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THE CRYSTAL STRUCTURE OF A TRICARBONYLIRON-SUBSTITUTED CYCLOBUTADIENE COMPLEX: TRICARBONYL[1,2,2*a*,12*a*-η-5,10-DIMETHYLDIBENZO[*a*, *c*]-CYCLOBUTA[*f*]CYCLOOCTENE-3,12-DIONE] IRON

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Summary

The crystal structure of tricarbonyl[1,2,2*a*,12*a*-η-5,10-dimethyldibenzo-[*a*,*c*] cyclobuta[*f*] cyclooctene-3,12-dione] iron, $C_{20}O_2H_{14}Fe(CO)_3$, has been determined by the single crystal X-ray diffraction technique using data collected with a fully automated diffractometer. The unit cell is monoclinic, space group $P2_1/c$ with $a = 12.025(2)$, $b = 23.204(3)$, $c = 14.614(2)$ Å, $\beta = 102.16(2)°$, and contains eight molecules (two per asymmetric unit). The structure was elucidated to study the coordination of the iron atom and to correlate the conformation of the eight-membered ring with an NMR study. The final structure was obtained by Patterson-superposition and Fourier techniques and refined by full-matrix least-squares to a crystallographic residual of 0.070. In both independent molecules the iron atom is 1.77 Å from the cyclobutadiene ring to which it is coordinated. The eight-membered ring is flattened from a boat conformation and the six-membered rings are twisted from coplanarity by an angle of 74°. The twist is such that if one ring points above the eight-membered ring, the other ring will point below it with concomitant pointing in the opposite sense by neighboring carbonyl groups. Such a structure has conformational chirality. It is postulated that the stability of each enantiometer is due to the particularly high energy of the transition state through which each would pass to achieve interconversion.

Introduction

The synthesis and NMR studies of the title compound (I) have recently been reported by Kaplan and Roberts [1]. Its preparation was accomplished in the

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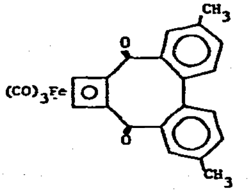

(I)

course of a research project the aims of which included the synthesis of 4,8 fused ring systems from irontricarbonyl cyclobutadiene derivatives. The NMR spectrum of I is of particular interest because of the nonequivalence of the protons of the four-membered ring; this spectrum indicated that the proton sets of the annelated six-membered rings were also nonequivalent. This result was explained by examination of a molecular model which revealed that a planar eight-membered ring with which the six-membered rings were coplanar produced steric interactions between the protons *ortho* to the bond joining these aromatic rings. Such an interaction, in addition to the strain imposed by a flattened eight-membered ring, could prevent the planarity of the system and, if the steric interaction between the protons is further relieved by a twist about the bond joining the aromatic rings, the mirror symmetry of the compound will be destroyed, creating nonequivalent environments at the above mentioned protons. A nonplanar geometry of this description will presumably be destabilized, however, by the minimization of the effects of the rather extensive conjugation found over the entire organic portion of the molecule.

The loss of mirror symmetry indicated the possibility that I had been prepared as a racemic mixture. This was confirmed by the NMR spectrum of I in absolute deuterochloroform recorded in the presence of tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III), a chiral shift reagent; distinct resonances appeared for each enantiomer. A temperature study was carried out to determine whether the enantiomers interconverted by conformational isomerism involving rotation about the carbon—carbon bond joining the six-membered rings. The NMR spectrum at 30°C in acetone-d_6, deuterochloroform, and DMSO-d_6 exhibited two distinct resonances for the protons of the four-membered ring. Were the enantiomers related by an appreciable equilibrium, one would have expected the peaks to coalesce. To determine whether this barrier could be surpassed at higher temperatures, spectra were recorded in DMSO-d_6 between 60 and 180°C. The resonances of the protons of the four-membered ring did not coalesce over this range but their difference did decrease from 19 to 12 Hz (spectrometer frequency: 100 MHz.) Hence, the barrier seemed to effectively prevent interconversion of the enantiomers.

Therefore, to confirm this interpretation of the observed NMR spectrum and to study in detail the geometry of the organic portion of the molecule and the coordination of the iron atom, we decided that the determination of the single-crystal X-ray diffraction structure of I was appropriate.

Experimental

Crystals of I, grown from cyclohexane, were provided by Dr. Fred A. Kaplan and Professor Bryan W. Roberts of the University of Pennsylvania. They were

TABLE I

CRYSTAL DATA [a]

a = 12.025(2) Å
b = 23.204(3) Å
c = 14.614(2) Å
β = 102.16(2)°
Z = 8
Space Group $P2_1/c$
D = 1.42 g cm^{-3}

[a] Standard errors on the least significant figure are given in parentheses here and elsewhere in this paper.

yellow-gold needles elongated about what will be called the *c* axis; crystals were found to be hollowed out along the direction of the *c* axis; this, presumably, is a solvent effect. Preliminary photographic investigation, using Ni filtered Cu radiation indicated the uniquely determined space group $P2_1/c$ by the systematic absences $h0l$, l odd and $0k0$, k odd, and the observation of monoclinic diffraction symmetry. In order to minimize any difficulties which might be associated with data collection on a hollow crystal, a selected crystal was cleaved along the *c* axis such that its final dimensions were 0.35 mm X 0.05 mm X 0.05 mm. To insure that the crystal had not been damaged during the cleavage process, it was checked photographically. Because the preliminary photographic investigation indicated the absence of the iron fluorescence often observed on Cu irradiation, the data were collected using graphite monochromatized Cu-K_α radiation on a Picker four-circle automated diffractometer. Lattice constants obtained from a least-squares treatment of twelve automatically centered reflections with 2θ values greater than 50° are given in Table 1. With $Z = 8$ in space group $P2_1/c$ there are, thus, two independent molecules to be located. Three-dimensional data were collected out to a maximum 2θ value of 110° using the $\theta - 2\theta$ scan technique with a scan speed of 1° per minute over a dispersion corrected base width of 1°. A total of 5016 * intensities was measured and consequently corrected for Lorentz and polarization factors as well as attenuation of the diffracted beam by aluminum foil. No corrections were made for absorption ($\mu = 68.71$ cm^{-1} for the crystal used), which for a majority of reflections is negligible. Of the measured intensities, 1751 were considered to be unobserved, being less than 3.09 times their respective standard deviation. The variance in the structure factor is estimated to be $\sigma^2(|F|^2) = \sigma^2(I) + (0.02\ F^2)^2$ where the final term of the sum is included to account for the electronic instability of the counting instrument and where, for an unattenuated intensity, $\sigma^2(I) = N + m^2(b_1 + b_2)$; m is a factor which places the background counts, $(b_1 + b_2)$, on a common basis with the total counting time.

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* The table of structure factors has been deposited as NAPS Document No. 03059 (31 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 7.75 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

Solution and Refinement of the Structure

The positions of the two unique iron atoms were determined from a sharpened Patterson function. A structure factor calculation based on only these positions produced an R of 0.52 ($R = \Sigma|F_0| - |F_c|/\Sigma|F_0|$); an electron density map phased from the positions of the two iron atoms seemed uninterpretable. Superposition [2] of the sharpened Patterson function on the eight positions of the iron atoms in the unit cell produced an image of the two unique molecules from which the location of 41 of the lighter atoms could be determined. A structure factor calculation based on the positional parameters of the 43 located atoms produced an R of 0.38. The remaining 15 non-hydrogen atoms were located in a subsequent electron density map phased from the positions of the atoms already located.

Each molecule was refined by full-matrix least-squares using the program UCLALS4 [3]. The procedure was to allow the parameters of molecule A to refine through several cycles with the parameters of molecule B being held constant, and then refining the parameters of molecule B with the parameters of molecule A being held constant, During all cycles except the final two, the parameters of both iron atoms were allowed to refine. The function minimized was $\Sigma w[|F_0| - (1/k)|F_c|]^2$ where k is the scale factor for the observed structure factors. The data were given weights, w, inversely proportional to the square of the standard errors of the observed structure factor amplitudes, where $\sigma(F_0) = \{(F_0|^2 + \sigma(I)\}^{1/2} - |F_0|$. Atomic scattering factors for all atoms were taken from the International Tables [4] exclusively; no corrections were made for anomalous dispersion. Four cycles of isotropic refinement (two cycles for molecule A followed by two more for molecule B) reduced the R to 0.12. Another four cycles, allowing the iron atoms to refine anisotropically, reduced the R to 0.10. Another four cycles, including anisotropic temperature factors for all atoms produced an R of 0.08. A difference Fourier map was calculated at this point to determine the positions of the hydrogen atoms, all of which were easily located except those bonded to the four methyl groups. Around these methyl groups residual peaks appeared as ill-defined smears indicative of methyl group rotation or disorder. The 16 hydrogen atoms were assigned isotropic temperature factors of 5.0 Å^2 and included in subsequent calculations but not further refined. Four more least-squares cycles produced a final crystallographic residual of 0.070. In order to insure that convergence had been obtained, one cycle more was calculated for each molecule; from these final two cycles, an estimated standard deviation for each parameter was determined. A final difference density map revealed the presence of no spurious peaks.

Results

Fig. 1 illustrates the labelling of the atoms in I. Tables 2 and 3 list, respectively refined positional and thermal parameters; these parameters define the geometry of two molecules of the same chirality. Table 4 lists the unrefined positional parameters of the non-methyl hydrogen atoms as located in a difference electron density function. Fig. 2a and 2b are stereo ORTEP [5] drawings of the non-hydrogen atoms in molecules A and B, respectively. Table 5 lists bond distances and bond angles determined for I from this study. Fig. 3 is a stereo ORTEP drawing illustrating the packing of I in the unit cell.

(continued on p. 152)

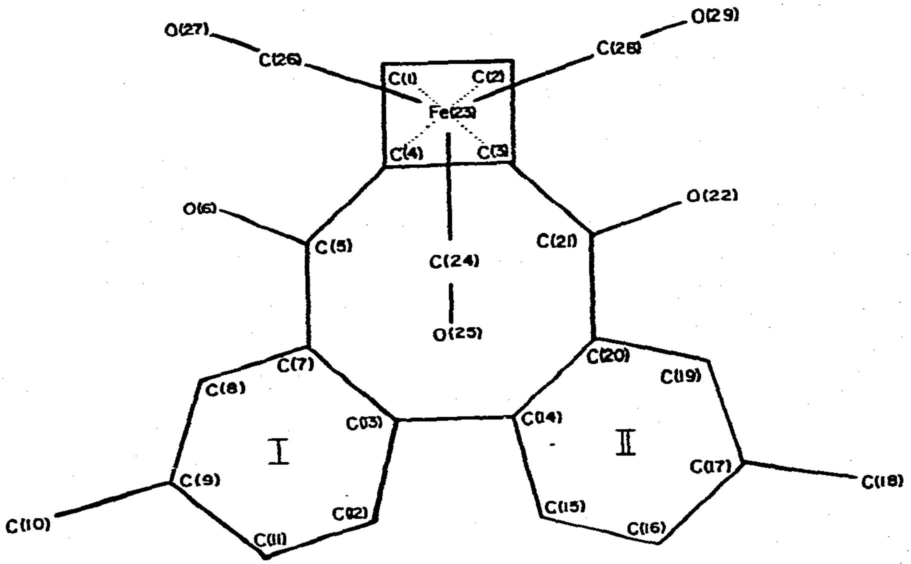

Fig. 1. Labelling of the atoms for I.

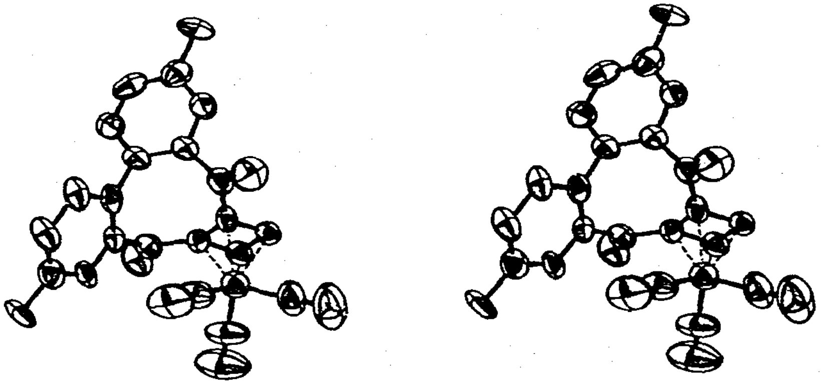

Fig. 2a. Stereo ORTEP drawing of molecule A.

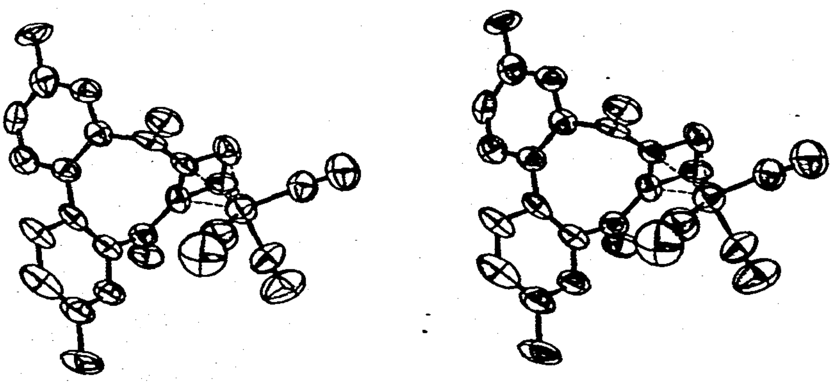

Fig. 2b. Stereo ORTEP drawing of molecule B.

TABLE 2

REFINED POSITIONAL PARAMETERS FOR I

Atom	x	y	z
C(1A)	0.1177(8)	0.2695(4)	0.5184(7)
C(2A)	0.1291(7)	0.2483(5)	0.4298(6)
C(3A)	0.1391(7)	0.1886(4)	0.4608(6)
C(4A)	0.1218(7)	0.2109(4)	0.5518(6)
C(5A)	0.1171(8)	0.1839(4)	0.6430(7)
O(6A)	0.1251(6)	0.2147(3)	0.7130(5)
C(7A)	0.0903(8)	0.1219(4)	0.6438(6)
C(8A)	−0.0053(8)	0.1081(4)	0.6768(6)
C(9A)	−0.0455(9)	0.0507(5)	0.6743(6)
C(10A)	−0.1556(9)	0.0358(5)	0.7047(7)
C(11A)	0.0158(9)	0.0084(5)	0.6432(7)
C(12A)	0.1202(9)	0.0213(5)	0.6093(7)
C(13A)	0.1558(8)	0.0800(5)	0.6094(6)
C(14A)	0.2668(8)	0.0879(4)	0.5813(7)
C(15A)	0.3641(9)	0.0655(5)	0.6380(7)
C(16A)	0.4657(9)	0.0642(5)	0.6078(8)
C(17A)	0.4766(9)	0.0825(4)	0.5186(8)
C(18A)	0.5884(8)	0.0784(5)	0.4869(8)
C(19A)	0.3775(9)	0.1043(4)	0.4624(6)
C(20A)	0.2748(8)	0.1083(4)	0.4911(6)
C(21A)	0.1803(8)	0.1371(4)	0.4262(7)
O(22A)	0.1544(6)	0.1240(3)	0.3437(5)
Fe(23A)	−0.02345(11)	0.22175(6)	0.45304(9)
C(24A)	−0.0968(9)	0.1553(5)	0.4536(8)
O(25A)	−0.1450(7)	0.1135(4)	0.4520(6)
C(26A)	−0.1171(9)	0.2645(5)	0.5040(7)
O(27A)	−0.1739(8)	0.2927(4)	0.5378(8)
C(28A)	−0.0854(10)	0.2396(7)	0.3365(9)
O(29A)	−0.1247(8)	0.2500(6)	0.2609(7)
C(1B)	0.3925(7)	0.2589(4)	0.1509(7)
C(2B)	0.3839(8)	0.2188(5)	0.2203(7)
C(3B)	0.3847(7)	0.1697(4)	0.1617(6)
C(4B)	0.3913(7)	0.2102(4)	0.0863(6)
C(5B)	0.3990(7)	0.2049(5)	−0.0118(7)
O(6B)	0.3941(6)	0.2484(3)	−0.0609(4)
C(7B)	0.4214(8)	0.1468(5)	−0.0465(6)
C(8B)	0.5171(8)	0.1432(5)	−0.0854(6)
C(9B)	0.5513(9)	0.0917(6)	−0.1167(7)
C(10B)	0.6620(9)	0.0869(5)	−0.1532(8)
C(11B)	0.4854(10)	0.0437(5)	−0.1129(7)
C(12B)	0.3845(9)	0.0441(5)	−0.0749(6)
C(13B)	0.3535(8)	0.0984(5)	−0.0406(6)
C(14B)	0.2449(8)	0.0968(4)	−0.0059(7)
C(15B)	0.1422(9)	0.0892(4)	−0.0696(7)
C(16B)	0.0418(9)	0.0816(4)	−0.0371(8)
C(17B)	0.0391(9)	0.0789(4)	0.0594(8)
C(18B)	−0.0693(8)	0.0699(5)	0.0646(8)
C(19B)	0.1423(9)	0.0863(4)	0.1200(6)
C(20B)	0.2438(8)	0.0959(4)	0.0951(6)
C(21B)	0.3459(8)	0.1103(5)	0.1641(7)
O(22B)	0.3857(6)	0.0763(3)	0.2274(5)
Fe(23B)	0.53775(11)	0.20916(6)	0.18696(9)
C(24B)	0.6126(9)	0.1475(6)	0.1601(8)
O(25B)	0.6604(7)	0.1073(4)	0.1440(7)
C(26B)	0.6214(9)	0.2655(5)	0.1481(8)
O(27B)	0.6701(7)	0.3012(4)	0.1228(6)
C(28B)	0.6053(8)	0.2119(5)	0.3071(7)
C(29B)	0.6482(6)	0.2133(4)	0.3830(5)

TABLE 3

REFINED THERMAL PARAMETERS X 10^4 FOR I

Temperature factor expression is $T = \exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - hk\beta_{13} - kl\beta_{23})$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1A)	81(9)	15(3)	59(7)	−6(7)	59(12)	−2(6)
C(2A)	51(8)	25(3)	51(7)	−14(7)	20(11)	17(7)
C(3A)	86(10)	19(3)	25(6)	0(8)	32(11)	5(6)
C(4A)	67(8)	17(3)	34(6)	−3(7)	22(10)	2(6)
C(5A)	79(10)	21(3)	44(7)	−5(8)	39(12)	−78(7)
O(6A)	152(8)	29(2)	45(5)	−21(7)	68(10)	−30(5)
C(7A)	100(10)	12(3)	36(6)	−4(8)	45(12)	2(6)
C(8A)	90(10)	21(3)	40(6)	−4(8)	62(12)	13(6)
C(9A)	108(11)	25(3)	38(6)	1(10)	45(13)	3(6)
C(10A)	97(11)	40(4)	84(8)	−24(10)	118(15)	25(8)
C(11A)	133(13)	24(3)	73(8)	−40(10)	94(17)	−1(7)
C(12A)	120(12)	22(3)	66(7)	−28(9)	69(15)	14(6)
C(13A)	86(10)	23(3)	27(6)	−8(9)	14(12)	12(6)
C(14A)	82(10)	17(3)	54(7)	−9(8)	52(13)	−7(7)
C(15A)	72(10)	30(3)	51(7)	14(9)	27(14)	13(7)
C(16A)	78(11)	31(4)	77(9)	31(9)	−23(16)	8(8)
C(17A)	103(12)	81(3)	68(8)	6(9)	31(16)	−4(7)
C(18A)	68(10)	41(4)	104(9)	9(10)	105(15)	3(9)
C(19A)	99(11)	18(3)	51(7)	−2(9)	55(14)	1(6)
C(20A)	73(9)	16(3)	40(6)	−7(7)	29(12)	−11(6)
C(21A)	85(10)	20(3)	41(7)	1(8)	45(13)	6(7)
O(22A)	159(9)	39(3)	37(5)	28(7)	13(10)	−24(5)
Fe(23A)	76(2)	24(1)	58(1)	−8(2)	32(2)	7(1)
C(24A)	82(9)	24(3)	85(8)	−12(7)	46(13)	−17(7)
O(25A)	112(9)	27(3)	162(8)	−40(7)	41(13)	−15(7)
C(26A)	87(12)	23(3)	149(12)	2(9)	93(18)	−26(9)
O(27A)	144(11)	36(3)	229(11)	2(9)	163(17)	−66(9)
C(28A)	70(11)	96(7)	91(10)	−23(14)	−6(17)	121(14)
O(29A)	128(11)	149(7)	116(8)	−66(13)	−54(15)	171(13)
C(1B)	71(9)	21(3)	57(7)	14(8)	47(13)	6(7)
C(2B)	84(10)	27(3)	49(7)	18(9)	20(12)	−26(8)
C(3B)	83(10)	17(3)	27(6)	−1(8)	28(11)	0(6)
C(4B)	65(8)	18(3)	41(6)	16(7)	−1(11)	−11(7)
C(5B)	68(9)	25(3)	42(7)	0(8)	20(12)	−3(7)
O(6B)	118(6)	28(2)	47(5)	12(6)	49(9)	26(5)
C(7B)	81(10)	19(3)	36(6)	21(9)	30(12)	−31(6)
C(8B)	90(11)	27(3)	42(6)	3(9)	44(13)	−4(7)
C(9B)	110(12)	35(4)	47(7)	3(11)	56(14)	−14(8)
C(10B)	100(12)	56(5)	92(9)	18(12)	116(16)	−47(10)
C(11B)	139(14)	30(4)	36(7)	87(11)	29(15)	21(8)
C(12B)	115(12)	30(3)	30(6)	47(10)	33(13)	−7(7)
C(13B)	88(10)	24(3)	22(6)	21(9)	20(11)	−6(6)
C(14B)	79(10)	16(3)	46(7)	11(8)	37(13)	−1(6)
C(15B)	84(10)	21(3)	50(7)	17(9)	19(14)	−5(7)
C(16B)	75(10)	21(3)	76(8)	−10(8)	−11(15)	−28(7)
C(17B)	117(13)	13(3)	69(8)	7(9)	28(17)	−8(7)
C(18B)	69(9)	30(3)	110(9)	−19(9)	113(15)	−7(8)
C(19B)	91(10)	17(3)	46(7)	3(8)	47(14)	8(6)
C(20B)	78(10)	15(3)	35(6)	11(8)	12(12)	5(6)
C(21B)	80(10)	26(3)	31(6)	16(9)	62(13)	4(7)
O(22B)	115(8)	29(2)	47(5)	12(6)	29(9)	14(5)
Fe(23B)	78(2)	26(1)	53(1)	12(2)	22(2)	−6(1)
C(24B)	97(12)	34(4)	79(9)	18(11)	34(16)	−8(9)
O(25B)	146(10)	40(3)	150(8)	63(9)	60(14)	−34(8)
C(26B)	70(11)	30(4)	91(9)	−11(10)	15(15)	8(9)
O(27B)	135(10)	42(3)	129(8)	−32(8)	54(14)	45(8)
C(28B)	77(10)	34(4)	50(7)	−3(9)	−8(13)	−4(9)
O(29B)	122(8)	47(3)	56(5)	−1(8)	−26(11)	2(7)

TABLE 4

UNREFINED COORDINATES FOR THE HYDROGEN ATOMS IN I. HYDROGEN ATOMS OF THE METHYL GROUPS WERE NOT LOCATED

	x	y	z
H(1A)	0.105	0.315	0.55
H(2A)	0.15	0.27	0.375
H(8A)	−0.07	0.145	0.705
H(11A)	−0.015	−0.04	0.645
H(12A)	0.18	−0.02	0.60
H(15A)	0.35	0.045	0.72
H(16A)	0.54	0.045	0.65
H(19A)	0.365	0.13	0.39
H(1B)	0.395	0.315	0.13
H(2B)	0.38	0.22	0.275
H(8B)	0.585	0.185	−0.09
H(11B)	0.50	0.00	−0.14
H(12B)	0.33	0.00	−0.07
H(15B)	0.155	0.085	−0.155
H(16B)	−0.04	0.075	−0.09
H(19B)	0.15	0.085	0.19

TABLE 5

BOND DISTANCES AND ANGLES IN I

Atoms	Distance (Å)	
	Molecule A	Molecule B
C(1)—C(2)	1.42(2)	1.40(2)
C(2)—C(3)	1.45(2)	1.43(2)
C(3)—C(4)	1.46(2)	1.46(2)
C(4)—C(1)	1.44(2)	1.47(2)
C(4)—C(5)	1.48(2)	1.46(2)
C(5)—O(6)	1.23(2) 1.27[a]	1.23(2) 1.26[a]
C(5)—C(7)	1.48(2)	1.49(2)
C(7)—C(8)	1.38(2)	1.39(2)
C(8)—C(9)	1.41(2)	1.37(2)
C(9)—C(10)	1.52(2)	1.54(2)
C(9)—C(11)	1.36(2)	1.38(2)
C(11)—C(12)	1.48(2)	1.44(2)
C(12)—C(13)	1.43(2)	1.43(2)
C(13)—C(7)	1.41(2)	1.40(2)
C(13—C(14)	1.49(2)	1.50(2)
C(14)—C(15)	1.39(2)	1.39(2)
C(15)—C(16)	1.39(2)	1.40(2)
C(16)—C(17)	1.40(2)	1.42(2)
C(17)—C(18)	1.52(2)	1.52(2)
C(17)—C(19)	1.39(2)	1.38(2)
C(19)—C(20)	1.39(2)	1.39(2)
C(20)—C(14)	1.42(2)	1.43(2)
C(20)—C(21)	1.48(2)	1.48(2)
C(21)—O(22)	1.22(2) 1.27[a]	1.23(2) 1.26[a]
C(21—C(3)	1.47(2)	1.46(2)
Fe···C(1)	2.085(8)	2.070(8)
Fe···C(2)	2.032(7)	2.026(8)
Fe···C(3)	2.004(8)	2.022(8)
Fe···C(4)	2.036(8)	2.045(8)
Fe—C(24)	1.78(1) 1.79[a]	1.78(2) 1.79[a]
Fe—C(26)	1.78(1) 1.81[a]	1.81(1) 1.83[a]
Fe—C(28)	1.76(2) 1.83[a]	1.77(1) 1.78[a]

(Table continued)

TABLE 5 (continued)

Atoms	Distance (Å)	
	Molecule A	Molecule B
C(24)—O(25)	1.13(2) 1.18 [a]	1.15(2) 1.21 [a]
C(26)—O(27)	1.13(2) 1.19 [a]	1.12(2) 1.17 [a]
C(28)—O(29)	1.13(2) 1.23 [a]	1.12(2) 1.15 [a]

Atoms	Angle (°)	
	Molecule A	Molecule B
C(1)—C(2)—C(3)	92.7(7)	94.8(8)
C(2)—C(3)—C(4)	86.9(7)	87.0(7)
C(3)—C(4)—C(1)	91.6(7)	90.3(7)
C(4)—C(1)—C(2)	88.8(7)	87.6(8)
C(1)—C(4)—C(5)	134.2(8)	134.4(8)
C(3)—C(4)—C(5)	134.2(8)	135.2(8)
C(4)—C(5)—O(6)	119.3(8)	119.9(9)
C(4)—C(5)—C(7)	117.9(8)	117.6(8)
O(6)—C(5)—C(7)	122.4(8)	122.3(8)
C(5)—C(7)—C(8)	115.5(8)	114.7(8)
C(5)—C(7)—C(13)	122.0(7)	123.8(8)
C(8)—C(7)—C(13)	122.5(8)	121.5(9)
C(7)—C(8)—C(9)	121.2(8)	121.3(9)
C(8)—C(9)—C(10)	121.4(9)	121.3(10)
C(8)—C(9)—C(11)	118.6(8)	118.4(9)
C(10)—C(9)—C(11)	120.0(9)	120.3(11)
C(9)—C(11)—C(12)	121.7(9)	123.4(10)
C(11)—C(12)—C(13)	118.1(8)	116.4(9)
C(7)—C(13)—C(12)	117.8(8)	118.9(8)
C(7)—C(13)—C(14)	128.1(8)	127.0(8)
C(12)—C(13)—C(14)	113.8(8)	114.0(8)
C(13)—C(14)—C(15)	119.0(8)	119.5(8)
C(13)—C(14)—C(20)	122.4(8)	121.9(7)
C(15)—C(14)—C(20)	117.7(9)	118.1(9)
C(14)—C(15)—C(16)	120.7(9)	119.9(9)
C(15)—C(16)—C(17)	123.5(9)	123.0(9)
C(16)—C(17)—C(18)	121.9(9)	123.0(9)
C(16)—C(17)—C(19)	114.9(8)	115.3(8)
C(18)—C(17)—C(19)	123.3(9)	121.6(10)
C(17)—C(19)—C(20)	123.6(9)	124.0(9)
C(14)—C(20)—C(21)	123.4(7)	122.0(7)
C(19)—C(20)—C(14)	119.7(8)	119.6(8)
C(19)—C(20)—C(21)	116.8(8)	118.1(8)
C(20)—C(21)—O(22)	121.6(8)	121.8(9)
C(20)—C(21)—C(3)	117.1(8)	114.7(8)
O(22)—C(21)—C(3)	120.4(8)	123.0(8)
C(21)—C(3)—C(2)	130.9(7)	134.2(8)
C(21)—C(3)—C(4)	136.0(8)	133.9(8)
C(1)···Fe···C(2)	40.3(5)	39.9(5)
C(2)···Fe···C(3)	42.2(5)	41.3(5)
C(3)···Fe···C(4)	42.2(5)	42.2(5)
C(4)···Fe···C(1)	41.0(5)	42.9(5)
Fe—C(24)—O(25)	178.3(10)	178.9(10)
Fe—C(26)—O(27)	177.9(10)	177.9(9)
Fe—C(28)—O(29)	178.5(14)	179.6(10)
C(24)—Fe—C(26)	97.0(5)	99.8(5)
C(24)—Fe—C(28)	95.7(6)	95.7(5)
C(26)—Fe—C(28)	95.5(6)	96.6(5)

[a] Corrected for thermal motion.

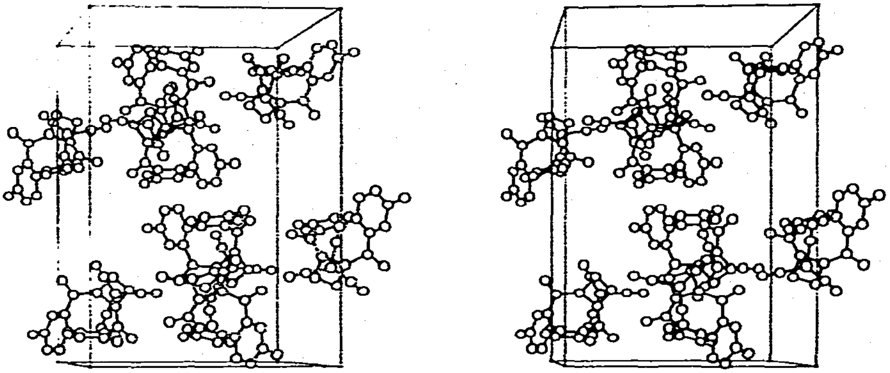

Fig. 3. Stereo ORTEP drawing of the packing as viewed down the a^* axis.

Discussion

The average C—C bond length in the cyclobutadiene rings is 1.44(2) Å; such a value falls between the average C—C bond lengths in the cyclobutadiene portions of tetraphenylcyclobutadiene iron tricarbonyl (TPCBIT) reported by Dodge and Schomaker [6] and 1,2,3,4-tetramethylcyclobutadienenickel dichloride reported by Dunitz, Mez, Mills and Shearer [7], where the average values were 1.46(1) and 1.43(2) Å, respectively. The general equivalence of these bond lengths is indicative of delocalized π bonding, the donation of two electrons from the iron coordinator creating an aromatic system of $(4n + 2)$ π electrons. As anticipated, the four-membered ring is square planar; the average C—C—C angle in the ring is 90(3)°, and the average deviation from the best least-squares planes is 0.005 Å. The perpendicular distance between the iron atoms and the best least-squares plane to which each is coordinated is 1.77 Å. The molecular orbital theory for such a system has been discussed by Longuet-Higgins and Orgel [8]. The average distance between the iron atoms and the carbon atoms of the four-membered rings which are coordinated to them is 2.04(3) Å; the corresponding value in TPCBIT is 2.07(2) Å. The average C···Fe···C angle where the carbon atoms are adjacent to each other is 41(1)°; the corresponding value for TPCBIT is 41.3(6)°.

The coordination of the carbon monoxide ligands is perhaps best described by referring to stereofigures 2a and 2b. The ligands are on a approximate three-fold axis which passes through the iron atom and is perpendicular to the four-membered ring. The projection of C(24)—O(25) on the cyclobutadiene ring roughly bisects the C(3)—C(4) bond; the average absolute O(25)—C(24)—Fe—C(3) and O(25)—C(24)—Fe—C(4) torsion angles are 96.0(2)° and 104.3(4)°, respectively. Of the remaining ligands, C(26)—O(27) projected onto the four-membered ring, cuts the C(1)—C(4) bond, and C(28)—O(29), similarly projected, cuts the C(2)—C(3) bond such that the average of the absolute O(27)—C(26)—Fe—C(1) and the O(29)—C(28)—Fe—C(2) torsion angles is 91(1)°. The average uncorrected C—O bond length in the carbon monoxide ligands is 1.13(1) Å; this value, corrected for thermal motion [9], is 1.19(3) Å. The uncorrected average

TABLE 6

TORSION ANGLES [a] AROUND THE EIGHT-MEMBERED RINGS IN I

Atoms	Torsion angle (°) in	
	Molecule A	Molecule B
C(3)—C(4)—C(5)—C(7)	−15.4	−10.4
C(4)—C(5)—C(7)—C(13)	55.8	56.1
C(5)—C(7)—C(13)—C(14)	7.8	4.6
C(7)—C(13)—C(14)—C(20)	−81.8	−79.4
C(13)—C(14)—C(20)—C(21)	16.0	14.8
C(14)—C(20)—C(21)—C(3)	59.4	65.5
C(20)—C(21)—C(3)—C(4)	−31.4	−39.8
C(21)—C(3)—C(4)—C(5)	−25.6	−24.6

[a] The values are given for one enantiomer. The enantiomer of opposite chirality has a corresponding set of torsion angles with opposite signs.

value in TPCBIT is 1.18(1) Å. Although the difference between the uncorrected values of 0.05 Å may seem substantial, the thermal motion described for TPCBIT is not as great as that reported for I such that our corrected average and the uncorrected average in TPCBIT are probably more closely comparable. The average Fe-C bond length is 1.78(2) Å; the comparable quantity reported for TPCBIT is 1.75(1) Å. The average Fe—C—O bond angle is 178.5(7)°, while the similar value reported for TPCBIT is 178.4(16)°.

The conformation of the eight-membered rings is greatly distorted from a boat shape; torsion angles about the rings of the two unique molecules are listed in Table 6. Approximate planarity about C(3) and C(4) is maintained by bond angles C(2)—C(3)—C(4) and C(3)—C(4)—C(1) of close to 90° and bond angles C(1)—C(4)—C(5), C(3)—C(4)—C(5), C(21)—C(3)—C(2) and C(21)—C(3)—C(4) of close to 135°, the angles of a regular octagon. Although, in order to meet requirements constraining sp^2 carbon atoms in a 4,8 fused ring system, the C(5)—C(4)—C(3)—C(21) torsion angles might be expected to be very nearly 0°, an average absolute value of 25° is reported, indicative, perhaps, of considerable strain about this bond. This has the effect of tilting one carbonyl group above, and the other below, the cyclobutadiene ring with corresponding tilting in the opposite sense by the neighboring aromatic six-membered rings; the average of the absolute O(6)—C(5)—C(7)—C(8) and O(22)—C(21)—C(20)—C(19) torsion angles is 118(4)°. Such a conformation probably results from the minimization of steric interactions between these neighboring groups and it is this aspect of the structure which induces chirality into the molecule. Were the C(5)—C(4)—C(3)—C(21) torsion angle even larger, the eight-membered ring would be in the boat conformation; as a result of constraint imposed by sp^2 bonding schemes and 4,8 fused ring systems, this area of the boat is flattened. The average angle between least-squares planes calculated using the coordinates of the atoms in the aromatic six-membered rings is 74.0(8)°; this large tilt is in accord with the NMR results reported by Kaplan and Roberts. Analysis of the stereochemistry in question reveals that were the aromatic six-membered rings to be coplanar, hydrogen atoms H(5) and H(12) (the hydrogen atoms which are substituents *ortho* to the bond joining the rings, C(13)—C(14) would approach too closely. The structure of biphenyl has been determined by Trotter [10] and Hargreaves and Rizvi [11]. The results indicate that the two rings are constrained to be coplanar; such a geometry implies that the hydrogens *ortho* to the bond joining the rings and on the same side of that bond are only 2.07 Å apart, indicating considerable interpenetration of their electron clouds. (The van der Waals radius of the hydrogen atom is given by Pauling [12] as 1.2 Å.) It has been suggested, however, that intermolecular forces are responsible for such a strained conformation. The vapor-phase electron diffraction studies of Almenningen and Bastiansen [13] on biphenyl and related compounds do indeed indicate that the interplanar angle is about 42°. In I, were the eight-membered ring to assume the geometry of a regular octagon with which the six-membered rings were coplanar, the valence angles about the eight-membered rings would be 135°; this geometry would force even greater interpenetration of the electron clouds of the hydrogens *ortho* to the bond joining the six-membered rings. The tilt of the rings is such that mirror symmetry is removed from the molecule leaving only an approximate two-fold axis through the organic portion of the molecule; this two-fold axis bisects both the C(3)—C(4) and the C(13)—C(14) bonds.

The average dihedral angle between least squares planes through the atoms of the cyclobutadiene rings and rings I (see Fig. 1) is 126.7(2)° while the same value for least-squares planes through the atoms of the cyclobutadiene rings and rings II is 105(5)°; this difference is perhaps indicative of interaction between the iron tricarbonyl portion and the six-membered rings since ring I, closer to the portion, is tilted away from the cyclobutadiene ring at a larger angle than is ring II.

In summary, the conformation of the eight-membered rings is influenced greatly by the requirements of the sp^2 bonding scheme in which each member of the rings participates, and by the non-coplanarity of the aromatic six-membered rings, apparently a favorable conformation as evidenced by the vapor-phase electron diffraction studies of related compounds. Presumably, however, this conformation must also minimize the effects of the rather extensive conjugation found throughout the molecule since extensive coplanarity is preserved only in the area of the four-membered ring. The fact that these conformational enantiomers do not interconvert is explicable in terms of this analysis of the geometry of eight-membered ring. Interconversion may be accomplished by a twist about the C(13)—C(14) bond (joining the aromatic six-membered rings) with concomitant twisting of the carbonyl groups. Such a conformational change in the molecule would require a transition state during which the six-membered rings were coplanar and during which the eight-membered ring would become planar, requiring valence angles of approximately 135°. The fact that the enantiomers do not interconvert even at higher temperatures provides a measure of the instability of such a transition state.

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