

## The Crystal and Molecular Structure of *trans,trans*-3,5-Heptadien-2-ol-Iron Tricarbonyl: the Hydrolysate of the *syn,syn*-1,5-Dimethylpentadienyliron Tricarbonyl Cation

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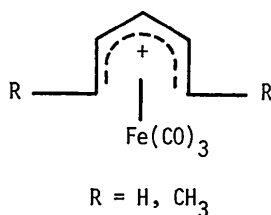
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(Received 3 April 1975; accepted 9 June 1975)

The crystal structure of *trans,trans*-3,5-heptadien-2-ol-iron tricarbonyl,  $(C_7H_{12}O)Fe(CO)_3$ , the hydrolysate of the *syn,syn*-1,5-dimethylpentadienyliron tricarbonyl cation, has been determined by single-crystal X-ray diffraction techniques using three-dimensional data gathered at  $ca -32^\circ C$  by counter methods. The irregularly shaped yellow crystals obtained by vacuum sublimation are monoclinic, space group  $P2_1/c$ , and at  $ca -32^\circ C$ ,  $a = 16.885$  (3),  $b = 17.831$  (3),  $c = 8.275$  (2) Å,  $\beta = 111.91$  (1)°. At  $ca -32^\circ C$  the calculated density for eight formula units of  $(C_7H_{12}O)Fe(CO)_3$  per unit cell is  $1.455$  g cm<sup>-3</sup>, in adequate agreement with the measured value (at  $22^\circ C$ ) of  $1.430$  (1) g cm<sup>-3</sup>. The structure consists of monomeric  $(C_7H_{12}O)Fe(CO)_3$  molecules linked by hydrogen bonds between the hydroxyl groups. Each Fe atom is coordinated by three CO ligands and the planar butadiene residue of a dimethylpentadienyl moiety. The hydrolysis (yielding the alcohol complex) is stereospecific, giving a racemic mixture of the alcohol with configurations *RR* and *SS*. Full-matrix least-squares refinement has converged with a weighted *R* index (on  $|F|$ ) of 0.033 for the 2791 symmetry-independent reflections with  $I_0 > 2.0\sigma(I_0)$ .

### Introduction

Investigations of the synthesis and properties of the acyclic cations *syn*-1-methylpentadienyliron tricarbonyl  $[(C_6H_9)Fe(CO)_3]^+$  and *syn,syn*-1,5-dimethylpentadienyliron tricarbonyl  $[(C_7H_{11})Fe(CO)_3]^+$  indicated (principally from n.m.r. data) that these species – like similar cyclic species [cyclohexadienyliron tricarbonyl cation, for example (Fischer & Fischer, 1960)] – possess an entirely *cisoid* arrangement of pentadienyl carbon atoms (Mahler & Pettit, 1963; Mahler, Gibson & Pettit, 1963). Hence all five pentadienyl carbons are bonded directly (and 'equivalently') to the  $Fe(CO)_3$  moiety as shown below.



Moreover, the hydrolyses of these cations were shown to be stereospecific, yielding only one of two possible diastereoisomers, with conformations *RR* and *SS* rather than *RS* and *SR*. (Two diastereoisomers in these compounds derive from the presence of two asymmetric centers in the alcohol, one at the C atom bonded to the hydroxyl function and the other resulting from the unsymmetrical diene-iron tricarbonyl group.)

Recently the report of an n.m.r. study (Foreman, 1972) employing the lanthanide shift reagent technique has questioned the conformation assigned by Pettit and co-workers to the alcohols formed upon hydrolysis of these pentadienyl cations. In particular it was suggested that although the hydrolysis is indeed

stereospecific the conformation of the resulting alcohols is that of the alternative diastereoisomer – *i.e.*, enantiomers *RS* and *SR* rather than enantiomers *RR* and *SS*. In order to resolve this controversy we have determined the structure of one of these alcohols, the 1,5-dimethyl species, by single-crystal X-ray diffraction methods.

### Experimental

Hydrolysis of the *syn,syn*-1,5-dimethylpentadienyliron tricarbonyl cation was effected as described by Mahler & Pettit to give the resulting alcohol *trans,trans*-3,5-heptadien-2-ol-iron tricarbonyl,  $C_7H_{12}OFe(CO)_3$ . Spectroscopic and analytical characterization of this compound is presented in the paper of Mahler & Pettit. Yellow plate-like crystals were obtained from pentane solution. Examination of several of these crystals *via* polarizing microscopy and Weissenberg photography indicated that they were not single, but composed of multiple thin plates. A single crystal suitable for study was eventually secured by vacuum sublimation methods ( $\sim 45^\circ C$ ), although the tendency to form as multiple thin plates persisted with these samples also.

Weissenberg photographs of the crystals initially selected, and subsequently found to be multiple, suggested monoclinic symmetry and systematic absences consistent with space group  $P2_1/c$ . However, owing to rapid decomposition of the crystals upon exposure to X-radiation at ambient conditions a satisfactory set of photographs for space-group determination could not be acquired. Later inspection of the diffractometer intensity data confirmed the space group as  $P2_1/c$ .

The prismatic crystal obtained by sublimation for data collection was bounded by seven faces consisting

of the planes (110), (1 $\bar{1}$ 0), ( $\bar{1}\bar{1}$ 0), ( $\bar{1}$ 21), ( $\bar{2}$ 10), (0 $\bar{2}$ 1) and (0 $\bar{2}$ 1), with extreme dimensions 0.38 mm parallel to the [010] direction, and maximum cross section of 0.30 × 0.39 mm, approximately orthogonal to the 0.38 mm dimension. The calculated volume of the data crystal was 0.0158 mm<sup>3</sup>. As an attempt to impede the steady decomposition of the crystal preliminary diffraction experiments and ensuing data collection were carried out with a Syntex P2<sub>1</sub> automated four-circle diffractometer equipped with the Syntex LT-1 low temperature flow system and a graphite monochromator. Temperatures of ca -32°C at the data crystal were maintained with a stream of cold nitrogen gas, and the crystal was found to be stable under these conditions.

At ca -32°C the unit-cell parameters were determined by least-squares refinement of 15 reflections with 25° ≤ 2θ ≤ 33° using graphite-monochromatized Mo Kα radiation. At the reduced temperature of data collection, the computed density for Z=8 is 1.455 g cm<sup>-3</sup>. The observed room temperature density [22 (1)°C] measured by flotation in aqueous ZnCl<sub>2</sub> solution is 1.430 (1) g cm<sup>-3</sup>. At the conclusion of all low-temperature diffraction work, lattice parameters were obtained at 22°C by least-squares refinement of the setting angles (80° ≤ 2θ ≤ 100°) of 19 reflections, determined on a General Electric XRD-5 diffractometer with Cu radiation, a narrow receiving slit (0.05°) and a takeoff angle of 3°. These cell data led to a calculated density at 22°C of 1.442 g cm<sup>-3</sup> for Z=8. The crystal data are summarized in Table 1.

Table 1. Crystal data for  
trans-trans-3,5-heptadien-2-ol-iron tricarbonyl,  
C<sub>10</sub>H<sub>12</sub>O<sub>4</sub>Fe

	22°C	-32°C
<i>a</i>	16.958 (8) Å	16.885 (3) Å
<i>b</i>	17.855 (8)	17.831 (3)
<i>c</i>	8.283 (5)	8.275 (2)
$\beta$	111.70 (4)°	111.91 (1)°
<i>V</i>	2330 (3) Å <sup>3</sup>	2311.3 (7) Å <sup>3</sup>
<i>D</i> <sub>cal</sub>	1.442 g cm <sup>-3</sup>	1.455 g cm <sup>-3</sup>
<i>D</i> <sub>meas</sub>	1.430 (1) g cm <sup>-3</sup>	

Systematic absences: *h*0*l*, *l*=2*n*+1; 0*k*0, *k*=2*n*+1

Space group P2<sub>1</sub>/c (No. 14)

Z=8; F(000)=1040; F.W. 252.06

$\lambda_{\text{Cu}}$ :  $K\alpha_{\text{mean}}=1.54178$ ;  $K\alpha_1=1.54050$ ;  $K\alpha_2=1.54433$  Å

$\lambda_{\text{Mo}}$ :  $K\alpha_{\text{mean}}=0.71069$  Å

$\mu(\text{Mo } K\alpha_{\text{mean}})=13.3$  cm<sup>-1</sup>

Intensity data were collected by the  $\omega$  scan technique at a constant speed of 3° min<sup>-1</sup> to minimize possible crystal decomposition.

Each peak was scanned symmetrically over a range of 1.0° through the calculated  $K\alpha_{1,2}$  position. Backgrounds were counted for a time equal to half the scan time, in positions offset by +1.0° and -1.0° in  $\omega$ .

4068 reflections in the octants *hkl* and  $\bar{h}\bar{k}\bar{l}$  were examined in the Mo Kα shell defined by 2° ≤ 2θ ≤ 50°. The intensities of four reflections in diverse regions of reciprocal space were recorded after every 96 reflections

as a measure of crystal decomposition and/or instrument instability. An analysis of the 47 sets of observations of these four standard reflections according to a scheme described earlier (Henslee & Davis, 1975) showed no significant trend over the 56 h of data collection. All correction factors in this analysis scheme were computed to be less than 2σ, so no decay correction was applied to the data. Perhaps sublimation of the crystal at room temperature rather than decay due to radiation is responsible for the decomposition observed while gathering Weissenberg photographs (see above).

Standard deviations were assigned to the intensity data in accordance with the expression  $\sigma(I)=[S^2(CT+B_1+B_2)+(pI)^2]^{1/2}$  where *S* is the scan rate, *CT* is the total integrated count, *B*<sub>1</sub> and *B*<sub>2</sub> are the background counts, and the intensity is  $I=S[CT-(B_1+B_2)]$ . A value of 0.02 was assigned to the empirical parameter *p* to account for instrument instabilities (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967). The net intensities *I* were corrected for Lorentz and polarization effects (including those due to reflection of the incident beam by the monochromator) and for absorption. The linear absorption coefficient  $\mu$  is 13.3 cm<sup>-1</sup>, and the transmission factors ranged from 0.67 to 0.78. The 2791 reflections for which  $I > 2.0\sigma(I)$  were then used in the succeeding computations leading to the solution and refinement of the structure.

#### Solution and refinement of the structure

The positions of the two Fe atoms were determined from a sharpened Patterson map. An electron density synthesis phased with these two positions revealed all nonhydrogen atoms. Isotropic refinement of this model structure by full-matrix least-squares methods converged at 0.089 and 0.090 for the error indices  $R = \sum |F_o| - |F_c| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ , respectively. The function minimized in refinement is  $\sum w(|F_o| - |F_c|)^2$ , where the weights *w* are  $\sigma(|F_o|)^{-2}$ , the reciprocal square of the standard deviation of each observation,  $|F_o|$ . Neutral atom scattering factors for Fe, O, C (Cromer & Waber, 1965) and H (Stewart, Davidson & Simpson, 1965) were used. Corrections for the real ( $\Delta f'$ ) and imaginary ( $\Delta f''$ ) parts of anomalous scattering were made to the Fe scattering function (Cromer, 1965). Full anisotropic refinement was then carried out nearly to convergence ( $R=0.064$ ,  $R_w=0.071$ ), and from an ensuing difference density map all H atoms (peaks with heights 0.4 to 0.7 e Å<sup>-3</sup>) were located. Continuation of least-squares refinement, now including positional and isotropic thermal parameters for 24 H atoms (12 per crystallographically independent molecule of the asymmetric unit) converged smoothly with final error indices  $R=0.042$ ,  $R_w=0.033$ , and a standard deviation of an observation with unit weight,  $[\sum w(|F_o| - |F_c|)^2 / (m-s)]^{1/2}$ , of 1.28, where *m*(2791) is the number of observations ( $|F_o|$ ), and *s*(367) the number of variables in least-squares

refinement.\* If all 4068 symmetry-independent reflections are used in structure factor computation,  $R=0.075$  and  $R_w=0.036$ . In the final cycles of refinement the number of independent variables exceeded the storage capacity of the computer, so that when least-squares refinement was expanded to include the H atom contributions the atomic variables were divided into two structurally related blocks. That is, the parameters describing the two Fe atoms and their coordination spheres were refined simultaneously as one block, while the remaining parameters (including some parameters common to both blocks) were treated in a second block. In the final cycle of least-squares refinement no nonhydrogen atom positional parameter shifted by more than 0.04 of its estimated standard deviation, and no thermal parameter by more than 0.09 of its e.s.d. For the H atoms, only the shifts of 0.14 and 0.11 of an e.s.d. in the  $x$  and  $z$  coordinates, respectively, of methyl H(7A3) exceeded 0.07 of an e.s.d. in this final cycle, and no isotropic thermal parameter

shifted by more than 0.04 of its e.s.d. A final difference Fourier map showed a few (*ca* 8) peaks of 0.3–0.4 e Å<sup>-3</sup>. With the exception of one peak close to methyl carbon C(7A) these peaks are about 1 Å from atoms Fe(A) or Fe(B), clearly chemically unreasonable sites. For comparison, the density of a C atom of a previous difference Fourier map is 5.5 e Å<sup>-3</sup>. There are no indications that the two independent molecules per asymmetric unit are related by pseudosymmetry, and correlation coefficients between chemically equivalent atoms of these two molecules did not exceed 0.6 during least-squares refinement.

Final positional and thermal parameters, along with corresponding estimated standard deviations as obtained from the inverse matrix, are presented in Table 2.

#### Principal computer programs

Absorption correction, *SYABS*, a local version of *ORABS* by W. R. Busing and H. A. Levy as modified by J. M. Williams; Fourier program, *RFOUR* by S. T. Rao, modified locally by R. E. Davis; full-matrix least-squares, *NUCLS*, J. A. Ibers's version of *ORFLS*; molecular geometry, *DAESD* by D. R. Harris, modified locally by R. E. Davis; least-squares plane, *LSMP* by M. E. Pippy; *ORTEP II*, thermal

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31194 (20 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Positional and thermal parameters

(a) Fractional atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\times 10^4$ ) with estimated standard deviations. See Fig. 1 for the atom-numbering sequence. Numbers in parentheses are the estimated standard deviations in the units of the least significant digits for the corresponding parameter. The anisotropic temperature factor is

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

For atoms Fe(A) and Fe(B), the positional parameters are given  $\times 10^5$ , and the thermal parameters  $\times 10^5$ .

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Fe(A)	-3787 (4)	9381 (3)	22548 (7)	289 (3)	243 (2)	1475 (12)	36 (2)	222 (4)	10 (4)
C(1A)	603 (3)	457 (2)	3373 (5)	42 (2)	30 (2)	223 (10)	4 (2)	29 (4)	4 (3)
O(2A)	1238 (2)	153 (2)	4069 (4)	45 (2)	56 (2)	344 (9)	22 (1)	27 (3)	28 (3)
C(3A)	-949 (3)	72 (2)	1961 (5)	35 (2)	32 (2)	219 (10)	6 (2)	37 (4)	-1 (3)
O(4A)	-1294 (2)	-486 (2)	1792 (4)	62 (2)	31 (1)	411 (10)	-9 (1)	73 (3)	-9 (3)
C(5A)	-291 (2)	1097 (2)	202 (6)	36 (2)	22 (2)	235 (10)	1 (1)	36 (4)	-11 (3)
O(6A)	-260 (2)	1212 (2)	-1138 (4)	86 (2)	47 (1)	211 (7)	2 (1)	89 (3)	3 (2)
C(7A)	1117 (4)	2144 (4)	4099 (10)	40 (3)	51 (3)	322 (18)	-12 (2)	18 (6)	-30 (6)
C(8A)	167 (3)	1998 (2)	3260 (6)	34 (2)	27 (2)	194 (10)	0 (2)	19 (4)	-14 (3)
C(9A)	-284 (3)	1683 (2)	4214 (6)	35 (2)	37 (2)	128 (9)	7 (2)	12 (4)	-7 (3)
C(10A)	-1145 (3)	1479 (2)	3318 (5)	37 (2)	27 (2)	140 (8)	3 (1)	33 (4)	2 (3)
C(11A)	-1498 (2)	1601 (2)	1502 (5)	34 (2)	23 (1)	131 (8)	4 (1)	30 (3)	4 (3)
C(12A)	-2379 (2)	1312 (2)	428 (5)	30 (2)	28 (2)	125 (8)	4 (1)	21 (3)	6 (3)
C(13A)	-2499 (4)	1148 (3)	-1442 (6)	37 (3)	53 (3)	155 (10)	3 (2)	21 (4)	-13 (4)
O(14A)	-3009 (2)	1863 (2)	369 (4)	34 (1)	39 (1)	143 (6)	12 (1)	29 (2)	17 (2)
Fe(B)	42194 (4)	12197 (3)	20702 (7)	331 (3)	224 (2)	1473 (12)	10 (2)	334 (5)	68 (4)
C(1B)	3143 (3)	1251 (2)	1980 (5)	49 (2)	38 (2)	216 (10)	1 (2)	53 (4)	12 (3)
O(2B)	2467 (2)	1267 (2)	1975 (5)	45 (2)	79 (2)	412 (10)	8 (2)	89 (4)	24 (3)
C(3B)	4584 (3)	1100 (2)	4383 (6)	48 (2)	22 (2)	210 (10)	-4 (1)	56 (4)	-1 (3)
O(4B)	4806 (2)	1010 (2)	5839 (4)	87 (2)	42 (1)	141 (6)	-6 (1)	53 (3)	10 (2)
C(5B)	4270 (2)	288 (2)	1299 (5)	31 (2)	34 (2)	133 (8)	-4 (1)	20 (3)	8 (3)
O(6B)	4296 (2)	-291 (2)	751 (4)	70 (2)	29 (1)	207 (7)	-6 (1)	38 (3)	-20 (2)
C(7B)	3016 (4)	1546 (4)	-1914 (8)	40 (3)	64 (3)	221 (13)	1 (2)	17 (5)	45 (5)
C(8B)	3907 (3)	1600 (3)	-546 (5)	33 (2)	37 (2)	156 (9)	1 (2)	28 (4)	25 (3)
C(9B)	4138 (3)	2184 (3)	-660 (6)	43 (3)	27 (2)	247 (12)	8 (2)	55 (5)	28 (4)
C(10B)	4931 (3)	2152 (2)	2081 (6)	45 (2)	21 (2)	181 (10)	-3 (1)	50 (4)	-2 (3)
C(11B)	5457 (2)	1522 (2)	2183 (5)	32 (2)	22 (1)	131 (8)	-5 (1)	31 (3)	-1 (3)
C(12B)	6261 (2)	1402 (2)	3755 (5)	35 (2)	32 (2)	109 (8)	-5 (1)	25 (3)	-9 (3)
C(13B)	6555 (3)	593 (3)	3974 (7)	44 (3)	36 (2)	173 (11)	2 (2)	19 (5)	5 (4)
O(14B)	6938 (2)	1848 (2)	3605 (4)	39 (2)	37 (1)	179 (6)	-12 (1)	42 (3)	-24 (2)

Table 2 (cont.)

(b) Fractional atomic coordinates ( $\times 10^3$ ) and isotropic temperature factors for hydrogen atoms. Numbers in parentheses are the estimated standard deviations in the units of the least significant digits for the corresponding parameters. Isotropic thermal parameters are in units of  $\text{\AA}^2$ . The sequence number of a hydrogen atom corresponds to that of the carbon or oxygen atom to which it is bound.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(7A1)	121 (3)	264 (3)	452 (6)	7 (1)
H(7A2)	140 (3)	210 (3)	332 (7)	9 (2)
H(7A3)	136 (3)	182 (3)	504 (7)	8 (2)
H(8A)	-11 (2)	238 (2)	233 (4)	3.1 (8)
H(9A)	0 (2)	157 (2)	540 (5)	3.3 (9)
H(10A)	-141 (2)	120 (2)	394 (4)	3.1 (9)
H(11A)	-139 (2)	203 (2)	102 (4)	1.4 (7)
H(12A)	-250 (2)	83 (2)	99 (4)	1.8 (7)
H(13A1)	-305 (3)	101 (2)	-207 (5)	4 (1)
H(13A2)	-232 (2)	160 (2)	-199 (5)	4 (1)
H(13A3)	-213 (2)	73 (2)	-160 (4)	3.5 (9)
H(14A)	-303 (2)	189 (2)	133 (4)	3 (1)
H(7B1)	296 (3)	186 (2)	-286 (6)	6 (1)
H(7B2)	264 (3)	173 (2)	-147 (6)	6 (1)
H(7B3)	286 (3)	101 (3)	-226 (6)	8 (2)
H(8B)	432 (2)	137 (2)	-95 (4)	2.4 (8)
H(9B)	372 (2)	234 (2)	58 (4)	2.9 (8)
H(10B)	507 (2)	251 (2)	304 (4)	2.6 (8)
H(11B)	551 (2)	131 (2)	105 (4)	2.5 (7)
H(12B)	620 (2)	156 (2)	484 (4)	2.3 (7)
H(13B1)	612 (3)	26 (2)	425 (5)	5 (1)
H(13B2)	664 (2)	42 (2)	298 (5)	3.3 (9)
H(13B3)	716 (3)	55 (2)	500 (6)	7 (1)
H(14B)	697 (3)	224 (2)	404 (6)	5 (1)

Table 3. Bond lengths ( $\text{\AA}$ )

Numbers in parentheses are the estimated standard deviations in the last significant digit. See Fig. 1 for identity of the atoms.

	Molecule <i>A</i>	Molecule <i>B</i>
Fe—C(1)	1.788 (4)	1.793 (5)
Fe—C(3)	1.788 (4)	1.792 (5)
Fe—C(5)	1.783 (5)	1.793 (4)
Fe—C(8)	2.131 (4)	2.139 (5)
Fe—C(9)	2.057 (5)	2.054 (5)
Fe—C(10)	2.057 (4)	2.050 (4)
Fe—C(11)	2.116 (4)	2.127 (4)
C(1)—O(2)	1.147 (6)	1.141 (6)
C(3)—O(4)	1.136 (5)	1.133 (6)
C(5)—O(6)	1.148 (6)	1.136 (5)
C(7)—C(8)	1.515 (8)	1.512 (8)
C(8)—C(9)	1.403 (6)	1.394 (7)
C(9)—C(10)	1.412 (6)	1.416 (7)
C(10)—C(11)	1.412 (6)	1.415 (6)
C(11)—C(12)	1.511 (6)	1.505 (6)
C(12)—C(13)	1.513 (6)	1.514 (6)
C(12)—O(14)	1.437 (5)	1.437 (5)
C(7)—H(7,1)	0.95 (5)	0.93 (5)
C(7)—H(7,2)	0.94 (6)	0.90 (5)
C(7)—H(7,3)	0.94 (5)	1.01 (5)
C(8)—H(8)	1.00 (4)	0.98 (3)
C(9)—H(9)	0.94 (4)	0.93 (4)
C(10)—H(10)	0.94 (4)	0.98 (3)
C(11)—H(11)	0.92 (3)	1.05 (3)
C(12)—H(12)	1.03 (3)	0.98 (3)
C(13)—H(13,1)	0.92 (4)	1.03 (4)
C(13)—H(13,2)	1.02 (4)	0.94 (4)
C(13)—H(13,3)	1.00 (4)	1.06 (5)
O(14)—H(14)	0.81 (4)	0.78 (4)

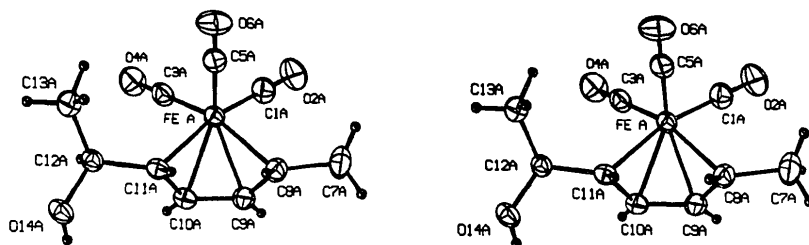


Fig. 1. A stereo view of molecule *A*, illustrating the atom numbering scheme employed for both independent molecules of the structure. Ellipsoids of 30% probability are shown for nonhydrogen atoms; hydrogen atoms are drawn as spheres of radius 0.1  $\text{\AA}$ .

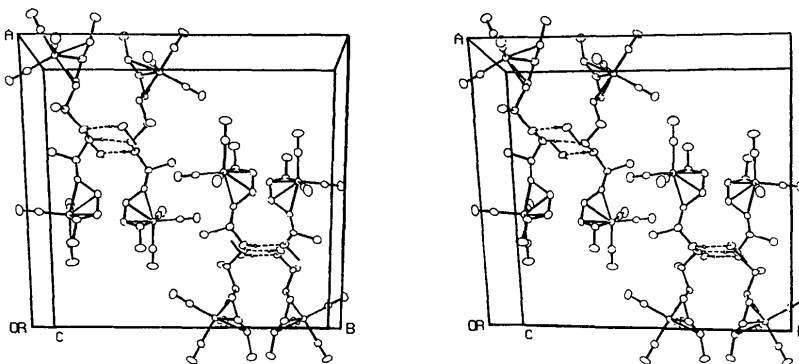


Fig. 2. A stereo view of the unit cell. Ellipsoids of 20% probability are shown for nonhydrogen atoms. Hydrogen atoms not participating in hydrogen bonding are omitted for the sake of clarity. Hydrogen bonds are indicated by dashed lines. Hydrogen-bond hydrogen atoms are presented as spheres of radius 0.1  $\text{\AA}$ .

ellipsoid plotting program by C. K. Johnson; and various data processing programs of local origin.

### Discussion

Fig. 1 provides a stereo view of molecule *A*, and illustrates the atom numbering scheme. The same numerical sequence applies to the atoms of molecule *B*. Fig. 2 presents a stereo view of the packing of the molecules in the unit cell. Fractional coordinates and

thermal parameters for all atoms are given in Table 2. Bond lengths and bond angles are in Tables 3 and 4.

The crystal structure consists of discrete  $C_{10}H_{12}O_4Fe$  monomers linked together in an infinite chain parallel to the crystallographic *z* direction at  $x \sim 0.7$  by hydrogen bonds between alternating *A* and *B* molecules (see Fig. 2). The two independent hydrogen bonds are 1.91 (4) and 1.94 (4) Å for the  $O(14B) \cdots H(14A)$  and  $O(14A) \cdots H(14B)$  interactions, respectively. The two independent  $O(14A) \cdots O(14B)$  separations of 2.707 (4) and 2.713 (4) Å are in agreement with  $R-O-H \cdots OH_2$  distances of 2.75 Å reported for the structure of 5,5-dihydroxybarbituric acid trihydrate (Mootz & Jeffrey, 1965). The angles subtended at  $H(14A)$  and  $H(14B)$  of the Fe-containing compound are 174 (4) and 171 (5)°, respectively. As shown in Figs. 1 and 2 each Fe atom fulfills its coordination requirements by bonding with three CO molecules and the (four)  $\pi$  electrons of the butadiene group. From the bond angles of Table 4 the butadiene carbon atoms here, as in related structures (see below), are clearly  $sp^2$ -hybridized.

The molecular geometries of the two crystallographically independent butadiene- $Fe(CO)_3$  moieties in this structure are in excellent agreement with one another (see Tables 3, 4, and 5) and with similar portions of other structures that have been reported previously: *e.g.*, butadiene-iron tricarbonyl (Mills & Robinson, 1963), sorbic acid-iron tricarbonyl (Eiss, 1970), (vitamin-A aldehyde)-iron tricarbonyl (Mason & Robertson, 1970), and the (-)-2-(*S*- $\alpha$ -methylbenzylammonium)-*cis,trans*-hepta-3,5-dienyliron tricarbonyl cation (Maglio, Musco, Palumbo & Sirigu, 1971).

The least-squares planes formed by the butadiene atoms [C(8)-C(9)-C(10)-C(11)] of molecules *A* and *B* indicate that these portions of the molecules are indeed

Table 4. Bond angles (°)

Numbers in parentheses are the estimated standard deviations in the last significant digit. See Fig. 1 for identity of the atoms. Angles involving the methyl groups of molecules *A* and *B*: H-C(methyl)-H, range = 103 (3) to 113 (4)°, mean = 108 (3)°; C-C(methyl)-H, range = 108 (3) to 115 (2)°, mean = 111 (2)°.

	Molecule <i>A</i>	Molecule <i>B</i>
C(1)—Fe—C(3)	90.2 (2)	89.3 (2)
C(1)—Fe—C(5)	100.3 (2)	101.3 (2)
C(3)—Fe—C(5)	103.9 (2)	103.1 (2)
C(1)—Fe—C(8)	92.3 (2)	94.8 (2)
C(1)—Fe—C(9)	96.8 (2)	95.6 (2)
C(3)—Fe—C(10)	94.0 (2)	97.1 (2)
C(3)—Fe—C(11)	93.8 (2)	92.4 (2)
C(5)—Fe—C(8)	93.1 (2)	87.7 (2)
C(5)—Fe—C(11)	90.8 (2)	94.3 (2)
C(8)—Fe—C(9)	39.1 (2)	38.8 (2)
C(8)—Fe—C(10)	70.5 (2)	70.7 (2)
C(8)—Fe—C(11)	80.1 (2)	80.3 (2)
C(9)—Fe—C(10)	40.2 (2)	40.4 (2)
C(9)—Fe—C(11)	70.7 (2)	70.7 (2)
C(10)—Fe—C(11)	39.5 (2)	39.5 (2)
C(7)—C(8)—Fe	124.1 (4)	122.7 (4)
H(8)—C(8)—Fe	107 (2)	106 (2)
C(7)—C(8)—C(9)	121.0 (5)	121.3 (5)
C(7)—C(8)—H(8)	110 (2)	111 (2)
Fe—C(8)—C(9)	67.6 (2)	67.3 (3)
H(8)—C(8)—C(9)	121 (2)	121 (2)
C(8)—C(9)—Fe	73.3 (3)	73.9 (3)
H(9)—C(9)—Fe	123 (2)	120 (2)
C(8)—C(9)—C(10)	118.5 (4)	119.3 (4)
C(8)—C(9)—H(9)	120 (2)	117 (2)
Fe—C(9)—C(10)	69.9 (3)	69.6 (3)
H(9)—C(9)—C(10)	121 (2)	123 (2)
C(9)—C(10)—Fe	69.9 (3)	70.0 (3)
H(10)—C(10)—Fe	119 (2)	120 (2)
C(9)—C(10)—C(11)	117.6 (4)	117.4 (4)
C(9)—C(10)—H(10)	117 (2)	121 (2)
Fe—C(10)—C(11)	72.5 (2)	73.2 (2)
H(10)—C(10)—C(11)	124 (2)	121 (2)
C(10)—C(11)—Fe	68.0 (2)	67.3 (2)
H(11)—C(11)—Fe	108 (2)	107 (2)
C(10)—C(11)—C(12)	120.4 (4)	120.6 (4)
C(10)—C(11)—H(11)	121 (2)	119 (2)
Fe—C(11)—C(12)	123.9 (3)	123.8 (3)
H(11)—C(11)—C(12)	110 (2)	112 (2)
C(11)—C(12)—C(13)	113.3 (4)	112.9 (4)
C(11)—C(12)—O(14)	110.0 (3)	109.7 (3)
C(11)—C(12)—H(12)	109 (2)	112 (2)
H(12)—C(12)—C(13)	109 (2)	107 (2)
H(12)—C(12)—O(14)	108 (2)	107 (2)
C(13)—C(12)—O(14)	106.4 (4)	107.6 (4)
C(12)—O(14)—H(14)	108 (3)	112 (4)
Fe—C(1)—O(2)	178.8 (4)	177.9 (4)
Fe—C(3)—O(4)	178.5 (4)	178.5 (3)
Fe—C(5)—O(6)	177.7 (4)	177.4 (4)

Table 5. Butadiene group [C(8)-C(9)-C(10)-C(11)] least-squares planes and distances from these planes

Orthonormal (Å) coordinate system with axes *X*, *Y*, and *Z* parallel to unit-cell vectors *a*, *b*, and *c*\*, respectively. Coordinates of atoms marked with asterisks were used to define the planes. A negative deviation from the plane indicates that the atom with coordinates given in Table 2 lies between the plane and the origin. The subscripts *A* and *B* refer to molecules *A* and *B* respectively. Numbers in parentheses are the e.s.d.'s in the last significant digits.

$$0.3760X_A - 0.9138Y_A - 0.1538Z_A + 3.9118 = 0$$

$$0.6857X_B + 0.4799Y_B - 0.5473Z_B - 6.2402 = 0$$

Deviations in Å  $\times 10^3$  from planes

	Molecule <i>A</i>	Molecule <i>B</i>
C(8)*	-1 (4)	-2 (5)
C(9)*	2 (4)	4 (5)
C(10)*	-2 (4)	-4 (5)
C(11)*	1 (4)	2 (4)
C(7)	169 (7)	-214 (7)
C(12)	163 (4)	-164 (4)
Fe	1615 (1)	-1619 (1)
H(8)	-584 (34)	531 (34)
H(9)	91 (35)	-128 (36)
H(10)	144 (33)	-139 (34)
H(11)	-526 (30)	605 (32)

planar (see Table 5), and that the other atoms bound to the four butadiene carbons deviate from these planes in the same regular fashion and to about the same extent as observed in sorbic acid-Fe(CO)<sub>3</sub> (Eiss, 1970). That is, atoms H(9), H(10), C(7), and C(12) lie *ca* 0.1 to 0.2 Å on the 'Fe side' of the planes (see Fig. 1), while H(8) and H(11) lie *ca* 0.5 to 0.6 Å to the opposite side. These deviations correspond to rotations of 7.4 and 9.8° about the C(8)–C(9) bonds in molecules *A* and *B*, respectively, and in the same order, of 7.3 and 7.0° about the C(10)–C(11) bonds. It has been suggested (Churchill, 1965) that such rotations result from an apparent enhancement of the overlap between the filled *d* orbitals of the Fe atoms and the  $\pi$ -acceptor orbitals of the butadiene residues of these kinds of compounds. Also, since the terminal hydrogen atoms of the butadiene groups are separated by about the van der Waals distance in this *cisoid* conformation [H(8*A*)...H(11*A*)=2.13 (5), H(8*B*)...H(11*B*)=2.07 (5), H...H van der Waals  $\sim$ 2.0 Å (Baur, 1972)], the consequent H...H repulsions may be somewhat diminished by the observed rotations.

The (intramolecular) dihedral angle between the least-squares planes defined by the carbonyl carbons and the butadiene carbons is 20.3° for molecule *A* and 21.2° for molecule *B*, in agreement with the value of 21° found in octafluorocyclohexa-1,3-diene-iron tricarbonyl (Churchill & Mason, 1967). This may be contrasted to the 0.01° angle noted in the more symmetrical ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>3</sub>PF<sub>6</sub> complex (Gress & Jacobson, 1973).

The objective of this study was to determine the stereochemistry of the alcohol which forms upon hydrolysis of the 1,5-dimethylpentadienyliron tricarbonyl cation (or, analogously, the 1-methylpentadienyliron tricarbonyl hydrolysate). The configuration about the asymmetric C atom C(12) as determined by this endeavor, is consistent with the original prediction of Mahler & Pettit (1963). Hence hydrolysis of these acyclic pentadienyl cations yields the *RR* and *SS* racemate, corroborating the (hydrolytic) mechanism proposed by Pettit and co-workers. A detailed critique of the application of lanthanide shifted n.m.r. spectral interpretation (Foreman, 1972) appears elsewhere (Willcott, Bearden, Davis & Pettit, 1975).

This work was supported by the Robert A. Welch Foundation (Grant No. F-233). We are also indebted to the National Science Foundation for the purchase of the Syntex P<sub>2</sub> diffractometer (Grant No. GP-37028), to the University of Texas at Austin Computation Center, and to Professor Rowland Pettit for supplying the crystals and describing the chemistry of these systems.

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