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CONFORMATIONS OF FUSED CYCLOALKANES IN ORGANOMETALLIC COMPLEXES

IV*. THE CRYSTAL AND MOLECULAR STRUCTURE OF TRICYCLO-[6.4.0.0^{2,7}]DODECA-3,5-DIENETRICARBONYLIRON

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Summary

The precise molecular structure of the title compound has been determined by single crystal X-ray diffractometry. It consists of a cyclohexadiene ring fused at the 5 and 6 positions to a cyclobutane ring which is in turn fused to a cyclohexane ring. The two six-membered rings are *trans* to each other with respect to the shared four-membered ring. The $Fe(CO)_3$ moiety is bound in the usual way to the conjugated diene portion of the cyclohexadiene ring. The feature of greatest interest is the mutual influence of the conformations of the two fused cycloalkane rings, whose intrinsically preferred conformations are mutually incompatible. Under the influence of the fused cyclohexadiene ring the C_4 ring would tend to be planar, while the cyclohexane ring would tend, of itself, to have a chair conformation. The actual result is a compromise, with the C_4 ring being folded by 15° along its diagonal and the C_6 ring having a conformation intermediate between planarity and a chair. Crystallographic data: space group, $P2_1$, $Z = 2$. Unit cell dimensions at 3°C are $a = 6.176(1)$, $b = 11.307(2)$, $c = 9.781(2)$ Å and $\beta = 92.89(2)°$. A set of 1733 reflections having $2\theta(\text{Mo-}K_\alpha) < 63.7°$ and $I > \sigma(I)$ was refined to convergence ($R_1 = 0.055$, $R_2 = 0.034$) with hydrogen atoms refined isotropically and all others anisotropically.

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* For part III see ref. 3.

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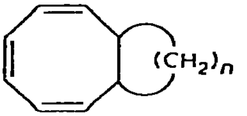
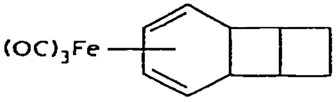
Introduction

Previous work in these laboratories has led to the preparation and structural characterization of a series of compounds formed by the reaction of polyolefins of type I with $Fe_2(CO)_9$ and $Mo(CO)_3(CH_3CN)_3$ [1-4] Among these have been compounds II V These are of interest because of the opportunities they afford to study the conformational influence of one fused ring upon another Thus far, the structures of II [3], III [2] and IV [4] have been determined by X-ray crystallography and reported in detail Comparison of III and IV showed that conformations are not significantly sensitive to crystal environment



(I) (n = 2,3,4)



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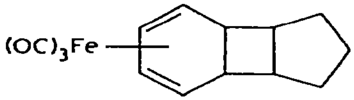

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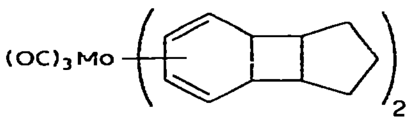

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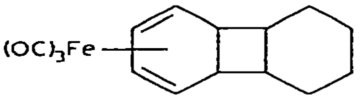

(V)

In this paper we report and discuss the detailed structure of compound V, in which the tendency of the central four membered ring to be essentially planar (as it is in II, III and IV) and thus constrain three consecutive C—C bonds in the saturated six-membered ring to be coplanar is in conflict with the inherent tendency of the six membered ring to adopt a chair conformation

Experimental

Tricyclo[6 4 0 $0^{2,7}$]dodeca-3,5 dienetricarbonyliron, $Fe(CO)_3(C_{12}H_{16})$ (compound V), was prepared and characterized in this laboratory by Dr G Deganello [1] Large, well shaped, yellow, single crystals suitable for diffraction studies were obtained by recrystallization from toluene Weissenberg and precession photographs used to determine the probable space group and a preliminary set of lattice constants indicated monoclinic, 2/*m*, symmetry The systematically absent reflections were those required by the noncentrosymmetric space group $P2_1$ C_2^2 (No 4) or the centrosymmetric space group $P2_1/m$ C_{2h}^2 (No 11) [5]

A crystalline specimen approximating a rectangular parallelepiped with dimensions of 0 46 X 0 30 X 0 25 mm was cut from a larger single crystal and glued to the end of a thin glass fiber having a tip diameter of 0 10 mm This crystal was then accurately centered optically on a computer-controlled four circle Syntex $P\bar{1}$ Autodiffractometer whose goniometer was located in a cold room maintained at a temperature of 3 ± 1°C A total of fifteen high angle [2θ(Mo-K_α) > 25°] reflections, chosen to give a good sampling of reciprocal space and diffractometer settings, were used to align the crystal and calculate angular settings for each reflection A least squares refinement of the diffraction geometry for these 15 reflections, recorded at a temperature of 3 ± 1°C with Nb filtered Mo-K_α radiation (λ = 0 71069 Å) gave the lattice constants a = 6 176(1), b = 11 307(2), c = 9 781(2) Å, and β = 92 89(2)° A unit cell content of two $Fe(CO)_3(C_{12}H_{10})$ molecules gives a calculated density of 1 46 g cm^{-3}, in good agreement with the observed density of 1 48 g cm^{-3} measured by flotation

Intensity measurements utilized Nb filtered Mo K_α radiation and the θ—2θ scanning technique with a 2° take-off-angle and a normal-focus X-ray tube A scanning rate of 2°/min was employed for the symmetrical scan between settings 1 0° above and below the calculated K_α doublet values [$\lambda(K_{\alpha_1})$ = 0 70926 Å and $\lambda(K_{\alpha_2})$ = 0 71354 Å] of each reflection Background counts, each lasting for half the total scan time, were taken at both ends of the scan range A total of 1926 independent reflections having 2θ(Mo K_α) < 63 7° (1 5 times the number of data in the limiting Cu K_α sphere) were measured in concentric shells of increasing 2θ containing approximately 650 reflections each The five standard reflections measured every two hundred reflections as a monitor for possible disalignment and/or deterioration of the crystal, gave no indication of either

The linear absorption coefficient of the crystal [6] for Mo-K_α radiation is 1 14 mm^{-1}, yielding a μR of 0 23 for a spherical crystal having the same volume as the specimen actually used Since the absorption of X-rays by a spherical crystal having μR = 0 23 is virtually independent of scattering angle [7], and deviations from this absorption occasioned by the use of a rectangular parallelepiped shaped specimen are practically negligible except for a trivial fraction of the reflections, no absorption corrections were made and the intensities of all reflections were reduced to a set of relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections

This set of observed structure factor amplitudes was used to calculate a Wilson plot and then reduced to a corresponding set of normalized structure factors, E_{hkl} The choice of $P2_1$ C_2^2 [5] as the most probable space group was indicated at this point by the positive results of sensitive tests for piezo electricity as well as by the values of the various statistical indicators calculated using these normalized structure factors — all of which were in agreement with a non centrosymmetric space group This choice was fully supported by the results at all stages of the subsequent structure determination and refinement

Of the 1926 reflections examined, 193 were eventually rejected as objectively unobserved by applying the rejection criterion, $I < \sigma(I)$, where $\sigma(I)$ is the standard deviation in the intensity computed from $\sigma^2(I) = (C_t + k^2B)$, C_t being the total count from scanning, k the ratio of scanning time to total background time (in this case, k = 1) and B the total background count The heavy-atom technique, difference Fourier syntheses, and full-matrix least-squares were used with the remaining 1733 observed intensities in the determination and refinement of the structure

The atomic coordinates of the iron atom were readily derived from a three-dimensional Patterson synthesis The remaining non-hydrogen atoms of the totally general position asymmetric unit were located from successive difference Fourier syntheses based on partial models of the molecule

Unit-weighted full-matrix least-squares minimization of the function $\Sigma w(|F_o| - K|F_c|)^2$ (where K is the scale factor and w is the weight assigned to each reflection) through refinement of the fractional atomic coordinates and isotropic thermal parameters of the 19 crystallographically independent non-hydrogen atoms resulted in a conventional unweighted residual, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0 095 and a conventional weighted residual, $R_2 = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, of 0 095 These and all subsequent structure factor calculations employed the atomic form factors compiled by Cromer and Mann [8] and an anomalous dispersion correction to the scattering factor of the iron atom [9] Utilization of anisotropic thermal parameters for all atoms in further cycles of least squares refinement gave R_1 = 0 064 for 1733 independent reflections having $2\theta(\text{Mo-}K_\alpha) < 63\ 7^\circ$ and $I > \sigma(I)$

In order to determine the absolute configuration of the molecule, it was necessary at this point to make a choice between the two possible enantiomorphs Refinement of the enantiomorph produced by mirroring perpendicular to the b axis gave R_1 = 0 069 for 1733 reflections, thereby indicating the correctness of the original description as the absolute configuration for the molecule A difference Fourier synthesis based on the correct absolute configuration revealed the sixteen hydrogen atoms in chemically anticipated positions

Further unit-weighted cycles of full-matrix least squares refinement which employed anisotropic thermal parameters for non hydrogen atoms and isotropic thermal parameters for hydrogen atoms gave R_1 = 0 056

Empirical weights ($w = 1/\sigma^2$) were then calculated from

$$\sigma = \sum_{o}^{3} a_n|F_o|^n = 1\ 397 - 8\ 12 \times 10^{-2}F_o + 3\ 71 \times 10^{-3}F_o^2 - 3 \times 10^{-5}F_o^3$$

the a_n being coefficients derived from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_{o}^{3} a_n|F_o|^n$$

where the F_c values were calculated from the fully refined model using unit weighting and an $I > \sigma(I)$ rejection criterion

Since the shifts in hydrogen atom parameters were somewhat erratic and approximately equal to their estimated standard deviations, their values were fixed and only parameters for the anisotropic non hydrogen atoms were varied in the final cycles of full-matrix least-squares refinement which utilized empirical weights and converged to final values of 0 055 and 0 034 for R_1 and R_2, respectively, for 1733 independent reflections During the final cycle of refinement, no parameter for a non hydrogen atom shifted by more than 0 09 σ_p with the average shift being 0 04 σ_p, where σ_p is the estimated standard deviation of the parameter. Since a careful examination of the final F_o and F_c values indi cated the absence of extinction effects, extinction corrections were not made. The esd of an observation of unit weight was 1.87, indicating a slight under estimation of $\sigma(F_o)$[*]. A final difference map showed no electron density peaks greater than 0.40 e Å^{-3}.

The following programs were used on an IBM 370/155 computer for this work: MAGTAPE and SCTFT2, data reduction programs written by V. W. Day, FORDAP II, Fourier and Patterson synthesis program by Zalkin, ORFLSE, full-

TABLE 1

ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS IN CRYSTALLINE $Fe(CO)_3(C_{12}H_{16})$[a]

Atom[b] type	10^4x	10^4y	10^4z	Isotropic thermal parameter[c] B (Å^2)
Fe	1512(1)	0	4705(1)	2.78
O(1)	4236(13)	2079(6)	4311(8)	4.4
O(2)	−1867(16)	366(1)	2533(11)	6.8
O(3)	3820(13)	−1690(7)	3026(8)	4.8
C(1)	2259(16)	517(9)	9013(8)	4.0
C(2)	3053(11)	706(7)	7531(7)	2.9
C(3)	3192(12)	−367(7)	6645(8)	3.2
C(4)	1334(17)	−1090(7)	6397(11)	3.7
C(5)	−579(17)	−456(11)	6144(13)	3.8
C(6)	−513(18)	817(9)	6167(10)	3.8
C(7)	1014(11)	1444(7)	7183(8)	3.1
C(8)	499(17)	1452(11)	8731(11)	4.6
C(9)	929(28)	2681(15)	9352(15)	5.9
C(10)	2194(23)	2668(15)	10717(13)	6.1
C(11)	4297(24)	1946(15)	10594(15)	6.0
C(12)	3811(22)	677(12)	10249(9)	5.1
C(13)	3178(13)	1276(8)	4468(8)	3.3
C(14)	−524(15)	205(8)	3388(11)	4.2
C(15)	2968(13)	−1051(7)	3734(9)	3.4
	10^3x =	10^3y =	10^3z =	
H(1)	233(9)	−20(8)	937(11)	6(1)
H(2)	444(10)	116(9)	771(9)	6(1)
H(3)	472(7)	−71(8)	665(9)	4(1)
H(4)	175(7)	−212(9)	639(9)	2(1)
H(5)	−206(13)	−80(8)	598(8)	1(1)
H(6)	−206(8)	121(7)	560(6)	5(1)
H(7)	83(6)	207(6)	689(8)	4(1)
H(8)	−141(9)	128(12)	871(10)	4(1)
H(9.1)	237(13)	344(9)	937(12)	8(1)
H(9.2)	1(9)	302(12)	1019(15)	3(1)
H(10.1)	250(12)	381(8)	1085(16)	3(1)
H(10.2)	50(12)	215(14)	1130(9)	3(1)
H(11.1)	430(13)	286(15)	998(15)	6(1)
H(11.2)	550(9)	230(11)	1140(13)	2(1)
H(12.1)	375(10)	35(14)	1145(12)	4(1)
H(12.2)	550(9)	39(10)	1017(8)	1(1)

[a] Figures in parentheses are the estimated standard deviations. Coordinate listed without a standard deviation is symmetry required. [b] Atoms numbered to agree with Figures 1 and 2. [c] Isotropic thermal parameters for non hydrogen atoms are calculated from the dimensionless β_{ij}'s employed during refinement as $B = 4[V^2\det(\beta_{ij})]^{1/3}$ and are given without standard deviations.

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[*] The table of structure factors will be deposited as a NAPS Document. Order from ASIS/NAPS c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016.

matrix least-squares structure refinement program, a highly modified version of Busing, Martin and Levy's original ORFLS, ORFFE, a function and error program by Busing, Martin and Levy, ORTEP, thermal ellipsoid plotting program by Johnson, and PUB, a modification of Snyder's structure factor table program, LIST.

Results

Atomic coordinates and equivalent isotropic thermal parameters for all non hydrogen atoms, derived from the final cycle of empirically-weighted full matrix least squares refinement, are given in Table 1 The atomic coordinates and isotropic thermal parameters given in Table 1 for hydrogen atoms represent values obtained from the last refinement cycle in which these parameters were varied Fully refined anisotropic thermal parameters for non-hydrogen atoms are given in Table 2 Bond lengths and angles are given with their estimated standard deviations in Tables 3 and 4, respectively The equations of least-squares mean planes which partially characterize important subgroupings of atoms in the molecule specified by the coordinates of Table 1 are given in Table 5 along with selected atomic displacements from these planes

The perspective ORTEP drawing of Fig 1 shows a side view of the $Fe(CO)_3(C_{12}H_{16})$ molecule and illustrates the numbering scheme used for the non hydrogen atoms which are represented by ellipsoids having shape, orientation, and relative size consistent with the thermal parameters listed in Table 2

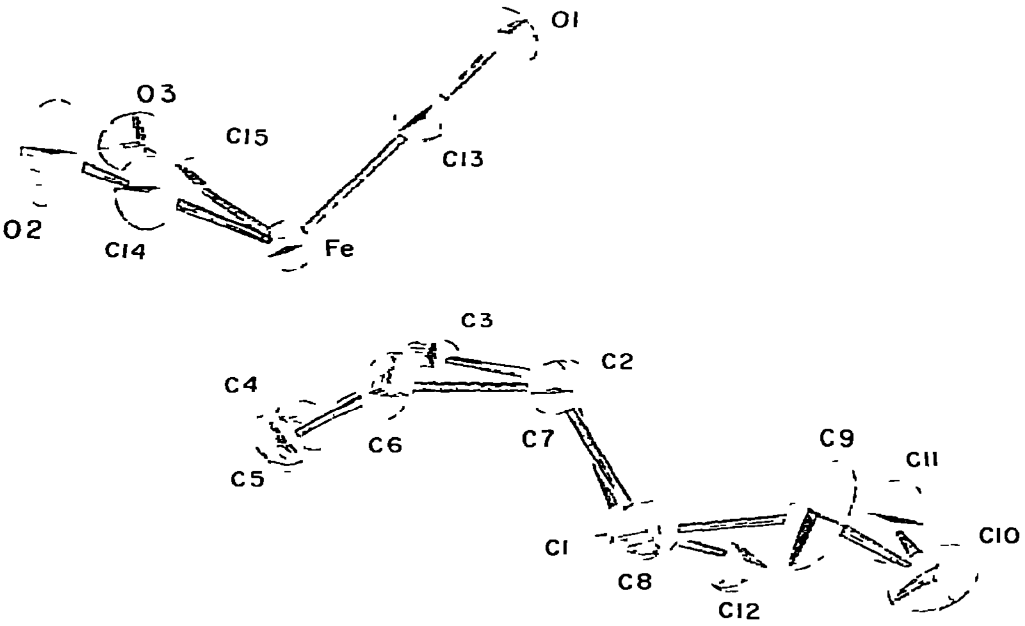

Fig. 1 A view of the molecule (hydrogen atoms omitted) in which each atom is represented by an ellipsoid proportional to its thermal vibrational amplitude as given in Table 2 The numbering scheme used is defined

TABLE 2

ANISOTROPIC THERMAL PARAMETERS FOR NON HYDROGEN ATOMS IN CRYSTALLINE $Fe(CO)_3(C_{12}H_{16})$[a]

Atom[b] Type	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe	183(2)	45(1)	88(1)	4(1)	6(1)	−8(1)
O(1)	435(25)	59(5)	146(9)	−71(9)	40(12)	−1(5)
O(2)	455(28)	152(13)	202(13)	48(15)	−138(16)	−38(10)
O(3)	442(25)	76(5)	141(8)	57(12)	74(12)	−9(5)
C(1)	384(28)	72(7)	86(7)	5(12)	55(11)	10(6)
C(2)	213(15)	56(5)	75(6)	−14(7)	9(8)	10(5)
C(3)	210(16)	65(5)	98(8)	29(7)	56(9)	4(5)
C(4)	377(27)	41(4)	149(10)	−11(9)	100(14)	−11(6)
C(5)	205(23)	94(9)	149(14)	−78(11)	46(14)	−26(8)
C(6)	271(26)	85(9)	101(9)	20(11)	5(12)	−41(7)
C(7)	227(16)	52(5)	89(7)	14(7)	17(8)	−6(5)
C(8)	296(23)	113(10)	109(10)	−2(13)	52(12)	−13(8)
C(9)	612(54)	151(17)	146(14)	154(27)	−97(23)	−79(14)
C(10)	493(43)	142(15)	129(13)	66(23)	63(19)	−4 (12)
C(11)	449(41)	135(14)	143(14)	33(21)	−91(20)	−12(12)
C(12)	514(42)	113(12)	85(8)	77(18)	−13(15)	7(8)
C(13)	239(18)	67(6)	79(7)	5(8)	12(9)	−1(5)
C(14)	313(21)	63(9)	139(10)	39(10)	−34(12)	−11(6)
C(15)	279(21)	50(5)	99(9)	28(8)	10(11)	−10(5)

[a] Figures in parentheses are the estimated standard deviations of the last significant figure [b] Atoms numbered to agree with Figs. 1 and 2

This numbering scheme is in accord with that used for nomenclature Each hydrogen atom carries the same numerical subscript as the carbon atom to which it is covalently bonded, a second numerical subscript (with values of 1 or 2) is used to distinguish between hydrogen atoms bonded to the same carbon atom Front and side views of the terminal cyclohexane ring are shown in the perspective ORTEP drawings of Fig 2

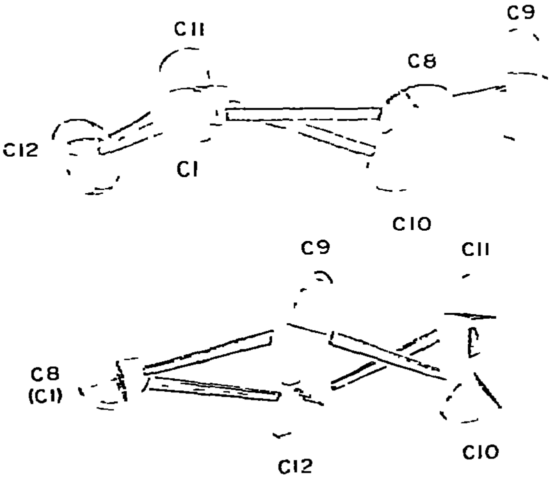

Fig 2 Front and side views of the cyclohexane ring to illustrate the twist-chair conformation

Discussion

The overall structure of the molecule is that which would have been expected from the known structures of the analogs [2,3] with 4- and 5-membered rings fused to the central cyclobutane ring The coordination polyhedron can be described in terms of idealized C_{4v} square pyramidal geometry with two carbonyl carbon atoms [C(14) and C(15)] and the midpoints of the two "outer" bonds of the butadiene portion of the cyclohexadiene ring [C(3)—C(4) and C(5)—C(6)] describing the "square" base and the third carbonyl group [C(13)—O(1)] lying on the idealized fourfold axis However, the dissimilarity of the ligands which comprise the base necessitates significant departures from idealized C_{4v} symmetry The coordination polyhedron (and to a large extent, the entire molecule) approximates rather closely its maximum possible symmetry of C_s *m* with Fe, C(13), O(1) and the midpoints of the C(14) C(15) and butadiene polyhedral edges describing a coplanar (to within 0 02 Å) array which coincides with the pseudo mirror plane The bond lengths and angles given in Tables 3 and 4 reflect this approximate symmetry

The structural parameters of the $Fe(CO)_3$ group are quite similar to those reported for this moiety in related compounds [2,3] Averaged values of 1.785(8,10,15) Å[*], 1 148(11,10,14) Å, and 177(1,2,2)° for the Fe—C(carbonyl) and C—O bond lengths, and the Fe—C—O bond angles, respectively, are typical The apical carbonyl [C(13)—O(1)] lies over the "open" side of the *cis* butadiene moiety and the other two carbonyls lie over the "outer" butadiene C—C bonds

TABLE 3

BOND LENGTHS FOR NON HYDROGEN ATOMS IN CRYSTALLINE $Fe(CO)_3(C_{12}H_{16})$[a]

Type[b]	Length (Å)	Type[b]	Length (Å)
Fe—C(2)	2 986(7)	Fe—C(13)	1 793(9)
Fe—C(3)	2 157(9)	Fe—C(14)	1 770(9)
Fe—C(4)	2 071(10)	Fe—C(15)	1 791(7)
Fe—C(5)	2 025(11)		
Fe—C(6)	2 155(10)	C(13)—O(1)	1 134(10)
Fe—C(7)	2 951(7)	C(14)—O(2)	1 162(13)
		C(15)—O(3)	1 147(11)
C(1)—C(2)	1 568(10)		
C(1)—C(8)	1 531(15)	C(5)—C(6)	1 440(17)
C(1)—C(12)	1 515(21)	C(6)—C(7)	1 511(15)
C(2)—C(3)	1 496(11)	C(7)—C(8)	1 563(12)
C(2)—C(7)	1 534(10)	C(8)—C(9)	1 533(17)
C(3)—C(4)	1 420(13)	C(9)—C(10)	1 513(19)
C(4)—C(5)	1 393(17)	C(10)—C(11)	1 544(18)
		C(11)—C(12)	1 500(21)

[a] The figure in parentheses following each individual distance is the estimated standard deviation [b] Atoms numbered to agree with Figs. 1 and 2 and Tables 1 and 2

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[*] The first number in parentheses is the rms estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the average value respectively

TABLE 4

INTRAMOLECULAR BOND ANGLES (DEG) FOR NON HYDROGEN ATOMS IN CRYSTALLINE $Fe(CO)_3(C_{12}H_{16})^a$

Type[b]	Angle	Type[b]	Angle
C(3)—Fe—C(4)	39 2(4)	C(13)—Fe—C(14)	101 0(4)
C(4)—Fe—C(5)	39 7(5)	C(14)—Fe—C(15)	93 4(4)
C(5)—Fe—C(6)	40 1(4)	C(15)—Fe—C(13)	99 1(4)
C(13)—Fe—C(3)	90 9(4)	C(14)—Fe—C(3)	163 4(5)
C(13)—Fe—C(6)	95 6(4)	C(15)—Fe—C(6)	163 7(5)
C(13)—Fe—C(4)	129 5(4)	C(14)—Fe—C(4)	126 5(4)
C(13)—Fe—C(5)	133 2(4)	C(15)—Fe—C(5)	123 7(4)
Fe—C(13)—O(1)	180 (3)	C(14)—Fe—C(5)	94 9(4)
Fe—C(14)—O(2)	178 (1)	C(15)—Fe—C(4)	94 4(4)
Fe—C(15)—O(3)	175 (1)		
		C(14)—Fe—C(6)	90 7(4)
		C(15)—Fe—C(3)	96 1(4)
Angles within cyclohexadiene ring at atom specified			
C(2)	112 5(6)	C(7)	111 6(6)
C(3)	119 8(6)	C(6)	119 7(11)
C(4)	113 9(7)	C(5)	119 2(10)
Angles within cyclobutane ring at atom specified			
C(1)	89 5(6)	C(8)	89 6(6)
C(2)	89 3(6)	C(7)	89 6(6)
Angles within cyclohexane ring at atom specified			
C(1)	118 4(9)	C(8)	116 6(9)
C(12)	113 9(9)	C(9)	114 3(13)
C(11)	111 3(13)	C(10)	109 6(10)
Inter ring angles			
C(1)—C(2)—C(3)	117 0(6)	C(6)—C(7)—C(8)	119 3(8)
C(2)—C(1)—C(12)	120 4(8)	C(7)—C(8)—C(9)	110 5(10)

[a] The figure in parentheses following each individual angle is the estimated standard deviation [b] Atoms numbered to agree with Fig 1 and 2 and Tables 1 and 2

The C—C bond lengths in the coordinated cyclohexadiene ring follow the pattern established for these rings in other molecules [2,3] The average value of 1 533(16,17,35) A for the C—C bond lengths in the two saturated rings is in good agreement with the generally accepted single bond value An average length of 1 11 Å was determined for the sixteen crystallographically independent C—H bonds which individually ranged from 0 88 to 1 35 Å and had esd's of ≈0 1 Å

One important structural difference does exist however between molecules of V and its analogues [2,3] Whereas in compounds II and III, the two fused, saturated rings were conformationally compatible with each one in its own preferred conformation, that is not the case in compound V In II, both four-membered rings have essentially planar configurations In compound III, the 5-membered ring adopts an envelope configuration which allows it to conform to the essential planarity of the 4-membered ring

The preferred conformations of the individual saturated 4- and 6-mem-

TABLE 5

MEAN PLANES FOR SELECTED GROUPINGS OF ATOMS AND ATOMIC DISPLACEMENTS THEREFROM IN CRYSTALLINE $Fe(CO)_3(C_{12}H_{10})$

Equations of Mean Planes[a]

I. 0 207 X + 0 007 Y − 0 978 Z = −6 01
II. −0 575 X − 0 782 Y − 0 240 Z = −3 19
III. 0 670 X + 0 299 Y − 0 679 Z = −5 28

Displacements (Å) from Mean Planes

Atom	Plane I	Plane II	Plane III
Fe	−1 66	−1 68	−2 63
C(1)	2 40	−0 07[b]	−0 11[b]
C(2)	0 86	0 07[b]	−1 53
C(3)	−0 00[b]	−1 01	−1 85
C(4)	0 00[b]	−2 36	−1 00
C(5)	−0 00[b]	−2 53	−0 60
C(6)	0 00[b]	−1 38	−1 05
C(7)	0 78	−0 07[b]	−1 18
C(8)	2 34	0 07[b]	0 11[b]
C(9)	2 88	1 44	−0 05[b]
C(10)	4 04	2 16	0 38
C(11)	3 65	2 24	−0 33
C(12)	3 39	0 88	0 06[b]
C(13)	−2 12	−0 01	−3 91
C(14)	−2 68	−2 50	−2 77
C(15)	−2 78	−2 30	−3 55

[a] X Y and Z are orthogonal coordinates measured in Å along a b and c* respectively of the crystallographic coordinate system Angles (deg) between the normals to pairs of planes are I—II 83 6 I—III 36 4 and II—III 62 9 [b] Displacements are those of the atoms used in determining the least squares mean plane

bered rings of V are however mutually incompatible The central 4-ring will tend to be locked into an essentially planar conformation as a result of being fused to the cyclohexadiene ring, whose conformation is rigidified by its binding to the $Fe(CO)_3$ unit Although a cyclohexane ring usually prefers a chair configuration in which no three contiguous C—C bonds are coplanar, fusion of such a ring to the planar 4 ring will tend to impose a planar arrangement for the five C—C bonds involving the two carbon atoms [C(1) and C(8)] shared by the rings

This incompatibility is resolved by a compromise in the conformation of each ring The cyclobutane ring is significantly non-planar, being folded by 15° along its diagonal An extensive comparison of cyclobutane ring conformations [10] shows that this is a compromise between the two extremes commonly observed for the resulting dihedral angle, namely ca 0° (planar) or ca 26°

The cyclohexane ring adopts a twist-chair conformation, as can be seen in Fig 2 This is a conformation intermediate between a chair and a twist In a chair conformation four carbon atoms [C(1),C(8),C(10), and C(11) in this case] would be coplanar with the others [C(9) and C(12)] on opposite sides of the plane In a twist conformation four consecutive carbon atoms [C(12), C(1),C(8), and C(9) in this case] would be coplanar, with the other two on opposite sides of this plane In both cases the symmetry is C_2, with the twofold axis bisecting the C(1)—C(8) and C(10)—C(11) bonds, so that there is a continuum of symmetry-preserving intermediate conformations The conformation observed here is midway between the twist, which would allow a planar cyclobutane ring and the chair which would require extreme nonplanarity of the cyclobutane ring

On the basis of this result it would be interesting to see the ring conformations in bicyclo[4 2 0]cyclooctane Here the 4 membered ring would be free to adopt a considerably more puckered conformation, and we would venture to predict that it would in fact do so, thus permitting the 6-membered ring to approach more closely its preferred chair configuration

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