

Within the  $\text{SeOCl}_4^{2-}$  units, the short Se-Cl bonds,  $2.246 \pm 0.004$  and  $2.244 \pm 0.004$  Å, are comparable to those found in  $(\text{C}_6\text{H}_5)_2\text{SeCl}_2$  ( $2.30 \pm 0.05$  Å),<sup>15</sup>  $(\text{CH}_3\text{-C}_6\text{H}_4)_2\text{SeCl}_2$  ( $2.38 \pm 0.02$  Å),<sup>16</sup>  $\text{C}_4\text{H}_8\text{Se}_2\text{Cl}_4$  ( $2.24 \pm 0.02$  Å),<sup>17</sup> and  $\text{C}_9\text{H}_8\text{NO}^+\text{SeCl}_3^-$  ( $2.234 \pm 0.004$  and  $2.271 \pm 0.004$  Å).<sup>5</sup> These Se-Cl bonds are usually considered as single covalent bonds. The other selenium-chlorine bonds, the 2.5-Å bonds ( $2.445$  and  $2.525$ ,  $2.502$  and  $2.431$  Å, all  $\pm 0.004$  Å) are rather unique. They are about the same as the average value of the bond lengths of the short and long Se-Cl bonds ( $2.39 \pm 0.02$  and  $2.57 \pm 0.02$  Å) found in  $\text{SeOCl}_2 \cdot 2\text{py}$ .<sup>18</sup>

The intermolecular environments of corresponding chlorine atoms for the two asymmetric units are very similar. Thus the packing features of Cl(1) and Cl(5) are dominated by the hydrogen bonding, and the remaining chlorine atoms have shortest intermolecular contacts with ring atoms of the cations. The one note-

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worthy exception is a 3.28-Å distance between Cl(3) and Cl(7).

The immediate environment of the selenium atoms can thus be considered a distorted square-pyramidal  $\text{SeOCl}_4^{2-}$  unit as shown in Figure 1 or a  $\text{SeOCl}_3^-$  unit which is approximately trigonal bipyramidal with axial chlorines at 2.5 Å, the oxygen, the chlorine at 2.2 Å, and a lone pair of electrons all being equatorial.

The occurrence of the three different Se-Cl lengths in the  $\text{SeOCl}_4^{2-}$  units is certainly the most significant feature of the structure. The explanation of the difference in bond character is very likely related to the manner in which the bonding orbitals on the selenium atom are being used, because there do not seem to be any structural features which would prevent the attainment of equal Se-Cl bond distances. Further aspects of the bonding in this and related selenium studies will be the subject of a future paper.

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## The Crystal and Molecular Structure of Sorbic Acid-Iron Tricarbonyl. Hybridization of the Butadiene Group in Metal Complexes

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The crystal and molecular structure of sorbic acid-iron tricarbonyl,  $(\text{C}_8\text{H}_8\text{O}_2)\text{Fe}(\text{CO})_3$ , has been determined from an X-ray diffraction study, with all hydrogen atoms being located and included in the least-squares refinement. The hybridization of all carbon atoms in the butadiene group is essentially  $sp^2$ , with a twist of about  $8.5^\circ$  about the terminal C-C bonds of the group in a direction to increase overlap between the  $\pi$ -electron orbitals of the butadiene group and the metal orbitals. The sorbic acid ligand consequently has four coplanar carbon atoms (those of the butadiene skeleton) and systematic deviations from the plane for the other ligand atoms, as predicted by Gutowsky, *et al.*, from  $^{13}\text{C}$  nmr. The presence of two crystallographically independent and essentially identical molecules in the unit cell gives strong evidence for the lack of distortion of bond lengths and bond angles within the monomeric unit by packing forces. The triclinic unit cell, space group  $P\bar{1}$ , contains two molecular dimers, each having a center of symmetry and held together by hydrogen-bonded carboxyl groups. Unit cell constants are  $a = 7.493$  (1),  $b = 22.885$  (5),  $c = 7.236$  (1) Å;  $\alpha = 81.70$  (1),  $\beta = 122.23$  (1),  $\gamma = 95.58$  (1)°. The observed density was  $1.60$  g/cm<sup>3</sup>, in agreement with  $1.61$  g/cm<sup>3</sup> calculated assuming four molecular units per unit cell. The structure was solved using 2086 statistically significant unique reflections collected by a counter method and refined to a final  $R$  factor of 0.047.

### Introduction

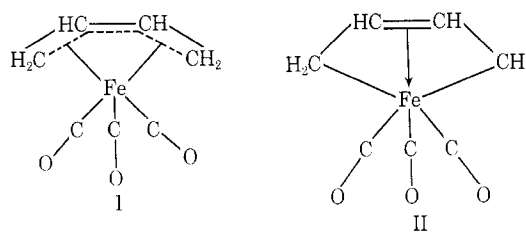
Since the synthesis of butadiene-iron tricarbonyl in 1930 by Rheilen, *et al.*,<sup>1</sup> and the subsequent treatment of bonding by Hallam and Pauson,<sup>2</sup> a great deal of attention has been directed to the elucidation of the nature of the very stable bond between the butadiene group and iron atom.<sup>3</sup>

(1) H. Rheilen, A. Gruhl, G. Hessling, and O. Pfrengle, *Justus Liebig's Ann. Chem.*, **482**, 161 (1930).

(2) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

(3) (a) M. Cais in "The Chemistry of Alkenes," S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1964, p 335; (b) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964); (c) M. R. Churchill and R. Mason, *ibid.*, **5**, 93 (1967).

The two leading models for the bonding in butadiene-iron tricarbonyl complexes are represented as I and II.



In I, the carbon atoms of the butadiene group have  $sp^2$  hybridization and the bonding to iron is *via* the de-

localized  $\pi$  electrons. In II the terminal carbon atoms are  $\sigma$  bonded to the iron atom and consequently should be closer to  $sp^3$  hybridization. The crystal structure determination of butadiene-iron tricarbonyl<sup>4</sup> was clearly consistent with I, while structures of related compounds involving cyclic dienes<sup>5-9</sup> have shown varying degrees of support for either I or II. This has led to the suggestion<sup>10</sup> that the problem may not even be suitable for crystallographic study, since it has not yet been established whether these differences are due to electronic factors or whether they may be controlled by packing effects.<sup>11</sup> Studies in solutions were initially very confusing with I being favored<sup>12,13</sup> on the basis of infrared and ultraviolet spectra while nmr seemed to support II.<sup>14,15</sup> More recently these and further data<sup>16,17</sup> have been interpreted as favoring I, but with a degree of distortion from the idealized planar butadiene arrangement. Two types of distortion have been proposed: (1) rotation about the "single" bond of the butadiene group,<sup>16</sup> resulting in a loss of planarity of the four carbon atoms, or (2) rotation about the two "double" bonds of the butadiene group,<sup>17</sup> leaving the four carbon atoms coplanar but causing the atoms bonded to the butadiene skeleton to be out of the plane.

Churchill and Mason<sup>8c</sup> considered the valence bond approach, permitting only I or II, to be an oversimplification and have used molecular orbital arguments to propose a smooth transition from I to II with an increasing contribution of the lowest antibonding orbital of the butadiene group to the molecular orbitals of the complex. In order to study further the bonding in these compounds and to determine the influence of packing forces on the geometry of the molecules, the single-crystal structure determination of two different crystal forms of sorbic acid-iron tricarbonyl has been undertaken. The structure of the crystal containing a racemic mixture is reported here.

### Experimental Section

Crystals of DL-sorbic acid-iron tricarbonyl,  $(C_6H_8O_2)Fe(CO)_3$ , supplied by Professor Alfredo Musco,<sup>18</sup> were examined and one, essentially a parallelepiped, having dimensions approximately  $0.5 \times 0.2 \times 0.08$  mm, with one corner truncated, was mounted and proved satisfactory for collection of all data. Precession photographs indicated the crystal was triclinic with possible

space groups P1 or  $P\bar{1}$ ; a Delauney reduction<sup>19</sup> indicated no higher symmetry was present. The crystal was moved to a Picker FACS-1 computer-controlled diffractometer where 12 reflections, having  $\theta$  for Cu  $K\beta_1$  values between 30 and 43°, were centered<sup>20</sup> in the detector window. The observed settings for  $2\theta$ ,  $\omega$ , and  $\chi$  were used to calculate the following unit cell parameters (Cu  $K\beta_1 = 1.39217 \text{ \AA}$ ):  $a = 7.493 \pm 0.001$ ,  $b = 22.885 \pm 0.005$ ,  $c = 7.236 \pm 0.001 \text{ \AA}$ ;  $\alpha = 81.70 \pm 0.01$ ,  $\beta = 122.23 \pm 0.01$ ,  $\gamma = 95.58 \pm 0.01^\circ$ ;  $V = 1038.3 \text{ \AA}^3$ . The observed density of 1.60 g/cm<sup>3</sup>, determined by flotation, agreed well with the calculated density of 1.61 g/cm<sup>3</sup>, assuming four formula units per unit cell. The observed faces were (010), (0 $\bar{1}$ 0), ( $\bar{1}$ 01), (10 $\bar{1}$ ), (001), and the unidentified face of the truncated corner.

A full sphere of data was collected, using niobium-filtered Mo  $K\alpha$  radiation, with  $\theta_{MoK\alpha} \leq 25^\circ$ , a takeoff angle of 4°, and the pulse-height discriminator set to accept 95% of the Mo  $K\alpha$  radiation, when centered on the  $K\alpha$  peak. The moving-crystal, moving-counter technique was used, with a  $2\theta$  scan rate of 1°/min and scan range of  $(1.33 + \Delta)$ , where  $\Delta$  is introduced to allow for the  $2\theta$  separation of the  $K\alpha_1$  and  $K\alpha_2$  peaks at increasing values of  $(\sin \sigma)/\lambda$ ; this range was more than sufficient to allow for the observed mosaic spread of the crystal. The crystal-source and crystal-detector distances were each approximately 24 cm; 1.5-mm diameter incident- and exit-beam collimators were used, without further restriction on the aperture. Background counts of 10 sec each were measured at the extremes of each  $2\theta$  scan. The observed intensities<sup>21</sup> were calculated using the formula  $I = A(P - (t/20)B)$ , where  $A$  is the correction factor for the attenuator inserted for those reflections having counting rates which would otherwise have exceeded the linear counting range of the detector,  $P$  is the number of counts during the scan,  $B$  is the sum of the background counts, and  $t$  is the counting time for the scan in seconds. Three standard reflections, measured after every 50 reflections, showed no fluctuations greater than  $\pm 2\%$  during the collection of the intensity data. A total of 7320 reflections were measured, of which 4305 were accepted as significant under the criterion  $I \geq 2.5(P + (t/400)B)^{1/2}$ , and averaging of the equivalent accepted reflections left 2086 unique reflections. The observed intensities were then corrected for Lorentz and polarization effects.

### Solution and Refinement of the Structure

A three-dimensional map of the Patterson function<sup>22</sup> readily gave the positions of the two unique iron atoms, under the assumption that the space group is  $P\bar{1}$ . A Fourier map phased on the iron atoms yielded the positions of all carbon and oxygen atoms and confirmed the presence of two independent hydrogen-bonded dimers in the unit cell. A structure factor calculation<sup>23,24</sup> phased on Fe, C, and O gave  $R_1 = \Sigma [|F_o| - |F_c|]/\Sigma |F_o| = 0.327$  where  $F_o$  is the observed and  $F_c$  the calculated structure factor. The weighted residual  $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/w|F_o|^2\}^{1/2}$  (where  $w = 4F_o^2/$

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TABLE II  
 FINAL ATOMIC COORDINATES<sup>a</sup> FOR (C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>)Fe(CO)<sub>3</sub>

Atom	x	y	z	B, <sup>b</sup> Å <sup>2</sup>
Fe <sub>1</sub>	0.24406 (14)	0.36703 (4)	0.22517 (14)	...
Fe <sub>2</sub>	0.09233 (14)	0.86124 (4)	0.86942 (14)	...
O <sub>11</sub>	-0.1993 (8)	0.40092 (22)	-0.0335 (8)	4.55 (11)
O <sub>12</sub>	0.2375 (9)	0.26933 (26)	0.5322 (9)	5.95 (13)
O <sub>13</sub>	0.1654 (10)	0.30092 (29)	-0.1240 (11)	7.22 (16)
O <sub>14</sub>	0.2086 (9)	0.44823 (23)	0.6513 (7)	...
O <sub>15</sub>	0.0582 (8)	0.49530 (22)	0.3119 (7)	...
O <sub>21</sub>	-0.3389 (9)	0.81641 (24)	0.7113 (8)	5.33 (12)
O <sub>22</sub>	0.1393 (9)	0.85140 (25)	0.5011 (9)	5.76 (13)
O <sub>23</sub>	0.2593 (9)	0.74599 (27)	1.1129 (9)	6.17 (14)
O <sub>24</sub>	-0.2736 (7)	1.00222 (21)	0.4791 (7)	...
O <sub>25</sub>	-0.3484 (7)	0.95297 (20)	0.7204 (7)	...
C <sub>11</sub>	-0.0213 (11)	0.38868 (30)	0.0686 (11)	3.41 (14)
C <sub>12</sub>	0.2399 (11)	0.30783 (33)	0.4059 (11)	3.76 (15)
C <sub>13</sub>	0.1985 (11)	0.32743 (34)	0.0163 (12)	4.23 (16)
C <sub>14</sub>	0.6854 (20)	0.31786 (61)	0.3325 (19)	5.90 (25)
C <sub>15</sub>	0.5797 (11)	0.39298 (33)	0.3771 (12)	3.79 (15)
C <sub>16</sub>	0.4956 (11)	0.41434 (32)	0.2319 (11)	3.67 (14)
C <sub>17</sub>	0.3729 (11)	0.45032 (33)	0.2597 (12)	3.49 (14)
C <sub>18</sub>	0.3444 (11)	0.43207 (29)	0.4396 (11)	2.91 (13)
C <sub>19</sub>	0.1918 (11)	0.46108 (31)	0.4602 (11)	3.51 (14)
C <sub>21</sub>	-0.1686 (11)	0.83452 (30)	0.7761 (11)	3.42 (14)
C <sub>22</sub>	0.1189 (11)	0.85552 (32)	0.6426 (12)	3.80 (15)
C <sub>23</sub>	0.1935 (11)	0.79217 (34)	1.0182 (11)	4.13 (16)
C <sub>24</sub>	0.6070 (14)	0.87411 (45)	1.1438 (15)	4.28 (18)
C <sub>25</sub>	0.3976 (10)	0.90501 (31)	1.0312 (11)	3.12 (13)
C <sub>26</sub>	0.2884 (10)	0.90576 (29)	1.1391 (11)	2.88 (13)
C <sub>27</sub>	0.0836 (12)	0.92806 (32)	1.0212 (11)	2.92 (14)
C <sub>28</sub>	-0.0010 (11)	0.95039 (30)	0.7940 (10)	2.82 (13)
C <sub>29</sub>	-0.2206 (10)	0.96796 (29)	0.6620 (10)	2.81 (12)
H <sub>14A</sub>	0.626 (11)	0.3155 (33)	0.151 (13)	7.1 (19)
H <sub>14B</sub>	0.654 (13)	0.2863 (43)	0.355 (14)	7.1 (25)
H <sub>14C</sub>	0.795 (14)	0.3357 (37)	0.391 (13)	8.1 (24)
H <sub>15</sub>	0.599 (9)	0.3619 (26)	0.517 (10)	4.2 (14)
H <sub>16</sub>	0.538 (10)	0.4205 (30)	0.086 (10)	5.9 (16)
H <sub>17</sub>	0.285 (10)	0.4810 (27)	0.150 (10)	4.5 (14)
H <sub>18</sub>	0.450 (8)	0.4142 (23)	0.564 (8)	2.9 (11)
H <sub>24A</sub>	0.597 (10)	0.8497 (31)	1.066 (11)	4.9 (16)
H <sub>24B</sub>	0.684 (9)	0.9037 (27)	1.207 (9)	3.7 (13)
H <sub>24C</sub>	0.625 (11)	0.8381 (36)	1.244 (13)	7.0 (19)
H <sub>25</sub>	0.383 (10)	0.9398 (30)	0.916 (10)	5.1 (15)
H <sub>26</sub>	0.334 (11)	0.8834 (30)	1.286 (11)	5.9 (16)
H <sub>27</sub>	0.012 (10)	0.9203 (29)	1.056 (10)	4.6 (16)
H <sub>28</sub>	0.076 (10)	0.9727 (28)	0.754 (10)	4.5 (15)
H <sub>140</sub>	0.069 (16)	0.4648 (45)	0.638 (15)	10.5 (30)
H <sub>240</sub>	-0.429 (15)	1.0220 (39)	0.416 (14)	8.9 (24)

<sup>a</sup> Estimated standard deviations (in parentheses) in this and following tables occur in the last significant digit in each case.  
<sup>b</sup> Thermal parameters for Fe and carboxyl oxygens are given in Table III.

 TABLE III  
 ANISOTROPIC TEMPERATURE PARAMETERS<sup>26</sup> FOR Fe  
 AND CARBOXYL OXYGEN ATOMS × 10<sup>6</sup>

	β <sub>11</sub>	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>
Fe <sub>1</sub>	1766 (29)	146 (2)	1576 (29)	74 (6)	866 (22)	-47 (6)
Fe <sub>2</sub>	1672 (28)	138 (2)	1690 (30)	118 (6)	889 (22)	18 (6)
O <sub>14</sub>	3386 (181)	240 (14)	2184 (153)	298 (39)	1733 (130)	46 (35)
O <sub>15</sub>	3247 (168)	219 (13)	2254 (146)	365 (38)	1419 (122)	48 (34)
O <sub>24</sub>	2031 (141)	212 (13)	2580 (153)	238 (34)	1292 (114)	268 (34)
O <sub>25</sub>	1990 (137)	178 (12)	2700 (149)	181 (31)	1350 (114)	200 (32)

Tables II and III, and all interatomic distances and bond angles, some of which are listed in Table IV, are reasonable<sup>27</sup> and show good agreement between the two independent molecules in the unit cell. Table II also lists positional parameters for all atoms.

### Discussion

**Description of the Structure.**—The unit cell contains two crystallographically unique dimers with the monomeric units contained in each being related by a crystallographic center of symmetry and held together by the two hydrogen bonds extending from the hydroxyl

(27) Only C-H distances, ranging from 0.71 (6) to 1.24 (6) Å, are sometimes shorter than would normally be expected.

 TABLE IV  
 PRINCIPAL INTRAMOLECULAR BOND DISTANCES  
 AND ANGLES IN (C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>)Fe(CO)<sub>3</sub>

Atoms	Molecule 1 (n = 1)		Molecule 2 (n = 2)
	A. Bond Distances, Å		
Fe <sub>n</sub> -C <sub>n1</sub>	1.761 (7)		1.771 (7)
Fe <sub>n</sub> -C <sub>n2</sub>	1.745 (7)		1.780 (7)
Fe <sub>n</sub> -C <sub>n3</sub>	1.740 (8)		1.755 (8)
Fe <sub>n</sub> -C <sub>n5</sub>	2.146 (7)		2.158 (7)
Fe <sub>n</sub> -C <sub>n6</sub>	2.061 (7)		2.063 (6)
Fe <sub>n</sub> -C <sub>n7</sub>	2.039 (7)		2.038 (7)
Fe <sub>n</sub> -C <sub>n8</sub>	2.104 (7)		2.117 (7)
C <sub>n1</sub> -O <sub>n1</sub>	1.167 (8)		1.156 (9)
C <sub>n2</sub> -O <sub>n2</sub>	1.176 (9)		1.131 (9)
C <sub>n3</sub> -O <sub>n3</sub>	1.161 (10)		1.162 (10)
C <sub>n4</sub> -C <sub>n5</sub>	1.527 (15)		1.518 (11)
C <sub>n5</sub> -C <sub>n6</sub>	1.395 (10)		1.403 (9)
C <sub>n6</sub> -C <sub>n7</sub>	1.399 (10)		1.402 (10)
C <sub>n7</sub> -C <sub>n8</sub>	1.425 (10)		1.436 (9)
C <sub>n8</sub> -C <sub>n9</sub>	1.460 (10)		1.455 (9)
C <sub>n9</sub> -O <sub>n4</sub>	1.309 (8)		1.307 (8)
C <sub>n9</sub> -O <sub>n5</sub>	1.233 (8)		1.204 (8)
C <sub>n4</sub> -H <sub>n4A</sub>	1.15 (8)		0.82 (7)
C <sub>n4</sub> -H <sub>n4B</sub>	0.76 (10)		0.82 (7)
C <sub>n4</sub> -H <sub>n4C</sub>	0.80 (9)		0.98 (8)
C <sub>n5</sub> -H <sub>n5</sub>	0.94 (6)		0.98 (8)
C <sub>n6</sub> -H <sub>n6</sub>	1.24 (6)		1.00 (7)
C <sub>n7</sub> -H <sub>n7</sub>	0.96 (6)		0.71 (6)
C <sub>n8</sub> -H <sub>n8</sub>	0.89 (5)		0.87 (6)
O <sub>n4</sub> -H <sub>n40</sub>	1.10 (10)		1.11 (10)
O <sub>n5</sub> <sup>a</sup> -H <sub>n50</sub>	1.59 (10)		1.53 (10)
O <sub>n4</sub> -O <sub>n5</sub> <sup>a</sup>	2.629 (7)		2.629 (6)
		B. Bond Angles, Deg	
C <sub>n1</sub> -Fe <sub>n</sub> -C <sub>n2</sub>	102.3 (3)		102.6 (3)
C <sub>n1</sub> -Fe <sub>n</sub> -C <sub>n3</sub>	89.7 (3)		90.7 (3)
C <sub>n2</sub> -Fe <sub>n</sub> -C <sub>n3</sub>	98.4 (3)		98.3 (3)
C <sub>n5</sub> -Fe <sub>n</sub> -C <sub>n6</sub>	38.7 (3)		38.7 (3)
C <sub>n5</sub> -Fe <sub>n</sub> -C <sub>n7</sub>	70.2 (3)		70.4 (3)
C <sub>n5</sub> -Fe <sub>n</sub> -C <sub>n8</sub>	79.7 (3)		79.9 (2)
C <sub>n6</sub> -Fe <sub>n</sub> -C <sub>n7</sub>	39.9 (3)		40.0 (3)
C <sub>n6</sub> -Fe <sub>n</sub> -C <sub>n8</sub>	70.6 (3)		70.8 (2)
C <sub>n7</sub> -Fe <sub>n</sub> -C <sub>n8</sub>	40.2 (3)		40.4 (3)
Fe <sub>n</sub> -C <sub>n1</sub> -O <sub>n1</sub>	177.5 (6)		178.3 (6)
Fe <sub>n</sub> -C <sub>n2</sub> -O <sub>n2</sub>	177.7 (6)		178.7 (7)
Fe <sub>n</sub> -C <sub>n3</sub> -O <sub>n3</sub>	179.2 (7)		178.6 (6)
C <sub>n4</sub> -C <sub>n5</sub> -C <sub>n6</sub>	120.6 (7)		121.1 (7)
C <sub>n5</sub> -C <sub>n6</sub> -C <sub>n7</sub>	119.1 (7)		119.4 (6)
C <sub>n6</sub> -C <sub>n7</sub> -C <sub>n8</sub>	117.0 (6)		117.1 (6)
C <sub>n7</sub> -C <sub>n8</sub> -C <sub>n9</sub>	120.7 (6)		118.1 (6)
C <sub>n8</sub> -C <sub>n9</sub> -O <sub>n4</sub>	114.5 (6)		115.4 (6)
C <sub>n8</sub> -C <sub>n9</sub> -O <sub>n5</sub>	123.4 (6)		122.7 (6)
O <sub>n4</sub> -C <sub>n9</sub> -O <sub>n5</sub>	122.0 (6)		121.8 (6)
H <sub>n5</sub> -C <sub>n5</sub> -C <sub>n6</sub>	177 (4)		119 (4)
C <sub>n5</sub> -C <sub>n6</sub> -H <sub>n6</sub>	112 (3)		123 (4)
H <sub>n6</sub> -C <sub>n6</sub> -C <sub>n7</sub>	128 (3)		116 (4)
C <sub>n6</sub> -C <sub>n7</sub> -H <sub>n7</sub>	124 (4)		122 (5)
H <sub>n7</sub> -C <sub>n7</sub> -C <sub>n8</sub>	118 (4)		118 (5)
C <sub>n7</sub> -C <sub>n8</sub> -H <sub>n8</sub>	119 (3)		121 (4)
C <sub>n4</sub> -C <sub>n5</sub> -H <sub>n5</sub>	121 (4)		113 (4)
C <sub>n9</sub> -C <sub>n8</sub> -H <sub>n8</sub>	116 (3)		111 (4)

<sup>a</sup> Atoms from the inversion-related (hydrogen-bonded) sorbic acid group.

hydrogen of the carboxyl group of one sorbic acid ligand to the carbonyl oxygen of the second. Figure 1 shows the formula unit of the molecule, including the center of symmetry and the related carboxyl group of the other molecule making up the dimer, and indicates the labeling of the atoms in the molecule. Figure 2 is the

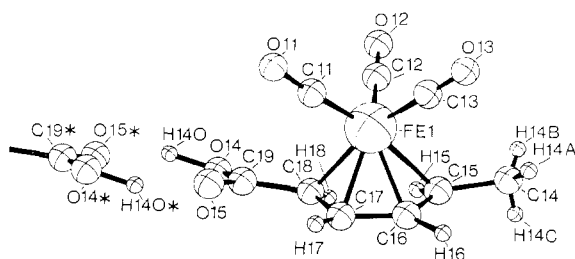


Figure 1.—A schematic representation of the structure indicating the atom-numbering scheme for molecule 1. Molecule 2 is specified by replacing the first integer in the subscript of each atom with an integer 2.

view of one of the dimers (molecule 1). Figure 3 shows the packing arrangement of the molecules in the unit cell.

**The Effect of Crystal Packing.**—Since the unit cell contains two unique dimeric units, each having a different packing environment (see Table V), it should be possible to determine the degree to which molecular parameters are affected by variations in crystal packing environment. As seen in Table IV, *the coordination within a monomer does not appear to be significantly affected by packing forces.* The only obvious difference in the two molecules, seen in Table VI, is the relative positions of the monomer with respect to the center of symmetry (that is, the relative positions of the monomers which constitute the dimeric unit). The distance from the inversion center to the carboxyl plane is 0.04 Å for molecule 1 and 0.16 Å for molecule 2; for the butadiene

Atom I	Molecule 1		Molecule 2	
	Atom J	Dist. Å	Atom J	Dist. Å
$O_{n1}$	$O_{15}$	3.34	$O_{12}$	3.21
	$O_{23}$	3.44	$C_{12}$	3.34
	$C_{14}$	3.46	$O_{13}$	3.45
$O_{n2}$	$O_{13}$	3.01	$O_{22}$	3.48
	$O_{21}$	3.21	$C_{26}$	3.39
	$O_{23}$	3.25	$O_{24}$	3.40
	$C_{21}$	3.32	$O_{21}$	3.44
	$O_{21}$	3.45	$O_{21}$	3.48
$O_{n3}$	$O_{12}$	3.01	$O_{12}$	3.25
	$O_{23}$	3.30	$O_{13}$	3.30
	$O_{21}$	3.45	$C_{13}$	3.38
$O_{n4}$	$O_{11}$	3.34	$O_{11}$	3.44
	$C_{11}$	3.43	$C_{11}$	3.48
	$O_{22}$		$C_{11}$	3.48
	$O_{22}$		$O_{22}$	3.40
	$O_{22}$		$C_{22}$	3.49
$O_{n5}$	$O_{11}$	3.34	$C_{27}$	3.38
	$C_{11}$	3.43	$C_{26}$	3.45
$C_{n1}$	$O_{15}$	3.43	$C_{24}$	3.47
	$O_{23}$	3.48	$O_{12}$	3.32
	$O_{21}$	3.34		
$C_{n2}$	$O_{21}$	3.34	$O_{24}$	3.49
$C_{n3}$	$O_{23}$	3.38		
$C_{n4}$	$O_{11}$	3.46	$O_{22}$	3.44
$C_{n5}$			$O_{25}$	3.47
$C_{n6}$			$O_{22}$	3.39
			$O_{25}$	3.45
$C_{n7}$	$C_{19}$	3.43	$C_{29}$	3.26
	$C_{18}$	3.49	$O_{25}$	3.38
			$O_{22}$	3.47
$C_{n8}$	$C_{17}$	3.49		
$C_{n9}$	$C_{17}$	3.43	$C_{27}$	3.26



Figure 2.—A stereoscopic view of one of the dimers (molecule 1) as drawn by the Calcplotter using the program ORTEP, by C. K. Johnson.

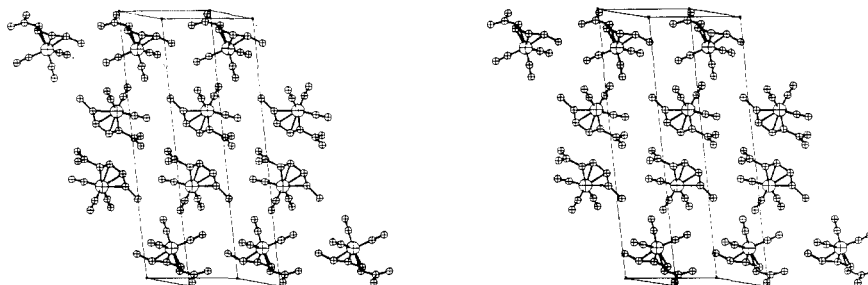


Figure 3.—The packing arrangement in  $(C_8H_8O_2)Fe(CO)_3$ , as viewed down the  $C^*$  reciprocal axis.

planes the distances are 0.46 and 0.14 Å, respectively. The independence of bond distances and angles within the monomeric unit from crystal packing forces cannot be extrapolated to other molecules, nor does it ensure that this molecule would be unaffected in other packing environments; another crystal structure determination of this compound under different packing conditions (the absolute configuration of (+)- $578$ -sorbic acid-iron tricarbonyl) will provide further information on this

effect. Finally, it is noted that no interdimeric contacts are less than the sum of the van der Waals radii.

**Bonding between the Butadiene Group and Iron.**—All bond lengths and bond angles for sorbic acid-iron tricarbonyl are similar to the corresponding values for butadiene-iron tricarbonyl,<sup>4</sup> so it is felt that the structural conclusions of this paper are thought to be generally applicable to the butadiene analog as well.

TABLE VI  
WEIGHTED LEAST-SQUARES PLANES<sup>a</sup> AND DISTANCES OF ATOMS  
FROM THESE PLANES FOR BUTADIENE AND CARBOXYL GROUPS

A. C <sub>15</sub> -C <sub>16</sub> -C <sub>17</sub> -C <sub>18</sub>			
$0.6012x + 0.5929y + 0.5929z = 7.551$			
C <sub>15</sub>	-0.002	C <sub>19</sub>	-0.227
C <sub>16</sub>	0.004	H <sub>15</sub>	0.330
C <sub>17</sub>	-0.004	H <sub>16</sub>	-0.028
C <sub>18</sub>	0.002	H <sub>17</sub>	-0.199
Fe <sub>1</sub>	-1.619	H <sub>18</sub>	-0.455
C <sub>14</sub>	-0.208	i <sup>b</sup>	-0.459
B. C <sub>25</sub> -C <sub>26</sub> -C <sub>27</sub> -C <sub>28</sub>			
$0.2929x + 0.9211y + 0.2566z = 21.191$			
C <sub>25</sub>	-0.003	C <sub>29</sub>	-0.152
C <sub>26</sub>	0.006	H <sub>25</sub>	0.539
C <sub>27</sub>	-0.007	H <sub>26</sub>	-0.181
C <sub>28</sub>	0.003	H <sub>27</sub>	-0.228
Fe <sub>2</sub>	-1.624	H <sub>28</sub>	0.531
C <sub>24</sub>	-0.172	i <sup>b</sup>	-0.137
C. O <sub>14</sub> -C <sub>19</sub> -O <sub>15</sub>			
$0.5461x + 0.7640y + 0.3437z = 9.135$			
H <sub>140</sub>	-0.211	i <sup>b</sup>	0.041
D. O <sub>24</sub> -C <sub>29</sub> -O <sub>25</sub>			
$0.0104x + 0.8713y + 0.4906z = 22.005$			
H <sub>240</sub>	0.091	i <sup>b</sup>	0.163

<sup>a</sup> Equations are referred to the following orthogonal axis system: the orthogonal *y* axis is coincident with the *y* axis of the triclinic unit cell, and the orthogonal *z* axis is perpendicular to the triclinic *xy* plane. <sup>b</sup> Inversion center.

If one assumes the iron to be bonded to the terminal carbon atoms of the butadiene group (bonding scheme II), the iron atom is reasonably close to having the angular values for a tetragonal pyramid (see Table IV). The bond lengths do not support such an interpretation, since the "axial" bond (Fe-C<sub>n2</sub>) and two of the "basal" bond lengths (Fe-C<sub>n1</sub> and Fe-C<sub>n3</sub>) are essentially equal ( $1.76 \pm 0.01$  Å), while the other two "basal" bond lengths (Fe-C<sub>n5</sub> and Fe-C<sub>n8</sub>) are considerably longer ( $2.13 \pm 0.03$  Å). Further, the Fe-C<sub>n6</sub> and Fe-C<sub>n7</sub> distances,  $2.05 \pm 0.01$  Å, do not provide any evidence that the bonding between iron and C<sub>n6</sub> or C<sub>n7</sub> is of a different nature than that between iron and C<sub>n5</sub> or C<sub>n8</sub>. The Fe-C<sub>n5</sub>-C<sub>n6</sub> and Fe-C<sub>n8</sub>-C<sub>n7</sub> angles ( $67.2 \pm 0.2^\circ$ ) do not support sp<sup>3</sup> bonding of the terminal butadiene carbon atoms.

The most significant contribution to the argument against bonding type II is that *the angles involving the carbon atoms of the butadiene group are all essentially 120°*, providing very strong evidence for a structure in which the butadiene carbons all have sp<sup>2</sup> hybridization and the iron is bonded *via* the π electrons. The greatest deviation is observed in the angle C<sub>n6</sub>-C<sub>n7</sub>-C<sub>n8</sub>, which is 117.0° or only 5 esd's less than 120°.

Examination of the distances of the atoms of the butadiene group from the best plane through the four carbon atoms of the group (Table VI) shows that the four carbons are essentially coplanar, and the carbon and hydrogen atoms bonded to these deviate from planarity in a regular manner; further, the deviations from planarity are in the same direction as predicted by Gutowsky and coworkers.<sup>17</sup> The carbon atoms C<sub>n4</sub> and C<sub>n9</sub> and the hydrogen atoms H<sub>n6</sub> and H<sub>n7</sub> are all roughly 0.2 Å below the butadiene plane, while H<sub>n5</sub> and H<sub>n8</sub> are roughly 0.4 Å above it. This is consistent with a rotation<sup>28</sup> about the C<sub>n6</sub>-C<sub>n5</sub> and C<sub>n7</sub>-C<sub>n8</sub> bonds of  $8.5 \pm 1.5^\circ$ , with the positions of H<sub>n6</sub> and H<sub>n7</sub> showing a resulting distortion in the other orbitals of C<sub>n6</sub> and C<sub>n7</sub>.

Two factors contribute to the twisting about the terminal butadiene bonds: (1) steric crowding of hydrogen atoms H<sub>n5</sub> and H<sub>n8</sub> and (2) distortion to provide increased overlap between butadiene orbitals and metal orbitals. The H<sub>n5</sub>-H<sub>n8</sub> distance (2.0 Å) is short and suggests the influence of van der Waals repulsion. Since this crowding would be more effectively relieved by reversing the direction of twist about *one* of the terminal bonds, leaving one hydrogen atom above and the other below the butadiene plane, it is felt that this cannot be considered a primary cause of the twisting.

Churchill<sup>29</sup> has treated the distortion of the butadiene group of cyclic ligands, in a direction to shorten the distance between the terminal carbon atoms of the group, in terms of increased overlap between the lowest antibonding orbital of the butadiene group and the filled metal orbitals to allow increased back-donation of metal electrons to the ligand. It should be noted that for a five-membered cyclic ligand this distortion must also involve a rotation about the terminal C-C bonds of the butadiene group, an effect that further increases the degree of overlap between the orbitals of interest. In the sorbic acid ligand the decrease in the distance between C<sub>n5</sub> and C<sub>n8</sub> is minimal, possibly owing to the crowding between H<sub>n5</sub> and H<sub>n8</sub>, but the rotation about the terminal butadiene carbon-carbon bonds, so that π-electron orbitals are no longer perpendicular to the butadiene plane but are turned in toward the metal atom, provides increased overlap between the π-electron orbitals and the metal d-electron orbitals.

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(28) Owing to the large esd's of the hydrogen atom positions, the calculation of the angle of rotation uses the C<sub>n4</sub> and C<sub>n9</sub> positions only.

(29) M. R. Churchill, *J. Organometal. Chem.*, **4**, 258 (1965).