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THE CRYSTAL AND MOLECULAR STRUCTURES OF THE COMPOUNDS $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_n$, WHERE $n = 3$ AND 4

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Summary

The crystal structures of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_n$, $n = 3$ and 4, have been determined.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_3$: $a = 21.20$, $b = 10.39$, $c = 7.88$ Å, $\beta = 101.6°$, $U = 1699$ Å^3, $C2/c$, $Z = 4$, $R = 0.059$, 1036 observed data.

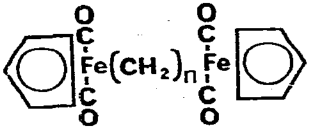
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_4$: $a = 7.63$, $b = 10.54$, $c = 21.87$ Å, $\beta = 96.4°$, $U = 1748$ Å^3, $P2_1/c$, $Z = 4$, $R = 0.051$, 1418 observed data.

In each compound the iron atoms are joined by simple chains of sigma bonded CH_2 groups. Bond lengths are similar in both: mean Fe—CO 1.75, C—O 1.15, Fe—C(cp) 2.11, Fe—CH_2 2.08, (cp)C—C(cp) 1.41, CH_2—CH_2 1.55 Å. The $(CH_2)_3$ compound retains a 2-fold axis of symmetry in the crystal. The $(CH_2)_4$ compound has no imposed symmetry, but closely approximates centrosymmetry. The effects of molecular symmetry on the IR spectrum between 2100 and 1900 cm^{-1} are discussed. The ^{13}C and ^{1}H (270 MHz) NMR spectra in solution are shown to be consistent with the structures found crystallographically.

Introduction

Compounds of the general formula $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_n$, $n = 3$—6, were originally prepared from $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ and the appropriate α,ω-dibromoalkane [1]. The structure of such a binuclear iron complex (I) with two Fe atoms linked by a polymethylene chain and each Fe atom σ-bonded to a CH_2 group was compatible with the NMR spectra.

Later work [2] showed that $NaMn(CO)_5$ and 1,3-dibromopropane reacted to yield $[Mn_2(CO)_{10}(CH_2)_3]$ which was subsequently shown [3] to be a cyclic carbene complex and structurally unrelated to I. A detailed study [4] showed that $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ would yield the mononuclear compound $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_3Br]$ which could undergo internal cyclisation to yield the cyclic oxacarbene complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_2PPh_3(\overline{CO(CH_2)_2CH_2})]^+Br^-$.



(I)

In the meanwhile, the compound $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (II) had been shown to exist in both *cis* and *trans* forms and their crystal structures had been determined [5]. The relative ease of conversion in solution from *cis* to *trans* form implied that the bridging Fe—C bonds were not particularly strong. The ability of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ derivatives to form cyclic carbene complexes had also been demonstrated [6].

These new results highlighted the previously unexplained anomalies in the physical properties of compounds of type I, i.e. their ^1H NMR spectra at 60 MHz showed the expected singlet at δ 4.65 associated with the cyclopentadienyl protons but only a singlet at ca. δ 1.4 for all of the methylene protons [1]. This singlet at δ 1.4 could be explained by any one (or more) of the following possibilities:

(i) the chemical shifts for the $Fe—\underline{CH_2}—$ protons and the $—CH_2—\underline{CH_2}—CH_2—$ protons are accidentally equivalent,

(ii) a fluxional process is causing the various methylene protons to rapidly exchange their sites and thus become equivalent,

(iii) a novel type of bonding of the polymethylene chain, possibly involving a cyclic carbene ligand, is present.

To resolve the situation, a crystallographic study and an investigation of the ^1H and ^{13}C NMR spectra of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_3$ (III) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_4$ (IV) were carried out.

Experimental

Crystals of III and IV were prepared both by the published method [1] and by reaction [27] of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2)_nBr]$ with $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, $n = 3$ and 4. Infrared spectra were recorded on a Perkin—Elmer 180 spectrophotometer. ^{13}C NMR spectra were recorded on a Varian Associates XL-100 spectrometer at 25.2 MHz; ^1H NMR spectra at 270 MHz were recorded on a super-conducting Bruker WH-270 spectrometer while those at 60 MHz were recorded on a Perkin—Elmer R12 spectrometer.

Preliminary oscillation, Weissenberg and precession photographs showed both compounds to be monoclinic. Accurate unit cell dimensions were obtained by least squares refinement of 2θ, x and ϕ angles for 25 reflections. Intensity data were measured on a Philips four-circle diffractometer with graphite-monochromated Mo-K_α radiation. Three reflections were used as standards and remeasured after every 60 reflections; no significant crystal decomposition was observed. Lorenz-polarization corrections were applied to the data but correc-

TABLE 1

CRYSTAL DATA OF III AND IV

	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_3$ (III)	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_4$ (IV)
a (Å)	21.20(2)	7.63(1)
b (Å)	10.39(1)	10.54(1)
c (Å)	7.88(1)	21.87(2)
β (degrees)	101.65(5)	96.38(5)
U (Å^3)	1699	1748
Space group	$C2/c$	$P2_1/c$
Z	4	4
D_m (g cm^{-3})	1.55(2)	1.55(2)
D_c (g cm^{-3})	1.553	1.563
Mol. wt.	396	410
Mol. symmetry	2	1
Range of $\theta°$ (degrees)	3-25	3-22
Measured reflections	1700	2219
Observed reflections: $I > 1.65\sigma(I)$	1036	1418
Scan time (sec)	24	30
Background count (sec)	24	30
Scan width (degrees)	1.2	0.9
μ (cm^{-1}) (Mo-K_α)	17.7	17.3
Final R	0.059	0.051

tions for absorption were considered unneccessary. Crystal data are tabulated in Table 1.

The structures were solved by the heavy atom method: a temperature-sharpened three-dimensional Patterson map [F^2 were multiplied by the appropriate value of $\exp(8.0 \sin^2\theta/\lambda^2)$] yielded the positions of the Fe atoms. The subsequent Fourier maps (phased on the Fe atoms) showed all C and O atoms. The structures were refined by the block-diagonal least-squares method for the observed data, weights proportional to $1/\sigma(F)$, first isotropically and then with only the Fe atoms anisotropic. (Residuals were 0.09 (III) and 0.08 (IV) at this stage.) The hydrogen atoms were now observable in the Fourier maps. They were therefore included at calculated positions 1 Å from their respective carbon atoms; the carbonyl C and O atoms were assigned anisotropic thermal parameters and the parameters of the non-hydrogen atoms were then refined to convergence; $R = 0.059$ (III), $R = 0.051$ (IV). The final difference Fourier maps were featureless.

All calculations were done with the local set of programs [7] on a Burroughs 5700 computer. Scattering factors were taken from the International Tables for X-ray Crystallography [8]; that of iron was corrected for anomalous dispersion. Lists of observed and calculated structure factors are available *.

The fractional atomic coordinates and isotropic thermal parameters are given

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* Lists of observed and calculated structure factors can be obtained from the authors.

TABLE 2

FRACTIONAL ATOMIC COORDINATES [a] AND ISOTROPIC THERMAL PARAMETERS [b] OF $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_3$

	x/a	y/b	z/c	B (Å^2)
Fe	0.12849(4)	0.26568(8)	0.01082(12)	
C(1)	0.1535(3)	0.2357(6)	−0.1823(8)	
C(2)	0.1693(3)	0.4132(7)	0.0418(9)	
O(1)	0.1709(2)	0.2147(5)	−0.3095(6)	
O(2)	0.1959(3)	0.5086(5)	0.0611(8)	
C(3)	0.0513(3)	0.3664(7)	−0.1349(9)	4.8(2)
C(4)	0.0(fixed)	0.2820(9)	−0.25(fixed)	5.0(2)
C(5)	0.1629(4)	0.0931(8)	0.1374(10)	6.3(2)
C(6)	0.1678(4)	0.1898(7)	0.2589(10)	6.0(2)
C(7)	0.1049(3)	0.2413(8)	0.2564(9)	5.9(2)
C(8)	0.0620(4)	0.1681(7)	0.1306(10)	5.6(2)
C(9)	0.0970(4)	0.0787(8)	0.0563(10)	5.9(2)
H(3.1)	0.030	0.417	−0.053	
H(3.2)	0.069	0.429	−0.212	
H(4.1)	0.021	0.224	−0.326	
H(5)	0.200	0.040	0.111	
H(6)	0.210	0.219	0.337	
H(7)	0.093	0.317	0.328	
H(8)	0.012	0.178	0.101	
H(9)	0.079	0.015	−0.040	

[a] C(4) was assigned a weight of 0.5 in the structure factor calculations because it is constrained to lie on a 2-fold axis in the unit cell. [b] All hydrogen atoms were assigned B = 6.0.

in Tables 2 (III) and 4 (IV) and the anisotropic thermal parameters are given in Tables 3 (III) and 5 (IV). In Tables 2—5, the estimated standard deviations in the last figure are shown in parentheses. The thermal ellipsoids and the direction cosines of their principal axes (derived from the data in Tables 3 and 5) are given in Table 6. Bond lengths and intramolecular non-bonded contacts are given in Tables 7 (III) and 8 (IV). Bond angles are given in Tables 9 (III) and 10 (IV). Parameters describing the planes of the cyclopentadienyl rings and polymethylene chain in IV are given in Table 11. The numbering systems are illustrated in Fig. 1 (IV) and 2 (III).

TABLE 3

ANISOTROPIC THERMAL PARAMETERS [a] OF: $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_3$ ($\times 10^5$ for Fe; $\times 10^4$ for C and O)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	196(2)	931(9)	1508(15)	−10(11)	86(9)	−46(29)
C(1)	26(2)	83(7)	203(14)	−10(7)	28(8)	28(19)
C(2)	24(2)	120(9)	196(15)	−6(7)	−15(9)	−27(19)
O(1)	51(2)	147(7)	220(11)	−23(6)	101(7)	−60(15)
O(2)	42(2)	122(7)	439(18)	−58(6)	5(9)	−125(17)

[a] The anisotropic temperature factor is defined as: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

TABLE 4

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS [a] OF $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_4$

	x/a	y/b	z/c	B (Å^2)
Fe(1)	1.01030(12)	0.11010(9)	0.11970(4)	
Fe(2)	0.48250(12)	0.09500(9)	0.38830(4)	
C(1)	0.8000(9)	0.0886(7)	0.0810(3)	
C(2)	1.0278(9)	0.2689(7)	0.0981(3)	
C(3)	0.6930(9)	0.1208(7)	0.4264(3)	
C(4)	0.4760(10)	−0.0637(7)	0.4087(3)	
O(1)	0.6643(6)	0.0707(5)	0.0546(2)	
O(2)	1.0382(8)	0.3739(5)	0.0852(3)	
O(3)	0.8289(7)	0.1384(5)	0.4533(2)	
O(4)	0.4753(8)	−0.1693(5)	0.4212(3)	
C(5)	0.8906(9)	0.1789(7)	0.1941(3)	3.4(2)
C(6)	0.7867(9)	0.0771(7)	0.2253(3)	3.3(2)
C(7)	0.7017(9)	0.1335(6)	0.2810(3)	3.3(2)
C(8)	0.5977(9)	0.0308(7)	0.3123(3)	3.5(2)
C(9)	1.0756(9)	−0.0797(7)	0.1407(3)	4.0(2)
C(10)	1.1173(9)	−0.0518(7)	0.0803(3)	3.9(2)
C(11)	1.2435(10)	0.0465(7)	0.0864(3)	4.3(2)
C(12)	1.2807(9)	0.0798(7)	0.1498(3)	4.2(2)
C(13)	1.1775(9)	−0.0009(7)	0.1827(3)	3.7(2)
C(14)	0.4125(9)	0.2859(7)	0.3696(3)	4.2(2)
C(15)	0.3751(10)	0.2530(8)	0.4301(3)	5.0(2)
C(16)	0.2515(10)	0.1546(7)	0.4248(3)	4.7(2)
C(17)	0.2117(10)	0.1242(7)	0.3613(3)	4.4(2)
C(18)	0.3100(9)	0.2076(7)	0.3275(3)	4.2(2)
H(5.1)	0.806	0.249	0.179	
H(5.2)	0.983	0.216	0.226	
H(6.1)	0.869	0.005	0.241	
H(6.2)	0.691	0.040	0.195	
H(7.1)	0.620	0.204	0.266	
H(7.2)	0.798	0.169	0.312	
H(8.1)	0.682	−0.042	0.326	
H(8.2)	0.503	−0.005	0.281	
H(9)	0.987	−0.148	0.152	
H(10)	1.065	−0.093	0.040	
H(11)	1.298	0.086	0.051	
H(12)	1.367	0.148	0.167	
H(13)	1.177	−0.002	0.229	
H(14)	0.500	0.354	0.359	
H(15)	0.428	0.293	0.470	
H(16)	0.201	0.110	0.460	
H(17)	0.128	0.056	0.343	
H(18)	0.306	0.210	0.281	

[a] All hydrogen atoms were assigned $B = 6.0$.

Discussion

In compounds III and IV the two Fe atoms are linked by simple polymethylene chains with the carbon of the α-methylene group σ-bonded to the iron atom, as was originally postulated [1]. There are no unusual bond lengths or angles; the mean values of the bond lengths in III and IV agree well with those (shown in parentheses) observed in similar molecules: Fe—CO 1.75 (1.75 [5], 1.74 [9],

(continued on p. 317)

TABLE 5

ANISOTROPIC THERMAL PARAMETERS [a] OF $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_4$ (× 10^5 for Fe; × 10^4 for C and O)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	1261(19)	702(11)	168(2)	0(29)	193(11)	1(10)
Fe(2)	1246(19)	751(11)	171(2)	85(30)	196(11)	—10(10)
C(1)	128(15)	78(9)	21(2)	19(19)	32(8)	—8(7)
C(2)	189(17)	70(8)	21(2)	0(20)	19(3)	—1(6)
C(3)	189(17)	80(9)	20(2)	68(20)	33(9)	1(7)
C(4)	230(19)	96(10)	23(2)	17(22)	39(10)	8(7)
O(1)	147(11)	117(7)	28(1)	—2(14)	—2(6)	—20(5)
O(2)	324(16)	85(7)	42(2)	—55(17)	—6(8)	28(6)
O(3)	195(13)	146(8)	35(2)	45(16)	—34(7)	—23(6)
O(4)	362(17)	99(7)	41(2)	—32(18)	30(9)	30(6)

[a] The anisotropic temperature factor is defined as: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

TABLE 6

THERMAL ELLIPSOIDS OF THE ATOMS OF THE CARBONYL GROUPS

	Atom	Amplitude (Å)	Direction cosines parallel to:		
			a	*b*	c^*
Compound III	C(1)	0.25	0.526	—0.395	—0.753
		0.24	0.777	—0.135	0.614
		0.20	—0.344	—0.909	0.236
	O(1)	0.35	0.808	—0.342	0.480
		0.28	0.396	0.918	—0.012
		0.22	—0.437	0.200	0.877
	C(2)	0.28	0.676	0.191	—0.711
		0.26	—0.281	0.960	—0.009
		0.20	0.681	0.206	0.703
	O(2)	0.38	0.403	0.148	—0.903
		0.34	—0.773	0.584	—0.249
		0.20	0.490	0.798	0.350
Compound IV	C(1)	0.23	0.294	—0.284	0.913
		0.21	0.477	0.871	0.117
		0.17	—0.828	0.401	0.391
	O(1)	0.28	0.194	0.644	—0.740
		0.24	—0.328	0.753	0.570
		0.20	0.925	0.132	0.357
	C(2)	0.24	0.904	—0.011	0.427
		0.22	0.427	0.045	—0.903
		0.20	—0.009	0.999	0.045
	O(2)	0.34	0.636	—0.281	—0.719
		0.29	0.753	0.026	0.657
		0.20	—0.166	—0.959	0.228
	C(3)	0.26	0.828	0.538	—0.160
		0.22	0.006	0.276	0.961
		0.19	0.561	—0.796	0.226
	O(3)	0.33	0.468	0.536	—0.702
		0.27	—0.242	0.842	0.481
		0.22	0.850	—0.055	0.524
	C(4)	0.27	0.794	0.259	0.550
		0.23	—0.458	0.850	0.260
		0.22	—0.400	—0.458	0.793
	O(4)	0.33	0.849	—0.287	—0.444
		0.32	0.508	0.212	0.835
		0.22	—0.146	—0.934	0.326

TABLE 7

BOND LENGTHS [a] AND INTRAMOLECULAR NON-BONDED SEPARATIONS (Å) (not corrected for thermal motion) OF $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_3$

Fe—C(1)	1.74	C(5)—C(6)	1.38
Fe—C(2)	1.75	C(6)—C(7)	1.43
Fe—C(3)	2.08	C(7)—C(8)	1.42
C(1)—O(1)	1.15	C(8)—C(9)	1.39
C(2)—O(2)	1.14	C(9)—C(5)	1.42
C(3)—C(4)	1.54	Fe—C(5)	2.11
		Fe—C(6)	2.12
C(1) ··· C(2)	2.53	Fe—C(7)	2.11
C(4) ··· C(8)	3.24	Fe—C(8)	2.11
C(4) ··· C(9)	3.54	Fe—C(9)	2.11

[a] Estimated standard deviations are approximately 0.01 Å for Fe—C and 0.02 Å for C—C and C—O distances.

TABLE 8

BOND LENGTHS [a] AND INTRAMOLECULAR NON-BONDED SEPARATIONS (Å) (not corrected for thermal motion) OF $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_4$

Fe(1)—C(1)	1.74	Fe(1)—C(9)	2.10
Fe(2)—C(3)	1.75	Fe(1)—C(10)	2.12
Fe(1)—C(2)	1.75	Fe(1)—C(11)	2.11
Fe(2)—C(4)	1.73	Fe(1)—C(12)	2.12
Fe(1)—C(5)	2.08	Fe(1)—C(13)	2.12
Fe(2)—C(8)	2.08	Fe(2)—C(14)	2.11
C(1)—O(1)	1.14	Fe(2)—C(15)	2.11
C(2)—O(2)	1.15	Fe(2)—C(16)	2.11
C(3)—O(3)	1.15	Fe(2)—C(17)	2.11
C(4)—O(4)	1.15	Fe(2)—C(18)	2.13
C(5)—C(6)	1.54	C(9)—C(10)	1.42
C(6)—C(7)	1.56	C(10)—C(11)	1.41
C(7)—C(8)	1.55	C(11)—C(12)	1.43
C(1) ··· C(2)	2.59	C(12)—C(13)	1.41
C(3) ··· C(4)	2.56	C(13)—C(9)	1.41
C(6) ··· C(13)	3.33	C(14)—C(15)	1.43
C(6) ··· C(9)	3.45	C(15)—C(16)	1.40
C(7) ··· C(18)	3.35	C(16)—C(17)	1.42
C(7) ··· C(14)	3.49	C(17)—C(18)	1.42
		C(18)—C(14)	1.41

[a] Estimated standard deviations are approximately 0.01 Å for Fe—C and 0.02 Å for C—C and C—O distances.

TABLE 9

BOND ANGLES IN DEGREES (±1°) OF $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_3$

Fe—C(1)—O(1)	179	C(5)—C(6)—C(7)	109
Fe—C(2)—O(2)	180	C(6)—C(7)—C(8)	106
Fe—C(3)—C(4)	115	C(7)—C(8)—C(9)	109
C(3)—C(4)—C(3)'	111	C(8)—C(9)—C(5)	108
C(1)—Fe—C(2)	93	C(9)—C(5)—C(6)	108
C(1)—Fe—C(3)	87		
C(2)—Fe—C(3)	87		

TABLE 10

BOND ANGLES IN DEGREES (±1°) OF $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_4$

Fe(1)—C(1)—O(1)	178	C(9)—C(10)—C(11)	107
Fe(1)—C(2)—O(2)	178	C(10)—C(11)—C(12)	109
Fe(2)—C(3)—O(3)	178	C(11)—C(12)—C(13)	107
Fe(2)—C(4)—O(4)	178	C(12)—C(13)—C(9)	109
C(1)—Fe(1)—C(2)	95	C(13)—C(9)—C(10)	109
C(3)—Fe(2)—C(4)	95		
C(1)—Fe(1)—C(5)	88	C(14)—C(15)—C(16)	108
C(3)—Fe(2)—C(8)	89	C(15)—C(16)—C(17)	108
C(2)—Fe(1)—C(5)	86	C(16)—C(17)—C(18)	107
C(4)—Fe(2)—C(8)	85	C(17)—C(18)—C(14)	108
Fe(1)—C(5)—C(6)	113	C(18)—C(14)—C(15)	108
Fe(2)—C(8)—C(7)	114		
C(5)—C(6)—C(7)	111		
C(6)—C(7)—C(8)	111		

TABLE 11

PARAMETERS DESCRIBING THE PLANES IN $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_4$

(a) CYCLOPENTADIENYL RINGS

Ring A. Direction cosines: 0.727; —0.679; 0.098
Ring B. Direction cosines: 0.742; —0.667; 0.065 } parallel to *a*, *b* and *c**

Deviation (Å)

	C(9)	C(10)	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)	C(17)	C(18)
Plane A	0.01	0.00	0.00	0.01	—0.01	6.22	6.18	6.16	6.19	6.25
Plane B	6.42	6.49	6.51	6.46	6.43	0.00	0.00	—0.01	0.01	—0.01

(b) THE $Fe_2(CH_2)_4$ SYSTEM

Direction cosines: 0.761; —0.234; 0.605

Deviation (Å)

Fe(1)	C(5)	C(6)	C(7)	C(8)	Fe(2)
0.02	—0.01	—0.01	—0.01	—0.01	0.02

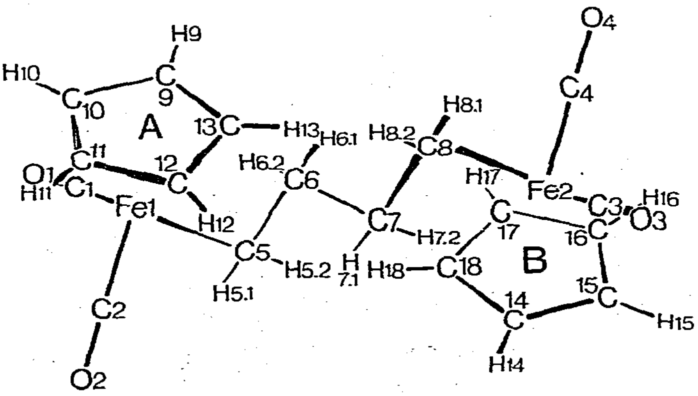


Fig. 1. Projection of compound IV down *y*, showing the numbering system.

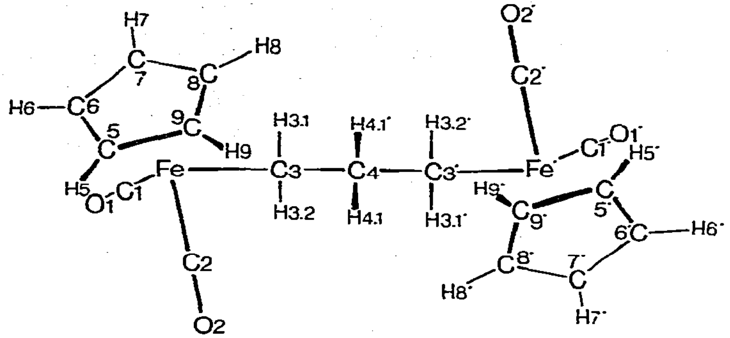


Fig. 2. Projection of compound III down y, showing the numbering system. C(4) lies on a 2-fold axis, and half of the molecule forms the asymmetric unit.

1.78 [11]); C—O 1.15 (1.55 [5], 1.17 [9], 1.12 [11]); Fe—C(cp) 2.11 (2.11 [5], 2.11 [9], 2.10 [11]); (cp)C—C(cp) 1.41 (1.41 [9], 1.43 [10], 1.40 [11]); Fe—CH_2 2.08 (2.06 [12], 2.10 [15]); CH_2—CH_2 1.55 Å. The Fe—CH_2 bond length lies between the extremes of 2.03 and 2.16 Å observed for the four Fe—CH bonds in the cyclohexadienyl system [$\overline{\mathrm{R{-}CH{=}CH{-}CH{=}CH{-}R}}$] [13], and is shorter than both the usual Fe—C(cp) length of 2.11 Å and the Fe—CH_2 length of 2.12 Å in $[(\eta^5\text{-}\overline{\mathrm{C_5H_4)Fe(CO)_2(CH_2}})\mathrm{Fe(CO)_4}]$ [14]. Thus, there seems to be little (or no) difference between the length of a σ Fe—C bond and that of an

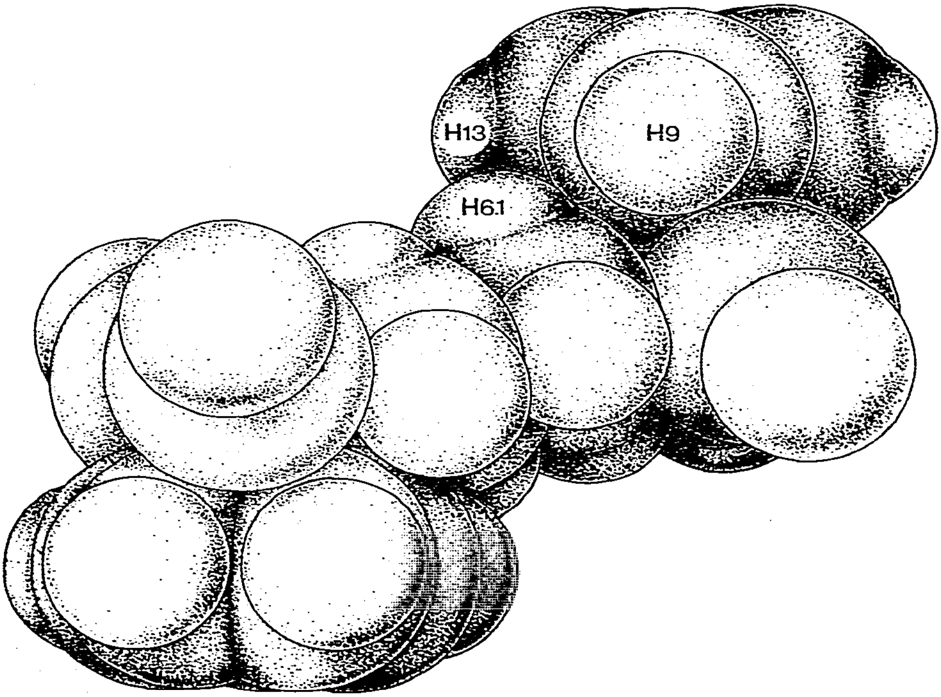


Fig. 3. Projection of compound IV showing van der Waals radii, the near-parallelism of the cyclopentadienyl rings and the conformation of the polymethylene chain.

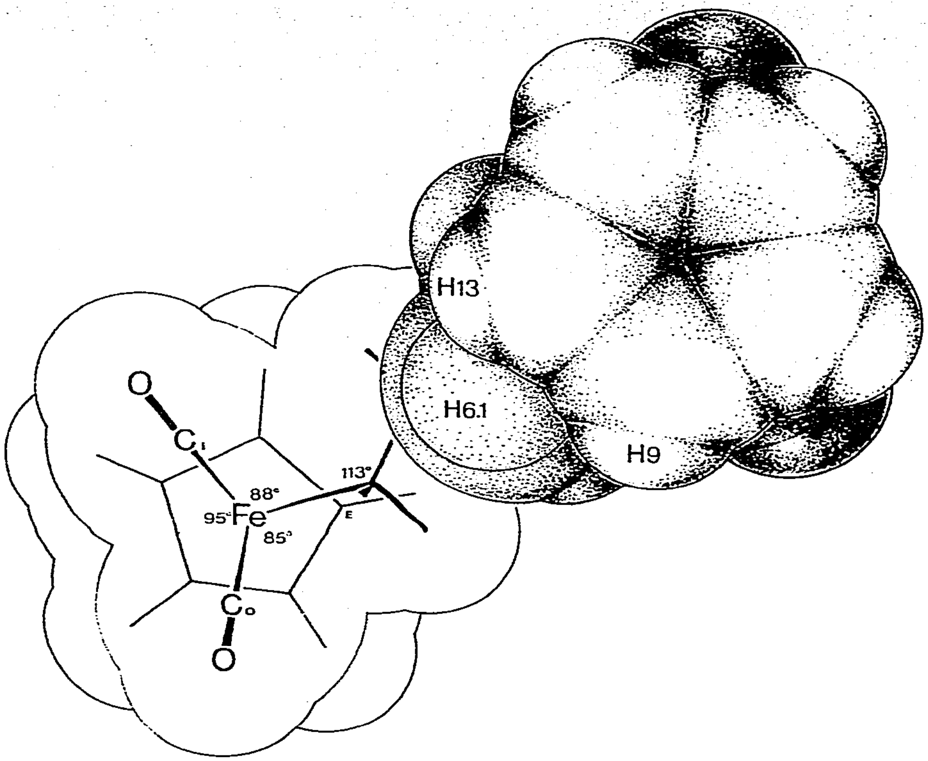


Fig. 4. Projection of compound IV onto the plane of the left-hand cyclopentadienyl ring, showing how H(6.1) fits between H(9) and H(13) on the cyclopentadienyl ring (compare Fig. 3).

Fe—C bond in a formally π-bonded system. The unique Fe—C bond in the complex [(η^5-C_5H_5)Fe$(CO)_2$CNB$(C_6H_5)_3$] is significantly shorter: 1.89 Å [11].

The arrangement of the groups bonded to the iron atoms is essentially identical in compounds III and IV. Intramolecular strains due to non-bonded repulsions

TABLE 12

SUMS OF FRACTIONAL COORDINATES FOR PAIRS OF ATOMS, SHOWING THE NEAR-CENTRE OF INVERSION IN IV

Atoms	*x/a*	*y/b*	*z/c*
C(5), C(8)	1.488	0.210	0.506
C(6), C(7)	1.488	0.211	0.506
Fe(1), Fe(2)	1.493	0.205	0.508
C(1), C(3)	1.493	0.209	0.507
O(1), O(3)	1.493	0.209	0.508
C(2), C(4)	1.504	0.205	0.507
O(2), O(4)	1.514	0.205	0.506
C(9), C(14)	1.488	0.206	0.510
C(10), C(15)	1.492	0.201	0.510
C(11), C(16)	1.495	0.201	0.511
C(12), C(17)	1.492	0.204	0.511
C(13), C(18)	1.488	0.207	0.510

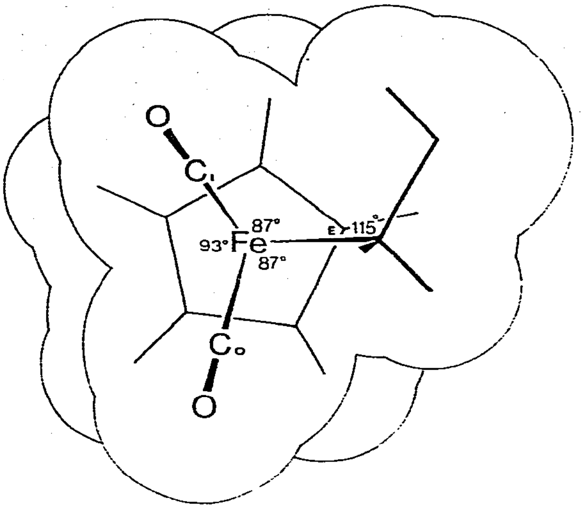


Fig. 5. Projection of compound III onto the plane of the cyclopentadienyl ring. The values of the C—Fe—C angles are shown, and may be compared with the mean values found in IV (see Fig. 4).

cause small but real deviations from ideality in the molecular geometry. The atoms in each of the cyclopentadienyl rings are coplanar within 0.01 Å. There are no unusually short intermolecular contacts in either compound.

The molecule IV has symmetry 1 in the crystal, yet it very closely approximates centrosymmetry (Fig. 3 and 4). The distortion is possible because there can be some rotation about the C—C bonds as well as bending of the polymethylene chain; and it arises because, by so doing, the molecule can reduce its effective volume and consequently pack more tightly in the crystal. The two iron atoms and the four carbons of the $(CH_2)_4$ chain are nearly coplanar, but there is a systematic distortion which places the two iron atoms on one side of the mean plane while the four carbons lie on the other (Table 11b). The magnitude of the distortion is also reflected in the differences between the direction cosines of the planes of the two cyclopentadienyl rings (Table 11a) and the small but systematic differences in sums of the *x*, *y* and *z* coordinates of analogous pairs of atoms (the sums would be identical if the molecule were ideally centrosymmetric, Table 12). The deviation from ideality is emphasised by comparing the

TABLE 13

^{1}H NMR SPECTRA AT 60 MHz FOR COMPOUNDS III AND IV USING TMS AS REFERENCE

Compound	Solvent	$\delta(C_5H_5)$ [b]	$\delta(CH_2)$ [b]
III	CCl_4	4.68 s, br	1.44 s, br
	$CDCl_3$	4.69 s	1.47 s
	C_6H_6	4.19 s	1.66 s [a]
IV	$CDCl_3$	4.73 s	1.48 s
	C_6H_6	4.19 s	1.62 s

ratios $(x/a)/(y/b)$ from Table 12: C(6), C(7) in the chain 7.05; O(2), O(4) of the carbonyls 7.38; and in the rings C(11), C(16) 7.44 and C(13), C(18) 7.19.

The close similarities between the two compounds are clearly seen by comparing the bond angles between groups on the Fe atom in III with the analogous angle about the two independent Fe atoms in IV (Fig. 4 and 5). OC—Fe—CO = 95, 95, 93°; OC_O—Fe—CH_2 = 85, 86, 87°; OC_I—Fe—CH_2 = 88, 89, 87°. The OC—Fe—CO angle exceeds 90° because the small C ··· C separations (mean value 2.55 Å) cause severe repulsion between the carbon atoms: the normal non-bonded C ··· C separation would exceed 3 Å. In both compounds, one carbon atom of the cyclopentadienyl ring is in contact with the β-methylene group [(cp)C ···CH_2 of 3.33 and 3.35 Å in IV, and 3.24 Å in III]. The effect of this repulsion can be seen in the enlarged Fe—CH_2(α)—CH_2(β) angle: 113 and 114° in IV and 115° in III. The angle at the β-carbon is uniformly smaller: 111° in each case. The similarities and subtle differences between the coordination about the iron atoms in III and IV, are illustrated in Fig. 4 and 5 which show projections of the $Fe(CO)_2CH_2$ groups onto the planes of the cyclopentadienyl rings. While there is no "free" rotation of the aromatic ring, its orientation in IV differs from that in III. The difference is best seen by considering two vectors, one defined by the line joining the centre of the cyclopentadienyl ring to carbon atom C_E and the second defined by the Fe—CH_2 bond. In projection onto the plane of the ring, the torsion angles in IV are 2.2 and 2.4° while in III the angle is 3.9° but in the opposite sense (see Fig. 4 and 5). It is imposible to state whether it is intramolecular repulsions or packing effects in the crystal that cause the difference.

A rationale can now be made for the systematic alternation of the melting point between compounds with even and odd n in the $(CH_2)_n$ chain [1]. In III the molecule occupies an effective volume of 425 Å^3 in the crystal; in IV the effective molecular volume is 437 Å^3. The addition of one CH_2 group thus increases the effective molecular volume by only 12 Å^3; a value of 18 Å^3 is more usual [16]. The molecules of IV with symmetry $\bar{1}$ are closer-packed in the crystal than those of III with their imposed 2-fold symmetry axis. It thus seems that the analogues with n = 5 and 6 will behave similarly, the $(CH_2)_5$ compound having a lower packing density than that of the $(CH_2)_6$ compound from which

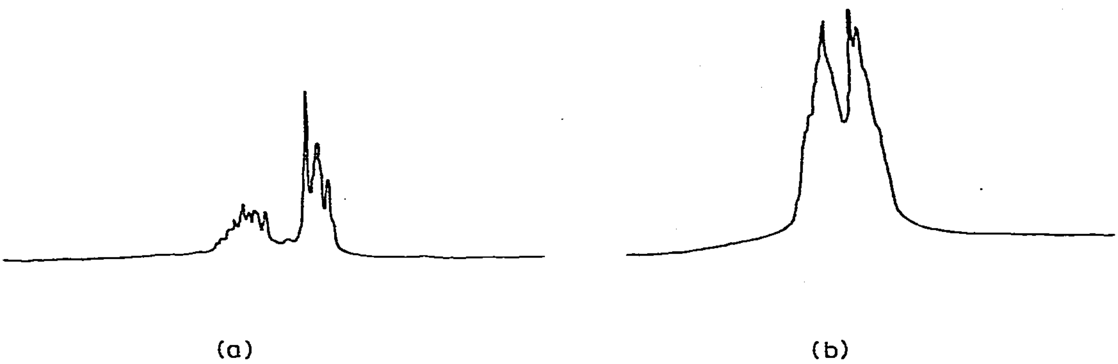

(a)
(b)

Fig. 6. ^{1}H NMR spectra at 270 MHz showing the fine structure of the methylene protons: (a) $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_3$; (b) $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_4$. Field increases to right (see Table 14). Scale: (a) 9 mm = 50 Hz; (b) 10 mm = 50 Hz.

TABLE 14

^1H NMR SPECTRA (270 MHz) FOR COMPOUNDS III AND IV IN C_6D_6 USING TMS AS REFERENCE

Compound	$\delta(C_5H_5)$ [a]	$\delta(CH_2)$ [a]
III	4.122 s	1.803 m, 1.636 m
IV	4.097 s	1.713 m, 1.660 m

[a] s, singlet; m, asymmetric multiplet.

would follow [17,18] the lower melting points for the compounds with *n* odd.

A marked difference between effective molecular volume in the crystal for *cis* and *trans* isomers, shown by the densities 1.728 (*cis*), 1.767 (*trans*) g cm^{-3}, was observed [5] in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. Such differences in density and packing can also be observed in differences in the thermal motion parameters of the atoms in the crystal. The effect is well illustrated by comparing the isotropic *B*'s and thermal ellipsoids for comparable pairs of atoms in III and IV. The vibration amplitudes in III are greater than those in IV: see Tables 2—6.

The crystallographic results show unequivocally that the α- and β-methylene groups have different environments, and there is no obvious reason for the various methylene hydrogen atoms to have similar chemical shifts as was observed at 60 MHz [1].

The ^1H NMR spectra of III and IV have been recorded in several solvents at 60 MHz (see Table 13). Only for III in benzene was any fine structure observed for the CH_2 resonance where two shoulders appeared on each side of the singlet. However, the ^1H NMR spectra of III and IV at 270 MHz (see Fig. 6 and Table 14) clearly show two sets of resonances for the methylene protons thus demonstrating that the chemical shifts of the α- and β-methylene protons at 60 MHz are accidentally equivalent. The ^{13}C NMR spectra of III and IV also have two resonances corresponding to the two different environments for the carbon atoms of the polymethylene chains (Table 15). These NMR results show quite unequivocally that, at ambient temperature and on the NMR time scale, there is no scrambling of the CH_2 groups.

In the related complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH)_4$, the two Fe atoms have been shown by X-ray crystallography to be σ-bonded *trans*-1,4 to the buta-1,3-diene chain [19—21]. A singlet was observed in this case for the four protons of the butadiene moiety in the ^1H NMR spectrum at 60 MHz [21], and the authors suggested that the complex was stereochemically non-rigid

TABLE 15

PROTON NOISE-DECOUPLED ^{13}C NMR SPECTRA OF III, IV AND $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ IN $CDCl_3$ SOLUTION AT AMBIENT TEMPERATURE [a]

Compound	$\delta(^{13}CO)$	$\delta(^{13}C_5H_5)$	$\delta(^{13}C\text{—Alkyl})$	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	218.4	85.3		—23.5
III	217.9	85.2	47.4	7.8
IV	217.8	85.4	43.8	3.8

[a] Chemical shifts in ppm downfield from TMS; $Cr(acac)_3$ has been added.

TABLE 16

IR DATA FOR COMPOUNDS III AND IV IN CYCLOHEXANE SOLUTION AND AS KBr DISC

Compound	Conditions	ν(CO) (cm^{-1})
III	Cyclohexane	2012(sh), 2007s, 2001vs, 1992vw(sh), 1957(sh), 1952vs, 1921vw
III	KBr disc	2047w, 1996vs, 1938vs
IV	Cyclohexane	2008(sh), 2006vs, 1993vw(sh), 1953vs, 1922vw
IV	KBr disc	2045vw, 1996vs, 1959s, 1950s, 1939vs

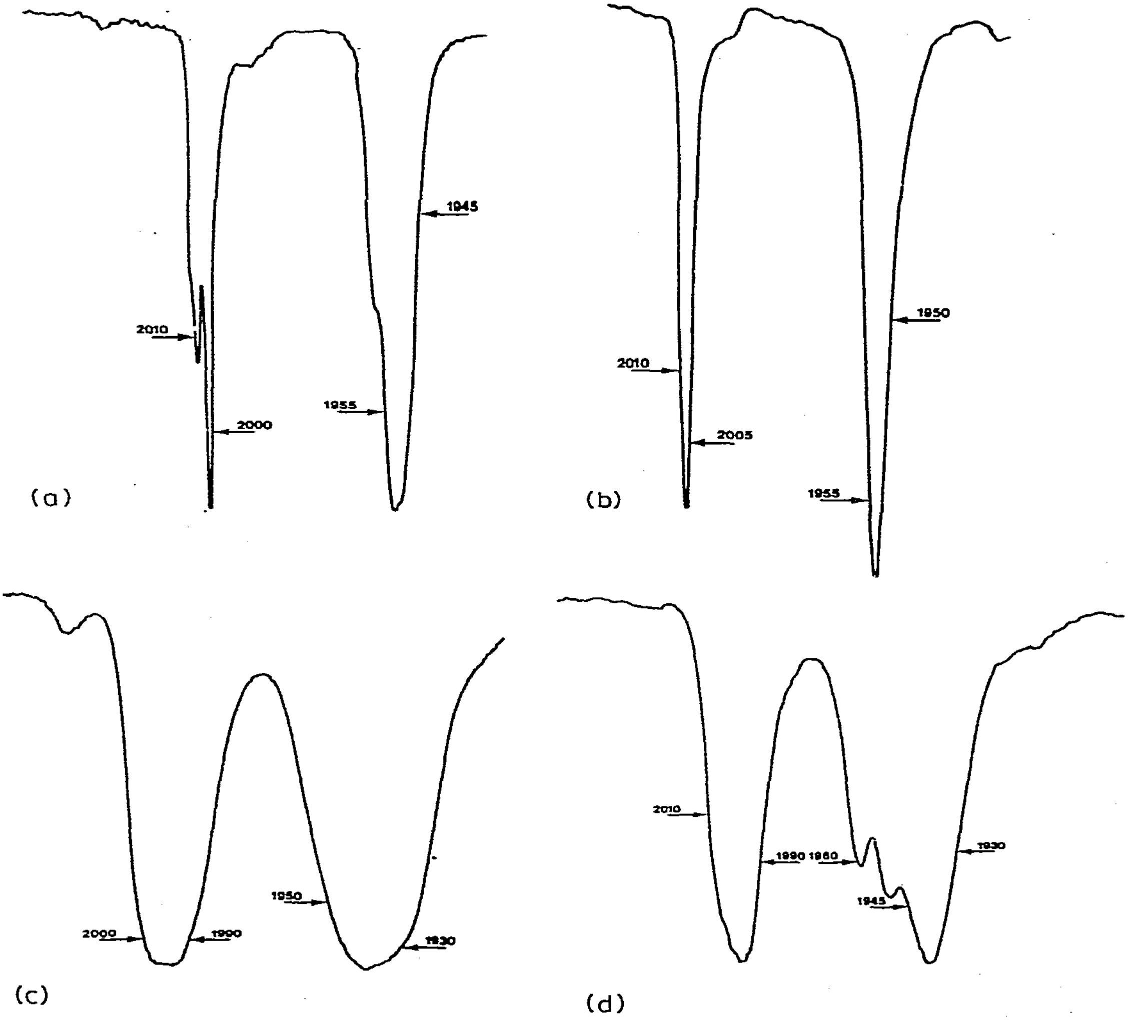


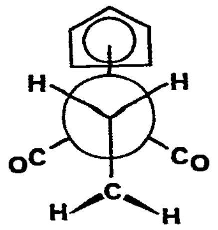
Fig. 7. Infrared spectra of compounds III and IV; (a) III in cyclohexane; (b) IV in cyclohexane; (c) III in KBr disc; (d) IV in KBr disc.

and also offered a mechanism for the interconversion of the various carbon atoms in the butadiene chain.

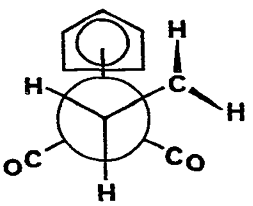
A similar situation exists for [$(C_5H_7O_2)Ni(PPh_3)C_2H_5$] for which a singlet was observed for all five protons of the C_2H_5 group at 100 MHz [22]. Cotton et al. [23] showed that the singlet was due to accidental equality of the proton chemical shifts and not to scrambling because the expected two resonances were observed for the carbon atoms of the ethyl group in the ^{13}C NMR spectrum. It is thus possible that in some cases, e.g. [21], the apparently anomalous singlets in the ^1H NMR spectra may also be caused by accidental equality of chemical shifts and not by rapid scrambling.

The infrared absorption spectra of III and IV differ noticeably in the region 1900—2100 cm^{-1} (see Table 16). In cyclohexane, the spectrum of IV consists of two strong peaks at 2006 and 1953 cm^{-1}, while that of III is more complex having peaks at 2007, 2001 and 1952 cm^{-1} with a shoulder at 1957 cm^{-1}. The KBr disc spectra are totally different. Now it is the spectrum of III which consists of only two strong peaks, 1996 and 1938 cm^{-1}, while the spectrum of IV is considerably more complex with peaks at 1996, 1959, 1950 and 1939 cm^{-1} (see Fig. 7). The differences between the spectra are caused by differences between the symmetry of the molecule in solution and in the crystal. Compound III has symmetry 2 in the crystal, there are two independent CO groups and therefore only two well-defined vibration frequencies are observed. In solution, the flexible $(CH_2)_3$ chain allows the molecule to distort and as a consequence, the absorption peaks are split. Conversely, IV will be centrosymmetric in solution and only two strong absorption peaks are expected. Its symmetry in the crystal is 1, the four CO groups are now independent and this results in an increase in complexity of the spectrum. Kettle et al. have given detailed discussions of the effect of change in environment on molecular symmetry and hence the carbonyl stretching absorption spectrum in this class of compound [24].

The presence of additional bands in the solution spectrum suggests that two different conformations may be present, caused by rotation about the Fe—C or C—C bonds. This behaviour was reported for the compound [$(\eta^5$-$C_5H_5)Fe(CO)_2SiMeCl_2$] [25]. The Newman projections a and b below show the two most likely possibilities for compounds of the type [$(\eta^5$-$C_5H_5)Fe(CO)_2]_2(CH_2)_n$.



(a)



(b)

Comparison with Fig. 4 and 5 shows that it is conformation b which is adopted by both III and IV in the crystalline state. Examination of scale models (CPK or Leybold) shows quite conclusively that conformation a is not favoured because two H atoms on the β-methylene group suffer large van der Waals repulsions as they eclipse the two carbonyl groups. A similar effect in compounds of the class $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2R$ has been discussed recently [26].

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