

for structures exhibiting short N...C=O or O...C=O contacts, the C atoms are generally displaced towards the N or O atoms respectively. The displacement exemplifies the effects of the interaction between a nucleophile and the electrophilic C atom of the carbonyl group.

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Tricarbonyl[2-5-η-(dimethyl 2,4-cyclohexadiene-1α,2-dicarboxylate)]iron(0) and Tricarbonyl[2-5-η-(dimethyl 2,4-cyclohexadiene-1β,2-dicarboxylate)]iron(0)

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Abstract. C₁₃H₁₂FeO₇, *M_r* = 336.09. Structures of both the 1α,2- (*A*) and 1β,2-bis(methoxycarbonyl) (*B*) isomers were determined. (*A*): monoclinic, *Pc*, *a* = 7.469 (2), *b* = 13.403 (5), *c* = 6.978 (2) Å, β = 93.85 (2)° (293 K), *U* = 697.0 Å³, *Z* = 2, *D_c* = 1.602 Mg m⁻³, *F*(000) = 344, μ(Mo *Kα*) = 1.143 mm⁻¹;

refinement converged with *R* = 0.019, *R_w* = 0.027 for 1665 diffractometer data [*I* ≥ 3σ(*I*)]. (*B*): triclinic, *P*1̄, *a* = 6.883 (1), *b* = 8.949 (1), *c* = 11.438 (2) Å, α = 91.50 (1), β = 101.78 (1), γ = 96.48 (1)° (293 K), *U* = 684.4 Å³, *Z* = 2, *D_c* = 1.631 Mg m⁻³, μ(Mo *Kα*) = 1.164 mm⁻¹; refinement converged with *R* = 0.026, *R_w* = 0.039 for 3309 diffractometer data. An unusually short O...C=O contact in (*B*) [2.652 (2) Å, O(2-methoxycarbonyl)...C=O(1β-methoxycarbonyl)] generates an appreciable pyramidal distortion [0.043 (1) Å] of the four-atom C-(1β-carboxylate) set.

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Introduction. Dimethyl 2,5-cyclohexadiene-1,2-dicarboxylate reacts with iron pentacarbonyl to yield a mixture of three isomeric complexes, (A), (B), and tricarbonyl[2-5- η -(dimethyl 3,5-cyclohexadiene-1 α ,2 β -dicarboxylate)]iron(0), (C), in the ratio 3:1:1 (Bandara, 1981). The present work serves to characterize the two first-mentioned isomers (A) and (B).

Data measurement and processing procedures follow those outlined in the preceding paper in this issue (Dunand & Robertson, 1982). 1796 independent reflections ($3^\circ < 2\theta < 56^\circ$) were recorded for (A) [linear decay rate $0.94(19) \times 10^{-5}$ per reflection measured] and 3638 for (B) (no significant decay). Reflections with $I \leq 3\sigma(I)$ were discarded. R_s values for the resultant data sets were 0.005 for (A) (1665 reflections) and 0.007 for (B) (3309 reflections). Crystal dimensions were $0.50 \times 0.55 \times 0.52$ mm (A) and $0.28 \times 0.35 \times 0.60$ mm (B).

Solution and refinement procedures also follow those outlined in the preceding paper. Refinements converged with $R = 0.019$ and $R_w = 0.027$ for (A) (cf. $R = 0.025$ and $R_w = 0.037$ for the enantiomorph), and $R = 0.026$

and $R_w = 0.039$ for (B). Extinction coefficients (Zachariassen, 1963) refined to $4.4(3) \times 10^{-7}$ and $5.3(12) \times 10^{-7}$ for (A) and (B) respectively and $[\sum w\Delta^2/(n-s)]^{1/2}$ values were 1.17 and 1.58. Final difference syntheses revealed no features higher than $0.24 e \text{ \AA}^{-3}$ in (A) and $0.40 e \text{ \AA}^{-3}$ in (B). Atom nomenclature is defined in Fig. 1 and the corre-

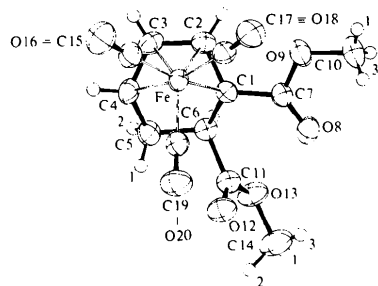


Fig. 1. The labelling scheme for (A) and (B).

Table 1. Atomic coordinates ($\times 10^5$ for Fe, $\times 10^4$ for C and O, $\times 10^3$ for H) and isotropic thermal parameters

	Isomer A				Isomer B			
	x	y	z	B_{eq}^* (\AA^2)	x	y'	z	B_{eq}^* (\AA^2)
Fe	0	20795 (1)	25000	2.87	-23637 (2)	22314 (2)	13438 (1)	2.53
C(1)	-2463 (2)	2630 (1)	3311 (2)	2.67	-1281 (2)	1207 (2)	2954 (1)	2.61
C(2)	-2518 (2)	2393 (1)	1306 (2)	3.06	-3414 (2)	888 (1)	2541 (1)	3.04
C(3)	-1227 (3)	2910 (2)	305 (3)	3.57	-4439 (2)	2166 (2)	2412 (1)	3.38
C(4)	-59 (3)	3538 (2)	1432 (3)	3.64	-3221 (2)	3563 (1)	2659 (1)	3.29
C(5)	-777 (3)	4233 (1)	2891 (4)	3.89	-1546 (2)	3790 (1)	3747 (1)	3.39
C(6)	-2303 (2)	3722 (1)	3897 (3)	2.88	-576 (2)	2342 (1)	4022 (1)	2.78
C(7)	-3432 (3)	2012 (1)	4660 (3)	3.08	-54 (2)	-52 (1)	2933 (1)	3.02
O(8)	-3551 (3)	2213 (2)	6318 (3)	4.74	1617 (2)	-51 (1)	3508 (1)	4.79
O(9)	-4159 (3)	1197 (1)	3829 (2)	4.33	-1018 (2)	-1214 (1)	2199 (1)	3.78
C(10)	-5034 (5)	530 (2)	5083 (6)	5.78	35 (3)	-2490 (2)	2137 (2)	4.61
C(11)	-4104 (3)	4235 (1)	3484 (3)	2.94	1680 (2)	2743 (1)	4360 (1)	2.97
O(12)	-5481 (2)	3818 (1)	3014 (3)	4.37	2663 (2)	3444 (1)	3771 (1)	4.07
O(13)	-3973 (2)	5215 (1)	3771 (2)	3.92	2407 (1)	2341 (1)	5462 (1)	4.17
C(14)	-5571 (3)	5793 (2)	3352 (4)	4.20	4534 (3)	2667 (3)	5865 (2)	5.66
C(15)	1875 (3)	1799 (2)	1121 (4)	3.96	-4005 (2)	2988 (2)	144 (1)	3.73
O(16)	3046 (3)	1653 (2)	207 (4)	5.96	-5052 (2)	3423 (2)	-631 (1)	5.87
C(17)	-417 (3)	773 (2)	2877 (3)	4.19	-2228 (2)	685 (2)	341 (1)	3.17
O(18)	-597 (5)	-57 (2)	3075 (5)	6.97	-2225 (2)	-251 (1)	-346 (1)	4.58
C(19)	1124 (3)	2428 (2)	4740 (3)	3.87	-113 (2)	3422 (1)	1266 (1)	3.25
O(20)	1735 (4)	2676 (3)	6181 (4)	6.42	1273 (2)	4172 (2)	1165 (1)	4.91
H(C2)	-322 (3)	187 (2)	66 (3)	2.5 (4)	-400 (3)	-6 (2)	231 (2)	3.4 (3)
H(C3)	-103 (4)	274 (2)	-103 (4)	3.2 (5)	-569 (3)	210 (2)	211 (2)	4.4 (4)
H(C4)	96 (4)	374 (2)	78 (5)	4.0 (6)	-395 (3)	438 (2)	236 (2)	3.6 (3)
H1(C5)	12 (5)	442 (3)	380 (5)	4.5 (6)	-51 (2)	459 (2)	364 (1)	3.1 (3)
H2(C5)	-129 (5)	480 (3)	231 (5)	5.3 (7)	-215 (4)	405 (3)	442 (2)	7.2 (6)
H(C6)	-199 (4)	371 (2)	525 (4)	3.1 (4)	-102 (2)	191 (2)	469 (1)	2.8 (3)
H1(C10)	-511 (8)	-2 (5)	441 (9)	9.2 (17)	-57 (5)	-295 (4)	147 (3)	7.8 (7)
H2(C10)	-589 (7)	88 (4)	589 (8)	7.3 (10)	24 (4)	-291 (3)	289 (2)	6.1 (5)
H3(C10)	-420 (6)	26 (3)	593 (7)	5.8 (8)	121 (4)	-220 (3)	193 (2)	6.3 (6)
H1(C14)	-521 (7)	646 (4)	385 (8)	8.4 (13)	476 (4)	258 (3)	670 (3)	6.3 (6)
H2(C14)	-655 (8)	557 (4)	426 (9)	9.1 (14)	499 (5)	380 (4)	575 (3)	9.1 (9)
H3(C14)	-598 (6)	561 (3)	211 (7)	6.6 (9)	482 (3)	195 (2)	551 (2)	3.2 (4)

* $B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$; actual B values for H atoms.

sponding atomic coordinates are listed in Table 1.* The figures were drawn with *ORTEP* (Johnson, 1976).

Discussion. Interest in the title compounds results from the continuing studies by A. J. Birch and co-workers (Birch *et al.*, 1981; Bandara, 1981) of substituted (1,3-cyclohexadiene)Fe(CO)₃ complexes as precursors in organic synthesis. The present results have been used to investigate correlations between stereochemistry and spectral properties and the usefulness of ¹H NMR data as a stereochemical probe in these systems (Birch & Bandara, 1982).

* Lists of structure amplitudes, anisotropic thermal parameters and deviations from planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36767 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

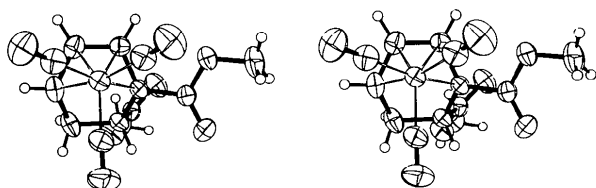


Fig. 2. Stereoscopic view of (A) perpendicular to the diene plane. Vibration ellipsoids correspond to 50% probability surfaces and H atoms are depicted as 0.1 Å radius spheres.

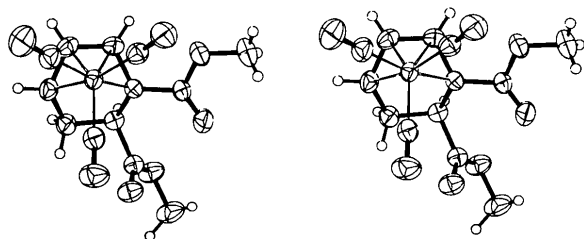


Fig. 3. Stereoscopic view of (B).

Except for the configurational difference at the 1 ring position (Figs. 2 and 3) both isomers exhibit almost identical stereochemistry. Bond lengths and bond angles are compared in Tables 2 and 3. They exhibit excellent internal agreement and are similar to those found in other (1,3-cyclohexadiene)tricarbonyl-iron derivatives (Dunand & Robertson, 1982, and references therein).

The dihedral angles between the C(1), C(2), C(3), C(4) and C(4), C(5), C(6), C(1) sets [42.1 for (A); 43.4° for (B)] are substantially exceeded only by that in (octafluoro-1,3-cyclohexadiene)Fe(CO)₃ (47.3°; Churchill & Mason, 1967). While the diene [C(1), C(2), C(3), C(4)] sets in both isomers are almost planar [torsion angles 2.4 (3) for (A), 2.5 (2)° for (B)], substantial torsion occurs about the C(5)–C(6) bonds [7.4 (2), (A); 12.7 (1)°, (B)]. As is usually observed the diene substituent atoms C(7), H(C2), H(C3) and H(C4) are each displaced out of the diene plane towards the metal.

The 2-methoxycarbonyl substituent exhibits an almost ideally staggered conformation in (B), with C(2)–C(1)–C(7)–O(9) = 19.1 (2) and C(6)–C(1)–C(7)–O(8) = –17.6 (2)°, but in (A) the group leans towards the plane of the diene with angles 6.2 (3) and –24.4 (3)° respectively. Consequently, the ester O(9) is in closer contact with carbonyl –C(17)≡O(18) in (B) [O(9)···C(17) = 2.808 (2), O(9)···O(18) = 3.025 (2) Å] than in (A) [O(9)···C(17) = 2.971 (3), O(9)···O(18) = 3.219 (4) Å]. The presence of the electron-withdrawing 2-methoxycarbonyl substituents modifies the geometry of the coordinated diene so as to remove the C(1)–C(2)/C(3)–C(4) bond-length equivalence. Thus, the C(1)–C(2) bond [1.433 (2) in (A); 1.441 (2) Å in (B)] is significantly longer in both isomers than the C(3)–C(4) bond [1.414 (3) in (A); 1.412 (2) Å in (B)]. The C(1)–C(6) and C(4)–C(5) bonds exhibit similar inequivalence [1.522 (2) and 1.505 (3) in (A); 1.530 (2) and 1.506 (2) Å in (B)]. All

Table 2. Bond lengths (Å) in the two isomers

	(A)	(B)		(A)	(B)
Fe–C(1)	2.095 (2)	2.115 (1)	C(7)–C(1)	1.480 (3)	1.484 (2)
Fe–C(2)	2.049 (2)	2.034 (1)	C(7)–O(8)	1.197 (3)	1.202 (3)
Fe–C(3)	2.058 (2)	2.058 (1)	C(7)–O(9)	1.336 (3)	1.341 (2)
Fe–C(4)	2.092 (2)	2.112 (1)	O(9)–C(10)	1.438 (3)	1.427 (2)
Fe–C(15)	1.791 (2)	1.790 (1)	C(11)–C(6)	1.521 (2)	1.521 (2)
Fe–C(17)	1.801 (2)	1.797 (1)	C(11)–O(12)	1.197 (3)	1.190 (2)
Fe–C(19)	1.786 (2)	1.798 (1)	C(11)–O(13)	1.331 (2)	1.332 (2)
C(15)–O(16)	1.134 (3)	1.130 (2)	O(13)–C(14)	1.437 (3)	1.436 (2)
C(17)–O(18)	1.130 (4)	1.134 (2)	C(2)–H(C2)	0.97 (3)	0.91 (2)
C(19)–O(20)	1.127 (3)	1.130 (2)	C(3)–H(C3)	0.98 (3)	0.85 (2)
C(1)–C(2)	1.433 (2)	1.441 (2)	C(4)–H(C4)	0.95 (3)	0.97 (2)
C(2)–C(3)	1.410 (3)	1.406 (2)	C(5)–H1(C5)	0.93 (4)	0.98 (2)
C(3)–C(4)	1.414 (3)	1.412 (2)	C(5)–H2(C5)	0.93 (4)	0.98 (3)
C(4)–C(5)	1.505 (3)	1.506 (2)	C(6)–H(C6)	0.96 (3)	0.95 (2)
C(5)–C(6)	1.539 (3)	1.535 (2)	C(Me)–H	0.96 ± 0.09	0.92 ± 0.13
C(6)–C(1)	1.522 (2)	1.530 (2)			

Table 3. Bond angles (°) in the two isomers

	(A)	(B)
C(15)–Fe–C(17)	91.36 (11)	88.57 (6)
C(15)–Fe–C(19)	100.75 (11)	97.77 (6)
C(17)–Fe–C(19)	101.68 (11)	100.76 (6)
Fe–C(15)–O(16)	177.4 (2)	177.9 (1)
Fe–C(17)–O(18)	176.5 (3)	175.6 (1)
Fe–C(19)–O(20)	175.6 (3)	177.0 (1)
C(2)–C(1)–C(6)	118.2 (2)	115.8 (1)
C(2)–C(1)–C(7)	120.9 (2)	118.1 (1)
C(6)–C(1)–C(7)	113.6 (1)	115.3 (1)
C(1)–C(2)–C(3)	113.5 (2)	114.7 (1)
C(1)–C(2)–H(C2)	126.3 (14)	121.0 (11)
C(3)–C(2)–H(C2)	119.6 (14)	123.9 (11)
C(2)–C(3)–C(4)	115.7 (2)	115.4 (1)
C(2)–C(3)–H(C3)	120.2 (18)	121.9 (14)
C(4)–C(3)–H(C3)	123.1 (18)	122.1 (14)
C(3)–C(4)–C(5)	120.7 (2)	120.1 (1)
C(3)–C(4)–H(C4)	112.9 (19)	111.3 (10)
C(5)–C(4)–H(C4)	118.5 (18)	121.2 (10)
C(4)–C(5)–C(6)	110.0 (2)	111.6 (1)
C(4)–C(5)–H1(C5)	110.8 (21)	111.0 (9)
C(4)–C(5)–H2(C5)	111.4 (23)	106.2 (16)
C(6)–C(5)–H1(C5)	109.3 (21)	108.4 (10)
C(6)–C(5)–H2(C5)	105.3 (24)	108.1 (16)
H1(C5)–C(5)–H2(C5)	109.9 (32)	111.5 (18)
C(1)–C(6)–C(5)	110.6 (1)	109.4 (1)
C(1)–C(6)–C(11)	109.3 (1)	114.0 (1)
C(1)–C(6)–H(C6)	104.6 (15)	107.6 (9)
C(5)–C(6)–C(11)	112.7 (2)	108.7 (1)
C(5)–C(6)–H(C6)	108.9 (16)	108.6 (10)
C(11)–C(6)–H(C6)	110.4 (16)	108.4 (9)
C(1)–C(7)–O(8)	124.1 (2)	124.6 (1)
C(1)–C(7)–O(9)	112.6 (2)	112.5 (1)
O(8)–C(7)–O(9)	123.4 (2)	122.9 (1)
C(7)–O(9)–C(10)	115.6 (2)	116.5 (1)
C(6)–C(11)–O(12)	125.0 (2)	125.0 (1)
C(6)–C(11)–O(13)	111.2 (2)	111.1 (1)
O(12)–C(11)–O(13)	123.7 (2)	123.5 (1)
C(11)–O(13)–C(14)	116.8 (2)	115.5 (1)
O–C(Me)–H	106.8 ± 5.8	105.4 ± 9.2
H–C(Me)–H	111 ± 21	113 ± 16

four methoxycarbonyl groups are slightly aplanar [maximum deviation 0.050 (3) Å], and each isomer exhibits a single short non-bonded O...C=O contact between its methoxycarbonyl substituents. In (A), the contact involves O(12)...C(7)=O(8) with O(12)...C(7) = 3.048 (3) Å and angles C(1)–C(7)...O(12) = 64.5 (1), O(8)–C(7)...O(12) = 96.7 (2), O(9)–C(7)...O(12) = 107.9 (1) and C(11)–O(12)...C(7) = 82.3 (1)°. The central atom C(7) does not deviate significantly from the plane of the C(1), O(8), O(9) set [0.002 (2) Å only]. In (B), the contact involves

O(8)...C(11)=O(12). The distance is substantially shorter [2.652 (2) Å], the relevant angles are closer to 90° [C(6)–C(11)...O(8) = 82.1 (1), O(12)–C(11)...O(8) = 101.8 (1), O(13)–C(11)...O(8) = 90.4 (1), C(7)–O(8)...C(11) = 91.6 (1)°], and the central atom C(11) is now significantly displaced from the plane of the C(6), O(12), O(13) carbonyl set towards O(8) [by 0.043 (1) Å]. Just such a result is expected. Bürgi, Dunitz & Shefter (1974) have investigated intra- and intermolecular O...C=O interactions and shown that when a nucleophilic O atom is less than about 3 Å from an electrophilic C atom (in C=O), the latter is displaced from the plane of the carbonyl group towards the nucleophile. The displacement tends to increase as the O...C distance decreases. The parameters which describe the O...C=O interactions in (A) and (B), and the magnitudes of the C-atom displacements, are in good agreement with that description. The 0.043 (1) Å displacement in (B) is amongst the largest observed for an interaction between ester groups. The ester O(12) in (B) is in close contact with the carbonyl –C(19)=O(20) [O(12)...C(19) = 3.101 (2), O(12)...O(2) = 3.050 (2) Å].

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