10,2) | 7.6(25) | | | | | |

[a] The anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

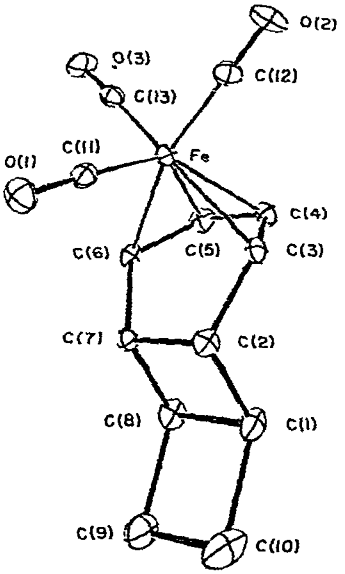


Fig. 1. A view of the structure of $(C_{10}H_{12})Fe(CO)_3$ showing the 50% probability ellipsoids and the atomic numbering scheme.

TABLE 3

BOND DISTANCES (Å) FOR $(C_{10}H_{12})Fe(CO)_3$

| Atoms | Distance | Atoms | Distance |
|---|---|---|---|
| Fe—C(2) | 2.963(6) | Fe—C(11) | 1.770(6) |
| Fe—C(3) | 2.116(6) | Fe—C(12) | 1.781(6) |
| Fe—C(4) | 2.039(6) | Fe—C(13) | 1.784(7) |
| Fe—C(5) | 2.052(7) | C(11)—O(1) | 1.140(6) |
| Fe—C(6) | 2.114(5) | C(12)—O(2) | 1.148(6) |
| Fe—C(7) | 2.963(6) | C(13)—O(3) | 1.144(7) |
| C(1)—C(2) | 1.552(8) | C(1)—H(1) | 0.87(5) |
| C(1)—C(8) | 1.547(9) | C(2)—H(2) | 0.94(4) |
| C(1)—C(10) | 1.511(11) | C(3)—H(3) | 0.85(5) |
| C(2)—C(3) | 1.490(8) | C(4)—H(4) | 0.96(5) |
| C(2)—C(7) | 1.532(7) | C(5)—H(5) | 0.88(4) |
| C(3)—C(4) | 1.401(8) | C(6)—H(6) | 1.01(4) |
| C(4)—C(5) | 1.386(7) | C(7)—H(7) | 0.91(5) |
| C(5)—C(6) | 1.404(7) | C(8)—H(8) | 0.92(4) |
| C(6)—C(7) | 1.505(7) | C(9)—H(9,1) | 0.88(5) |
| C(7)—C(8) | 1.557(8) | C(9)—H(9,2) | 1.06(4) |
| C(8)—C(9) | 1.547(9) | C(10—H(10,1) | 0.92(4) |
| C(9)—C(10) | 1.521(10) | C(10)—H(10,2) | 0.82(6) |

## Results

The molecular structure of $(C_{10}H_{12})Fe(CO)_3$ is consistent with that predicted from IR and PMR spectroscopy [1]. As shown in Fig. 1, the tricarbonyliron moiety is π-bonded to a hexadiene ring in *tetrahapto* fashion. The saturated portion of the cyclohexadiene is *cis*-fused to a cyclobutane ring, which in turn, is *cis*-fused to a second four-membered ring. Although not required crystallographically the molecule possesses approximate mirror symmetry.

The conformation of the three fused rings is *exo* as depicted in the figure. Tables 3 and 4 give bond distances and bond angles, respectively; Table 5 presents least-squares planes data.

TABLE 4

BOND ANGLES (deg) IN $(C_{10}H_{12})Fe(CO)_3$

| | | | |
|---|---|---|---|
| *Fe coordination sphere* | | | |
| C(3)—Fe—C(4) | 39.4(2) | C(5)—Fe—C(6) | 39.4(2) |
| C(3)—Fe—C(5) | 68.6(2) | C(5)—Fe—C(11) | 130.8(3) |
| C(3)—Fe—C(6) | 75.5(2) | C(5)—Fe—C(12) | 124.4(3) |
| C(3)—Fe—C(11) | 92.6(2) | C(5)—Fe—C(13) | 95.6(3) |
| C(3)—Fe—C(12) | 93.9(3) | C(6)—Fe—C(11) | 92.9(2) |
| C(3)—Fe—C(13) | 163.8(2) | C(6)—Fe—C(12) | 162.9(2) |
| C(4)—Fe—C(5) | 39.6(2) | C(6)—Fe—C(13) | 94.4(2) |
| C(4)—Fe—C(6) | 69.4(2) | C(11)—Fe—C(12) | 101.1(3) |
| C(4)—Fe—C(11) | 130.8(3) | C(11)—Fe—C(13) | 100.7(2) |
| C(4)—Fe—C(12) | 93.8(3) | C(12)—Fe—C(13) | 92.6(2) |
| C(4)—Fe—C(13) | 125.4(3) | | |
| | | Fe—C(11)—O(1) | 176.8(6) |
| | | Fe—C(12)—O(2) | 179.8(5) |
| | | Fe—C(13)—O(3) | 178.4(5) |

TABLE 4 (continued)

| | | | |
|---|---|---|---|
| *Angles at atom specified:* | | | |
| *6-membered ring:* | | | |
| C(2) | 110.8(5) | C(5) | 116.0(5) |
| C(3) | 121.9(6) | C(6) | 120.3(5) |
| C(4) | 114.8(6) | C(7) | 110.6(5) |
| *Central 4-membered ring:* | | | |
| C(1) | 89.8(5) | C(7) | 90.1(4) |
| C(2) | 90.4(4) | C(8) | 89.7(4) |
| *Terminal 4-membered ring:* | | | |
| C(1) | 89.4(6) | C(9) | 89.1(6) |
| C(8) | 89.6(5) | C(10) | 91.9(6) |
| *Angles between rings:* | | | |
| C(1)—C(2)—C(3) | 115.2(5) | C(8)—C(7)—C(6) | 114.3(5) |
| C(10)—C(1)—C(2) | 114.4(7) | C(9)—C(8)—C(7) | 115.4(6) |
| *Angles involving hydrogen atoms:* | | | |
| H(1)—C(1)—C(2) | 116(4) | H(7)—C(7)—C(6) | 120(3) |
| H(1)—C(1)—C(8) | 121(4) | H(7)—C(7)—C(8) | 105(3) |
| H(1)—C(1)—C(10) | 120(4) | H(8)—C(8)—C(1) | 123(3) |
| H(2)—C(2)—C(1) | 110(3) | H(8)—C(8)—C(7) | 118(2) |
| H(2)—C(2)—C(3) | 111(3) | H(8)—C(8)—C(9) | 116(2) |
| H(2)—C(2)—C(7) | 118(3) | H(9,1)—C(9)—C(8) | 108(4) |
| H(3)—C(3)—C(2) | 121(3) | H(9,1)—C(9)—C(10) | 117(4) |
| H(3)—C(3)—C(4) | 110(3) | H(9,1)—C(9)—H(9,2) | 115(5) |
| H(4)—C(4)—C(3) | 125(4) | H(9,2)—C(9)—C(8) | 108(3) |
| H(4)—C(4)—C(5) | 120(4) | H(9,2)—C(9)—C(10) | 115(3) |
| H(5)—C(5)—C(4) | 124(3) | H(10,1)—C(10)—C(1) | 104(4) |
| H(5)—C(5)—C(6) | 119(3) | H(10,1)—C(10)—C(9) | 109(3) |
| H(6)—C(6)—C(5) | 118(2) | H(10,1)—C(10)—H(10,2) | 115(7) |
| H(6)—C(6)—C(7) | 114(2) | H(10,2)—C(10)—C(1) | 116(5) |
| H(7)—C(7)—C(2) | 112(3) | H(10,2)—C(10)—C(9) | 118(6) |

## Discussion

### *The cyclohexadieneiron tricarbonyl moiety*

The coordination about the iron atom is tetragonal pyramidal if one considers the diene as a bidentate ligand attached to the iron atom at the midpoints of the formal double bonds. The four diene carbon atoms, C(3)—C(6), are coplanar to within 0.01 Å (Table 5). Similarly C(2), C(3), C(6), and C(7) are coplanar to within 0.002 Å. The dihedral angle between these two least-squares planes is 37.7°.

The structure of the (cyclohexadiene)iron tricarbonyl fragment has been determined in at least nine X-ray diffraction studies [3, 4, 7, 8, 12—15].

Table 6 compares bond distances and angles derived from these studies. The deviations from the mean are an average of 1.3 times the individual e.s.d.'s for distances. The average dihedral angle is 38.3(3)°. As might be expected, the perfluoro compound, XI, has structural parameters quite different from the other compounds. This is especially obvious in the dihedral angle of 47.3°. The structure is listed for comparison purposes and is not included in the average

TABLE 5

LEAST-SQUARES PLANES AND RELATED PARAMETERS FOR $(C_{10}H_{12})Fe(CO)_3$

| Plane | Atoms |
|---|---|
| I | C(3), C(4), C(5), C(6) |
| II | C(2), C(3), C(6), C(7) |
| III | C(1), C(2), C(7), C(8) |
| IV | C(1), C(8), C(9), C(10) |

*Equations of planes*[a]

| | |
|---|---|
| I | $0.216x - 16.212y + 1.797z = -4.648$ |
| II | $-5.767x - 11.231y + 3.425z = -4.144$ |
| III | $-9.515x + 5.689y + 2.911z = 1.416$ |
| IV | $-5.373x - 11.488y + 3.485z = -5.589$ |

*Deviations (Å) from planes*

| Plane I | | Plane II | | Plane III | | Plane IV | |
|---|---|---|---|---|---|---|---|
| C(3) | −0.006 | C(2) | −0.002 | C(1) | 0.005 | C(1) | −0.013 |
| C(4) | 0.011 | C(3) | 0.001 | C(2) | −0.006 | C(8) | 0.013 |
| C(5) | −0.011 | C(6) | −0.001 | C(7) | 0.006 | C(9) | −0.013 |
| C(6) | 0.006 | C(7) | 0.002 | C(8) | −0.005 | C(10) | 0.013 |
| C(2) | −0.860 | C(4) | −0.765 | C(3) | −1.252 | C(2) | 1.389 |
| C(7) | −0.854 | C(5) | −0.785 | C(6) | −1.251 | C(7) | 1.428 |
| | | C(1) | −1.394 | C(9) | 1.386 | | |
| | | C(8) | −1.383 | C(10) | 1.386 | | |

*Dihedral Angles (Deg.)*

| Planes | Angle | Planes | Angle |
|---|---|---|---|
| I, II | 37.7 | II, III | 63.3 |
| I, III | 101.0 | II, IV | 2.2 |
| I, IV | 36.0 | III, IV | 65.0 |

[a] $x$, $y$, and $z$ are fractional orthorhombic coordinates.

values listed in Table 6. The only other compound with a dihedral angle significantly different from the others is 6. This difference may be related to the puckering of the four-membered ring.

## *The conformation of the fused ring system*

Figure 2 illustrates the conformation of the organic ring system and identifies the four approximately planar sections (see Table 5). The dihedral angle

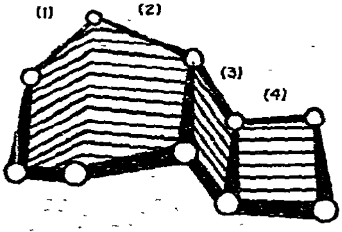
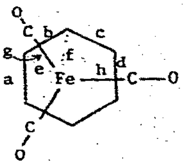
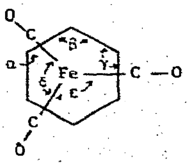


Fig. 2. An illustration of the conformation of the organic ring system with the least squares planes labeled.

TABLE 6

STRUCTURAL PARAMETERS FOR THE (CYCLOHEXADIENE)M(CO)$_3$ MOIETY





| Compound | *a* | *b* | *c* | *d* | *e* | *f* | *g* |
|---|---|---|---|---|---|---|---|
| III | 1.419(7) | 1.438(8) | 1.520(8) | 1.541(8) | 2.069(5) | 2.128(5) | 1.787(6) |
| IV | 1.387(8) | 1.404(7) | 1.505(7) | 1.532(7) | 2.039(6) | 2.114(5) | 1.770(6) |
|  |  | 1.400(8) | 1.492(8) |  | 2.053(7) | 2.116(6) | 1.784(7) |
| V | 1.411(4) | 1.417(3) | 1.500(3) | 1.545(3) | 2.053(2) | 2.132(2) | 1.788(3) |
|  |  | 1.412(3) | 1.504(3) |  | 2.053(2) | 2.139(2) | 1.783(2) |
| VI | 1.413(4) | 1.422(4) | 1.507(4) | 1.536(4) | 2.244(3) | 2.336(3) | 1.991(3) |
|  | 1.417(4) | 1.410(4) | 1.511(4) | 1.533(4) | 2.236(3) | 2.325(3) |  |
|  |  | 1.396(4) | 1.501(4) |  | 2.266(3) | 2.380(3) |  |
|  |  | 1.390(4) | 1.504(4) |  | 2.264(3) | 2.396(3) |  |
| VII | 1.39(2) | 1.42(1) | 1.50(1) | 1.53(1) | 2.03(1) | 2.16(1) | 1.770(9) |
|  |  | 1.44(2) | 1.51(2) |  | 2.07(1) | 2.16(1) | 1.791(7) |
| VIII | 1.41(2) | 1.42(2) | 1.47(2) | 1.58(2) | 2.07(1) | 2.12(1) | 1.75(1) |
|  |  | 1.46(2) | 1.53(2) |  | 2.10(1) | 2.14(1) | 1.80(1) |
| X | 1.38(4) | 1.38(4) | 1.50(3) | 1.55(3) | 2.01(2) | 2.10(2) | 1.70(3) |
|  |  | 1.40(4) | 1.50(3) |  | 2.02(2) | 2.10(2) | 1.70(3) |
| XI | 1.37(1) | 1.40(1) | 1.50(1) | 1.56(1) | 2.060(7) | 1.993(8) | 1.803(8) |
| XII | 1.37(2) | 1.40(2) | 1.50(2) | 1.52(2) | 2.04(1) | 2.10(1) | 1.77(1) |
|  | 1.41(1) | 1.52(2) |  |  | 2.04(1) | 2.12(1) | 1.76(2) |

|  | *h* | α | β | γ | δ | ε | Dihedral Angle | Ref. |
|---|---|---|---|---|---|---|---|---|
| III | 1.780(6) | 115.2(4) | 119.8(4) | 111.3(4) | 92.6(2) | 100.3(2) | 38 | 8 |
| IV | 1.770(6) | 114.9(6) | 121.8(6) | 110.8(5) | 92.6(2) | 101.1(3) | 37.7 | This work |
|  |  | 115.9(5) | 120.3(5) | 110.6(5) |  | 100.7(2) |  |  |
| V | 1.783(2) | 115.2(2) | 120.3(2) | 111.3(2) | 90.5(1) | 102.4(1) | 38.0 | 3 |
|  |  | 115.9(2) | 120.5(2) | 110.0(2) |  | 102.8(1) |  |  |
| VI | 1.991(3) | 114.3(2) | 119.7(2) | 117.6(2) | 95.5(1) |  | 38.0 | 7 |
|  |  | 114.6(2) | 120.0(2) | 115.7(2) |  |  | 39.0 | 7 |
|  |  | 117.5(2) | 120.1(2) | 115.2(2) |  |  |  |  |
|  |  | 116.7(2) | 119.5(2) | 114.7(2) |  |  |  |  |
| VII | 1.793(9) | 113.9(7) | 119.7(6) | 111.7(6) | 93.4(4) | 99.1(4) | 36.3 | 4 |
|  |  | 119.2(10) | 119.7(11) | 112.5(6) |  | 101.0(4) |  |  |
| VIII | 1.80(1) | 115(1) | 120(1) | 110(1) | 90.6(5) | 98.9(5) | 39 | 12 |
|  | 1.80(1) | 116(1) | 122(1) | 111(1) |  | 100.6(5) |  |  |
| X | 1.74(4) | 115(3) | 119(2) | 109(2) | 92(1) | 101(1) | 39.9 | 14 |
|  |  | 116(2) | 121(2) | 111(2) |  | 102(1) |  |  |
| XI | 1.799(3) | 114.4(7) | 116.7(7) | 108.9(7) | 89.6(4) | 97.8(4) | 47.3 | 15 |
| XII | 1.78(2) | 117(1) | 119(1) | 110(1) | 92.9(6) | 101.7(6) | 38.5 | 6 |
|  |  | 114(1) | 122(1) | 111(1) |  | 100.8(6) |  |  |

of 63° between the least-squares planas II and III compared with 60° in III [8], 59° in V [3] 62° in VI [7], 60° in VII [4], 64° in VIII [12] and 63° in X [14].

The dihedral angle between the four-membered rings (least-squares planes III and IV) is 65°. This is close to the dihedral angles of 67° [16] 68° [17], and

69° [18] found for the fused four-membered rings in Dewar benzene complex and is identical to that found in VII [4].

### *The four-membered rings*

Of primary interest in this compound is the geometry of the four-membered rings. The C—C bond lengths in these rings range from 1.511(11) to 1.557(8) Å with a mean value of 1.538(17) Å. This (as shown elsewhere [9]) compared favorably with the following mean* values: 1.549 Å for cyclobutane, 1.545(3) Å for substituted cyclobutanes, 1.551(3) Å for organic fused cyclobutanes, and 1.552(4) Å for organometallic fused cyclobutanes. For organic fused cyclobutanes the C—C bond that is common to two rings is typically ca. 0.024(8) Å shorter than the C—C bond that is part of only one four-membered ring [9]. The average C—C bond length [9] for the 109 individual determinations by X-ray diffraction methods is 1.547(2) Å. This represents a lengthening of ca. 0.01 Å over non-cyclic $C(sp^3)$—$C(sp^3)$ bonds [19].

The two four-membered rings in $(C_{10}H_{12})Fe(CO)_3$ are essentially planar (Table 5) with dihedral angles of 1.1(8) and 2.7(9)° for the central and terminal rings, respectively. (The corresponding torsional angles are 0.8(5) and 1.9(7)°.) Dihedral angles in other organometallic fused cyclobutane structures range [9] from 0.2(3) to 16.4(12)°.

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## References

1 F.A. Cotton and G. Deganello, (a) J. Organometal. Chem., 38 (1972) 147; (b) J. Amer. Chem. Soc., 94 (1972) 2142; (c) ibid., 95 (1973) 396.
2 F.A. Cotton, B.A. Frenz, G. Deganello and A. Shaver, J. Organometal Chem., 50 (1973) 227.
3 F.A. Cotton, V.W. Day, B.A. Frenz, K.I. Hardcastle and J.M. Troup, J. Amer. Chem. Soc., 95 (1973) 4522.
4 F.A. Cotton, V.W. Day and K.I. Hardcastle, to be submitted.
5 F.A. Cotton, B.A. Frenz, J.M. Troup and G. Deganello, J. Organometal. Chem., 59 (1973) 317.
6 F.A. Cotton, B.A. Frenz and J.M. Troup, J. Organometal. Chem., 61 (1973) 337.
7 F.A. Cotton and B.A. Frenz, Acta Crystallogr., in press.
8 F.A. Cotton and J.M. Troup, J. Organometal. Chem., in press.
9 F.A. Cotton and B.A. Frenz, Tetrahedron, in press.
10 D.T. Cromer and J.T. Waber, International Tables for X-ray Crystallography, Volume IV, in preparation
11 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
12 A. Robson and M.R. Truter, J. Chem. Soc. A, (1968) 794.
13 K.I.G. Reid and I.C. Paul, Chem. Commun., (1970) 1106.
14 A.H.-J. Wang, I.C. Paul and G.H. Schrauzer, J. Chem. Soc., Chem. Commun., (1972) 736.

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[*] The weighted mean of $N$ distances $d_i$ with e.s.d. $\sigma_i$ is defined as $(\Sigma_{i=1}^{N}(d_i/\sigma_i^2))/(\Sigma_{i=1}^{N}(1/\sigma_i^2))$ and the e.s.d. of the mean is $(1/\Sigma_i^N(1/\sigma_i^2))^{1/2}$. This formula for the e.s.d. produces values too small to be chemically meaningful (*ca.* 0.0005 Å). Therefore the following more conservative estimate of the error in the mean $d$ is used: $[(1/N(N-1))\Sigma_{i=1}^{N}(d_i-d)^2]^{1/2}$.

15 M.R. Churchill and R. Mason, Proc. Roy. Soc. A, 301 (1967) 433.
16 G. Huttner and O.S. Mills, Chem. Commun., (1968) 344.
17 J.F. Malone, W.S. McDonald, B.L. Shaw and G. Shaw, Chem. Commun., (1968) 869; J.F. Malone and W.S. McDonald, J. Chem. Soc. (A), (1970) 3124.
18 R. Mason, G.B. Robertson, P.O. Whimp, B.L. Shaw and G. Shaw, Chem. Commun., (1968) 868; R. Mason, G.B. Robertson and P.O. Whimp, J. Chem. Soc. (A), (1970) 535.
19 L.E. Sutton (Ed.), Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement, Chem. Soc. Special Publication No. 18, 1965.