Crystal Structures of *o*-, *m*-, and *p*-Nitrophenylferrocenes and their Relevance to other Sterically Crowded Phenylferrocenes†

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The crystal structures of the nitrophenylferrocenes $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4R)]$ [R = *o*- (**1**), *m*- (**2**), or *p*-$O_2NC_6H_4$ (**3**)] have been determined. All three structures consist of discrete molecules with the iron atom η^5-bonded to both cyclopentadienyl rings with bond lengths in the range 1.997(9)—2.120(10) Å. The steric constraints of the nitro group lead to different conformations in the three structures. Thus in the *ortho* structure, the *o*-nitro group intersects the phenyl ring at an angle (Θ') of 42.3(1)° and the phenyl ring intersects the cyclopentadienyl (cp) ring at an angle (Θ) of 43.6(1)°. Corresponding angles in the less crowded *meta* and *para* structures are 10.3(1), 17.4(1) (*meta*) and 2.9(1), 12.5(1)° (*para*) respectively. These structures are discussed in conjunction with that of 2,2′,5,5′-tetramethyl-1,1′-bis(2″,4″,6″-trimethylphenyl)ferrocene, (**4**), and other *ortho*-substituted phenylferrocenes. Iron-57 Mössbauer and ^{13}C n.m.r. data for (**4**) are presented and discussed. The ^{13}C data have been used in an estimation of Θ for a number of *ortho*-substituted phenylferrocenes. A critical survey of known structures of ferrocene derivatives is also presented.

There has been enormous interest in the structure of ferrocene and its derivatives and over 300 crystal structures of molecules containing the ferrocene fragment have been determined, including 18 of ferrocene itself (Cambridge Crystallographic Data Centre Files, 1986 update). In this paper we report the structures of the nitrophenylferrocenes $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4R)]$-[R = *o*- (**1**), *m*- (**2**), or *p*-$O_2NC_6H_4$ (**3**)], together with ^{13}C n.m.r. and Mössbauer data on the sterically crowded derivative 2,2′,5,5′-tetramethyl-1,1′-bis(2″,4″,6″-trimethylphenyl)-ferrocene, (**4**).[1] The main interest lies in the different orientations of the nitro and phenyl groups relative to the cyclopentadienyl rings (cp represents $\eta\text{-}C_5H_5$ and $\eta\text{-}C_5H_4R$ throughout).

Experimental

The nitrophenylferrocene derivatives were prepared by reaction of ferrocene with the corresponding isomers of the diazotised nitroanilines following published methods[2–5] with the modification that tetrahydrofuran was used as co-solvent instead of acetic acid or CH_2Cl_2.[6] The products were recrystallised from methanol. Compound (**4**) was synthesised by an established procedure.[1] Carbon-13 n.m.r. spectra were run on a Bruker WP 80 spectrometer. Mössbauer spectra were obtained and fitted as previously described.[6]

Crystal Data for (**1**).—$C_{16}H_{13}FeNO_2$, M = 307.1, monoclinic, space group $P2_1/a$, a = 14.112(8), b = 10.660(7), c = 8.905(8) Å, β = 101.5(1)°, U = 1 312.7 Å^3, D_m = 1.55, D_c = 1.55 g cm^{-3}, λ(Mo-K_α) = 0.7107 Å, μ = 11.78 cm^{-1}, F(000) = 632, Z = 4.

Table 1. Atomic co-ordinates (× 10^4) for (**1**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Fe	1 188(1)	2 243(2)	4 316(2)
C(1)	−107(10)	3 133(18)	3 771(20)
C(2)	−95(12)	2 274(17)	2 660(21)
C(3)	699(14)	2 609(19)	2 035(15)
C(4)	1 107(12)	3 694(18)	2 809(17)
C(5)	610(10)	3 991(14)	3 874(16)
C(11)	1 374(8)	1 203(11)	6 236(13)
C(12)	1 470(10)	456(13)	5 070(17)
C(13)	2 251(10)	926(13)	4 521(16)
C(14)	2 598(8)	2 002(12)	5 415(13)
C(15)	2 065(8)	2 171(13)	6 544(12)
C(21)	2 189(7)	3 154(10)	7 701(11)
C(22)	1 368(7)	3 735(11)	7 986(13)
C(23)	1 433(8)	4 662(13)	8 995(13)
C(24)	2 327(9)	5 113(12)	9 709(13)
C(25)	3 149(8)	4 630(13)	9 558(13)
C(26)	3 058(6)	3 632(11)	8 543(11)
N(1)	3 982(6)	3 067(11)	8 437(11)
O(1)	4 062(6)	1 919(9)	8 422(10)
O(2)	4 650(5)	3 790(10)	8 391(11)

Crystal Data for (**2**).—$C_{16}H_{13}FeNO_2$, M = 307.1 orthorhombic, space group $Pbca$, a = 7.470(8), b = 11.780(9), c = 30.323(21) Å, U = 2 668.3 Å^3, D_m = 1.53, D_c = 1.53 g cm^{-3}, λ(Mo-K_α) = 0.7107 Å, μ = 11.59 cm^{-1}, F(000) = 1 264, Z = 8.

Crystal Data for (**3**).—$C_{16}H_{13}FeNO_2$, M = 307.1, monoclinic, space group $P2_1/a$, a = 9.692(8), b = 9.316(8), c = 14.570(13) Å, β = 93.3(1)°, U = 1 313.4 Å^3, D_m = 1.55, D_c =

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 2. Atomic co-ordinates (× 10⁴) for (**2**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Fe	5 326(1)	3 655(1)	9 222(1)
C(1)	2 678(12)	3 852(8)	9 177(3)
C(2)	3 322(15)	4 587(9)	9 496(3)
C(3)	4 550(14)	5 304(8)	9 295(3)
C(4)	4 656(13)	5 042(8)	8 853(3)
C(5)	3 482(13)	4 132(8)	8 774(3)
C(11)	5 769(11)	2 000(7)	9 373(3)
C(12)	6 469(12)	2 700(7)	9 710(3)
C(13)	7 785(11)	3 412(7)	9 509(3)
C(14)	7 850(9)	3 152(7)	9 056(2)
C(15)	6 583(9)	2 275(6)	8 960(2)
C(21)	6 225(9)	1 779(6)	8 526(2)
C(22)	5 324(10)	749(7)	8 487(3)
C(23)	5 028(12)	276(8)	8 081(3)
C(24)	5 545(11)	812(7)	7 698(3)
C(25)	6 408(9)	1 844(7)	7 735(2)
C(26)	6 772(9)	2 320(6)	8 137(2)
N(1)	6 864(9)	2 454(6)	7 337(2)
O(1)	7 820(9)	3 306(5)	6 985(2)
O(2)	6 338(9)	2 140(6)	6 985(2)

Table 3. Atomic co-ordinates (× 10⁴) for (**3**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Fe	−1 849(2)	−196(2)	6 530(1)
C(1)	−2 384(14)	−2 325(14)	6 501(11)
C(2)	−2 097(15)	−1 851(17)	5 633(11)
C(3)	−2 974(19)	−756(18)	5 378(10)
C(4)	−3 843(13)	−501(18)	6 111(15)
C(5)	−3 452(14)	−1 485(19)	6 793(10)
C(11)	−234(10)	24(13)	7 480(8)
C(12)	191(10)	371(14)	6 587(8)
C(13)	−629(11)	1 532(14)	6 231(9)
C(14)	−1 561(12)	1 889(12)	6 928(10)
C(15)	−1 352(11)	958(12)	7 691(8)
C(21)	−2 106(10)	968(11)	8 526(8)
C(22)	−1 643(11)	202(13)	9 296(7)
C(23)	−2 321(13)	257(14)	10 116(9)
C(24)	−3 488(12)	1 099(13)	10 140(9)
C(25)	−4 004(13)	1 796(14)	9 379(9)
C(26)	−3 347(12)	1 750(12)	8 596(9)
N(1)	−4 164(13)	1 203(13)	11 012(9)
O(1)	−5 199(10)	1 977(11)	11 026(8)
O(2)	−3 676(12)	533(14)	11 670(7)

Table 4. Molecular dimensions for (**1**)—(**3**) (distances in Å, angles in °)

	(**1**)	(**2**)	(**3**)
Fe–C(1)	2.030(13)	1.997(9)	2.050(12)
Fe–C(2)	2.094(13)	2.034(9)	2.027(13)
Fe–C(3)	2.048(13)	2.039(9)	2.016(12)
Fe–C(4)	2.036(16)	2.043(8)	2.013(11)
Fe–C(5)	2.041(13)	2.016(8)	2.018(12)
Fe–C(11)	2.011(11)	2.029(8)	2.040(11)
Fe–C(12)	2.033(14)	2.044(7)	2.043(12)
Fe–C(13)	2.036(12)	2.051(8)	2.059(12)
Fe–C(14)	2.052(11)	2.039(7)	2.042(11)
Fe–C(15)	2.120(10)	2.040(7)	2.038(11)
C(1)–C(2)	1.351(22)	1.385(12)	1.383(18)
C(1)–C(5)	1.354(20)	1.401(12)	1.385(19)
C(2)–C(3)	1.393(23)	1.389(13)	1.365(19)
C(3)–C(4)	1.410(22)	1.378(12)	1.418(21)
C(4)–C(5)	1.325(20)	1.406(12)	1.388(20)
C(1)–Fe–C(11)	114.8(6)	106.8(4)	107.1(5)
C(2)–Fe–C(11)	123.7(6)	123.1(4)	124.9(5)
C(3)–Fe–C(11)	155.4(7)	159.6(4)	161.5(7)
C(4)–Fe–C(11)	163.7(6)	158.7(4)	154.9(7)
C(5)–Fe–C(11)	130.3(5)	122.1(4)	120.0(6)
C(1)–Fe–C(12)	128.7(7)	121.8(4)	119.6(6)
C(2)–Fe–C(12)	109.4(6)	108.0(4)	107.6(4)
C(3)–Fe–C(12)	120.8(6)	124.4(3)	125.2(6)
C(4)–Fe–C(12)	155.7(6)	159.4(4)	163.5(7)
C(5)–Fe–C(12)	164.6(5)	157.9(4)	154.1(6)
C(1)–Fe–C(13)	162.9(6)	158.8(4)	154.2(5)
C(2)–Fe–C(13)	126.3(6)	124.2(4)	120.5(5)
C(3)–Fe–C(13)	108.5(6)	110.0(3)	108.5(5)
C(4)–Fe–C(13)	121.8(6)	124.3(6)	126.8(6)
C(5)–Fe–C(13)	145.9(6)	159.4(4)	164.4(6)
C(1)–Fe–C(14)	156.0(6)	158.9(4)	163.0(6)
C(2)–Fe–C(14)	163.3(6)	159.7(4)	156.4(6)
C(3)–Fe–C(14)	126.9(6)	124.5(6)	122.8(6)
C(4)–Fe–C(14)	109.3(5)	108.9(3)	109.5(5)
C(5)–Fe–C(14)	121.2(5)	123.1(4)	127.3(5)
C(1)–Fe–C(15)	124.8(6)	121.4(4)	125.1(5)
C(2)–Fe–C(15)	157.0(6)	158.2(4)	161.8(5)
C(3)–Fe–C(15)	162.4(7)	158.9(4)	156.6(6)
C(4)–Fe–C(15)	126.1(6)	122.4(4)	120.1(6)
C(5)–Fe–C(15)	110.5(5)	105.8(3)	107.6(5)
C(2)–C(1)–C(5)	112.9(15)	108.3(9)	107.1(13)
C(1)–C(2)–C(3)	104.3(14)	107.6(8)	109.4(13)
C(11)–C(12)	1.337(17)	1.412(11)	1.424(16)
C(11)–C(15)	1.410(16)	1.430(10)	1.437(14)
C(12)–C(13)	1.385(19)	1.429(12)	1.423(16)
C(13)–C(14)	1.426(16)	1.405(11)	1.437(16)
C(14)–C(15)	1.382(15)	1.432(11)	1.414(15)
C(15)–C(21)	1.456(16)	1.463(10)	1.455(15)
C(21)–C(22)	1.381(14)	1.393(11)	1.382(15)
C(21)–C(26)	1.400(14)	1.401(9)	1.415(15)
C(22)–C(23)	1.327(16)	1.370(11)	1.398(16)
C(23)–C(24)	1.405(16)	1.376(11)	1.379(17)
C(24)–C(25)	1.325(15)	1.380(11)	1.354(17)
C(25)–C(26)	1.386(16)	1.370(9)	1.340(15)
C–N(1)	1.456(13)	1.444(9)	1.466(18)
N(1)–O(1)	1.230(13)	1.237(8)	1.237(17)
N(1)–O(2)	1.225(13)	1.197(7)	1.217(17)
C(2)–C(3)–C(4)	107.3(14)	109.2(8)	107.9(13)
C(3)–C(4)–C(5)	108.8(16)	107.6(8)	106.2(13)
C(1)–C(5)–C(4)	106.6(15)	107.3(8)	109.3(13)
C(12)–C(11)–C(15)	114.4(11)	110.1(7)	108.6(10)
C(11)–C(12)–C(13)	105.6(12)	106.8(6)	108.7(9)
C(12)–C(13)–C(14)	107.7(11)	108.2(7)	106.2(11)
C(13)–C(14)–C(15)	109.5(11)	109.5(7)	110.2(10)
C(11)–C(15)–C(14)	102.7(10)	105.4(7)	106.2(10)
C(11)–C(15)–C(21)	130.2(10)	128.3(7)	127.1(10)
C(14)–C(15)–C(21)	127.1(11)	126.3(6)	126.6(10)
C(15)–C(21)–C(22)	117.8(9)	120.8(6)	121.4(10)
C(15)–C(21)–C(26)	127.6(9)	121.4(6)	122.2(10)
C(22)–C(21)–C(26)	114.6(10)	117.7(6)	116.4(10)
C(21)–C(22)–C(23)	120.7(9)	120.6(7)	121.9(11)
C(22)–C(23)–C(24)	122.3(10)	121.7(7)	117.9(12)
C(23)–C(24)–C(25)	120.7(11)	117.9(7)	121.1(12)
C(24)–C(25)–C(26)	115.7(10)	121.6(7)	120.7(11)
C(21)–C(26)–C(25)	125.9(9)	120.4(7)	121.7(11)
C(21)–C(26)–N(1)	121.0(10)		
C(25)–C(26)–N(1)	113.1(8)		
C(24)–C(25)–N(1)		118.8(6)	
C(26)–C(25)–N(1)		119.5(6)	
C(23)–C(24)–N(1)			117.9(12)
C(25)–C(24)–N(1)			121.0(11)
C–N(1)–O(1)	119.9(10)	117.5(6)	117.2(12)
C–N(1)–O(2)	116.5(11)	120.9(7)	118.5(12)
O(1)–N(1)–O(2)	123.6(10)	121.6(7)	124.4(13)

Table 5.

Angles between least-squares planes*

Plane 1: C(1), C(2), C(3), C4), C(5)
Plane 2: C(11), C(12), C(13), C(14), C(15)
Plane 3: C(21), C(22), C(23), C(24), C(25), C(26)
Plane 4: N(1), O(1), O(2)

Angles between planes

Compound	1—2	1—3	1—4	2—3	2—4	3—4
(**1**)	3.3(1)	40.9(1)	51.5(1)	43.6(1)	54.6(1)	42.3(1)
(**2**)	3.2(1)	15.4(1)	18.3(1)	17.4(1)	18.6(1)	10.3(1)
(**3**)	0.7(1)	11.8(1)	11.4(1)	12.5(1)	12.1(1)	2.9(1)

* All atoms are coplanar within experimental error.

1.55 g cm^{-3}, λ(Mo-K_α) = 0.7107 Å, μ = 11.78 cm^{-1}, F(000) = 632, Z = 4.

Needle crystals of approximate size 0.6 × 0.2 × 0.2 mm for (**1**), 0.4 × 0.2 × 0.2 mm for (**2**), and 0.5 × 0.2 × 0.15 mm for (**3**) were all mounted along the a axis of a Stoe STADI-2 diffractometer equipped with a graphite monochromator. Intensity data were measured by ω scans with a speed of 0.0333° s^{-1} and a background count of 20 s; 2 392, 2 600, and 2 373 independent reflections were measured with $2\theta < 50°$ for (**1**)—(**3**) respectively. Of these intensity data, 1 253, 1 358, and 1 149 respectively, all with $I > 2\sigma(I)$ were used in subsequent calculations. Neither absorption nor extinction corrections were applied. Structures were determined by normal heavy-atom methods. Non-hydrogen atoms were refined anisotropically; H atoms were fixed in trigonal positions at 0.95 Å from the C atoms to which they were bonded. All calculations were carried out using SHELX 76[7] on a CDC 7600 computer at the University of Manchester Regional Computing Centre. Scattering factors and dispersion corrections were taken from International Tables.[8] For all three refinements (on F) the weighting scheme was chosen as $w = 1/[\sigma^2(F) + 0.002\ F^2]$ where $\sigma(F)$ was taken from counting statistics. This gave similar values of $w\Delta^2$ over ranges of $\sin\theta/\lambda$ and F. In final cycles of refinement no shift/error was >0.1. Difference Fourier maps showed no significant peaks [in (**1**) max. 1.32, min. −0.43; in (**2**) max. 1.21, min. −0.77; in (**3**) max. 1.44, min. −0.73e Å^{-3}]. The final R values were 0.077 (R' = 0.081) for (**1**), 0.058 (R' = 0.059) for (**2**), and 0.079 (R' = 0.082) for (**3**).

Atomic co-ordinates for (**1**)—(**3**) are given in Tables 1—3 respectively and molecular dimensions are compared in Table 4. Figures 1—3 show the molecular structures and numbering schemes.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Discussion

The geometries of the co-ordination spheres of the iron atoms are very similar in all three structures, but the difference in position of the nitro group [*ortho* in (**1**), *meta* in (**2**), and *para* in (**3**)] has affected the conformation of the nitrophenylcyclopentadienyl ligands.

The Fe–C distances in (**2**) and (**3**) are very regular with ranges of 1.997(9)—2.051(8) and 2.013(11)—2.059(12) Å respectively. These distances are in the range of those found in ferrocene and its derivatives. We searched the Cambridge Data Centre Files (1986 update) for structures containing the phenylferrocenyl unit and located several molecules. In these, the Fe–C distances range from 1.957 to 2.212 Å with a mean of 2.041 Å. A larger range of distances is found in structures with more crowded co-ordination spheres and this is certainly true for (**1**). Thus Fe–C(15) is well above the mean at 2.120(10) Å. This must be due to the steric constraints of the *o*-nitro group on the phenyl ring. However, this has little effect on the relative positions of the two cp rings which are closely parallel in all three structures [angles of intersection 3.3(1) in (**1**), 3.2(1) in (**2**), and 0.7(1)° in (**3**)]. As is apparent from Figures 1—3 and the dimensions in Table 4, all three structures show the cp rings eclipsed rather than staggered. This is in common with most substituted ferrocenes.

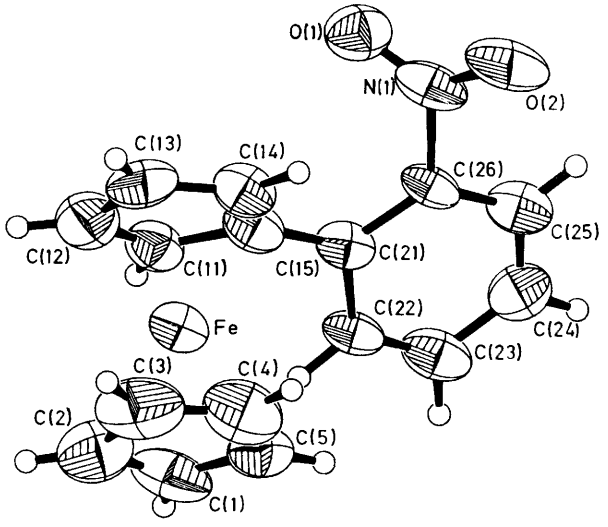


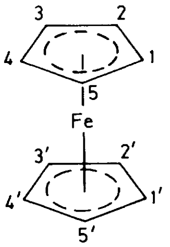
Figure 1. Molecular geometry and numbering scheme for (**1**)

Least-squares planes for (**1**)—(**3**) are given in Table 5. In (**1**) the *o*-nitro group is rotated by 42.3(1)° out of the plane of the phenyl ring. The phenyl ring itself is rotated such that it intersects the cp ring at an angle of 43.6(1)°. These large rotations, which clearly considerably reduce delocalisation between the two rings, are due to steric effects. If the rings and the nitro group had remained planar, then there would be a very close contact between the nitro group and the α-hydrogen H(14) of the cp ring The rotation has increased the O(1) ··· H(14) close distance to 2.95 Å, just outside the sum of the van der Waals radii. The effect of the *m*-nitro group in (**2**) is much less, but still significantly greater than that of the *p*-nitro group in (**3**). Thus the nitro group is rotated by 10.3(1)° from the phenyl ring plane [*cf.* 2.9(1)° in (**3**)] and the phenyl group intersects the cp ring by 17.4(1)° as against 12.5(1)° in (**3**). There are no distances less than the sum of the van der Waals radii in all three structures. The twist in the phenyl ring compared to the cp ring appears to have had little effect on the ligand geometry, in particular the C(15)—C(21) distance is similar in all three structures, a point which will be returned to later.

These twists are found in related structures. Thus in 4-biphenylylferrocene[9] and 2-biphenylylferrocene,[10] the angles between planes 1—2, 1—3, and 2—3 (numbering follows that in Table 5) are 5.4, 9.6, 8.8 and 7.8, 40.8, 47.6° respectively. These values are closely comparable to the variations between the present *o*-nitro [(**1**)] and *p*-nitro [(**3**)] compounds. The structure of 1,1″- (naphthalene-1,8-diyl)diferrocene (angles 0.9, 40.2, 39.6°)[11] shows a similar twist to the *para*-substituted compounds. However, in 1,1′-(tetraphenyl-*o*-phenylene)ferrocene,[12] the cp and some of the phenyl rings are forced to be almost perpendicular (angles 23.7, 88.4, and 85.1°).

One striking feature of the *ortho* derivative (**1**) is the marked distortion of the cp rings. Bond distances for the substituted ring range from 1.337 to 1.426 Å, with corresponding variation

Table 6. Carbon–carbon bond lengths (Å) for cyclopentadienyl rings and relevant exocyclic C–C bonds in substituted ferrocenes



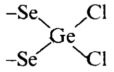
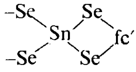
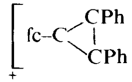
Entry no.		C–C						Average for unsubstituted cp	Exocyclic C–C	Average error	Ref.
		1–2^{a}	2–3^{a}	3–4	4–5^{a}	5–1^{a}	Average				
(A)	Monosubstituted ferrocenes Substituent at C^{1}										
1	H	1.407					1.407	1.407	—	0.007	17
2	COMe^{b}	1.428	1.416	1.420	1.415	1.432	1.422	1.413	1.466	0.004	*c*
		1.422	1.415	1.408	1.399	1.437	1.416	1.409	1.469		
3	CHO						1.402	1.397	1.481	0.014	*d*
4	CO(fc)^{e}	1.412	1.409	1.416	1.463	1.476	1.435	1.426	1.451	0.025	*f*
5	$\mathrm{CO_2}^{-\,b,g}$	1.411	1.422	1.407	1.411	1.410	1.412	1.393	1.457	0.015	*h*
		1.435	1.399	1.390	1.429	1.440	1.419	1.400	1.467		
6	$\mathrm{C_6H_4NO_2}$-*o*	1.410	1.337	1.385	1.426	1.382	1.388	1.366	1.456	0.019	*i*
7	$\mathrm{C_6H_4NO_2}$-*m*	1.430	1.412	1.429	1.405	1.432	1.422	1.391	1.463	0.011	*i*
8	$\mathrm{C_6H_4NO_2}$-*p*	1.437	1.424	1.423	1.437	1.414	1.427	1.389	1.455	0.017	*i*
9	$\mathrm{C_6H_4Ph}$-*p*	1.44	1.42	1.43	1.43	1.43	1.43	1.38	1.54, 1.56	0.030	9
10	$\mathrm{CH{=}C(NO_2)CO_2Et}$	1.432	1.428	1.422	1.419	1.443	1.428	1.414	1.456	0.007	*j*
11	C(Ph)=CHPh	1.434	1.415	1.413	1.415	1.422	1.420	1.405	1.484	0.006	*k*
12	$\mathrm{CH{=}C(CN)_2}$	1.47	1.42	1.42	1.42	1.46	1.44	1.42	1.39	0.01	*l*
13	$\mathrm{CH_2CH_2(fc)}^{e}$	1.413	1.416	1.433	1.417	1.433	1.422	1.404	1.509	0.009	*m*
14	$\mathrm{CH_2NHCHO}$	1.419	1.409	1.406	1.415	1.420	1.416	1.365	1.498	0.004	*n*
15	CH(Me)SC(O)SMe	1.415	1.418	1.404	1.405	1.440	1.416	1.365	1.485	0.007	28
16	fc^{e}	1.38	1.35	1.40	1.41	1.45	1.40	1.41	1.48	0.01	27
17	$\mathrm{AlMe_2AlMe_2Cl}$	1.482	1.409	1.405	1.409	1.482	1.437	1.419		0.011	*o*
18	$\mathrm{SiHPh_2}$	1.429	1.425	1.414	1.426	1.435	1.426	1.391		0.007	*p*
19	$\mathrm{N(fc)_2}^{e}$	1.420	1.435	1.409	1.423	1.423	1.422	1.425		0.006	26
		1.431	1.422	1.408	1.435	1.416	1.422	1.419			
		1.431	1.431	1.433	1.424	1.439	1.431	1.425			
20	$\mathrm{C_{10}H_6(fc)}^{e,q}$	1.431	1.422	1.406	1.415	1.420	1.419	1.395	1.489	0.006	11
		1.416	1.416	1.401	1.401	1.425	1.412	1.396	1.486		
(B)	Disubstituted (homo) ferrocenes Substituents										
21	1-$\mathrm{PPh_2}$, 2-$\mathrm{CH(Me)NMe_2}$	1.44	1.45	1.40	1.39	1.43	1.42	1.40	1.48	0.01	*r*
22	1-Ag, 2-$\mathrm{CH_2NMe_2}$	1.48	1.46	1.42	1.46	1.45	1.45	1.32	1.45	0.035	*s*
23	1-Cu, 2-$\mathrm{CH_2NMe_2}$	1.45	1.49	1.49	1.46	1.51	1.48	1.40	1.50	0.050	*t*
(C)	Disubstituted (hetero) ferrocenes Substituents at C^{1}, C$^{1'}$										
24	COMe, COMe	1.438	1.417	1.422	1.407	1.454	1.428		1.468	0.014	*u*
		1.436	1.407	1.424	1.427	1.422	1.423		1.474		
25	$\mathrm{CO_2H}$, $\mathrm{CO_2H}$	1.436	1.420	1.394	1.422	1.436	1.422		1.461	0.013	*v*
		1.437	1.420	1.413	1.429	1.425	1.425		1.455		
(D)	Bridged ferrocenes Bridge between C^{1}, C$^{1'}$										
26	$-\mathrm{C_5H_8}-^{w}$	1.416	1.401	1.409	1.427	1.430	1.417		1.491	0.030	*x*
									1.495		
27	>PPh	1.452	1.391	1.420	1.408	1437	1.422			0.015	*y*
		1.440	1.414	1.400	1.404	1.451					
28	$\begin{smallmatrix}-\mathrm{S}\\-\mathrm{S}\end{smallmatrix}\!>\mathrm{AsPh}$	1.424	1.423	1.430	1.408	1.441	1.425			0.005	*z*
		1.422	1.429	1.425	1.408	1.437					
29	>$\mathrm{SiPh_2}$	1.445	1.417	1.440	1.409	1.415	1.435			0.016	*aa*
30	>$\mathrm{GePh_2}$	1.449	1.387	1.422	1.404	1.421	1.417			0.018	*y*
31		1.426	1.414	1.415	1.411	1.421	1.419			0.007	*bb*
		1.429	1.398	1.427	1.420	1.432					

Table 6 (*continued*)

Entry no.		C–C 1–2[a]	2–3[a]	3–4	4–5[a]	5–1[a]	Average	Average for unsubstituted cp	Exocyclic C–C	Average error	Ref.
	Bridged ferrocenes Bridge between C¹, C¹′										
32	 fc′[e]	1.431 1.423	1.421 1.430	1.421 1.428	1.431 1.428	1.436 1.418	1.427			0.005	*cc*
33	C_6Ph_4-*o*	1.443 1.441	1.431 1.433	1.401 1.411	1.431 1.437	1.431 1.439	1.427 1.432		1.514 1.508	0.008	12
34	$-CMe_2CMe_2-$	1.450 1.464	1.425 1.420	1.401 1.425	1.445 1.447	1.443 1.431	1.433 1.437		1.54 1.55	0.017	*dd*
(E)	Polysubstituted ferrocenes Substituents										
35	Me_{10}	1.419	1.418	1.418	1.410	1.419	1.419		1.502	0.004	*ee*
	Me_{10}[ff]						1.439		1.503	0.003	*gg*
36	2,2′,3,3′,4,4′,5,5′-Me_8	1.425	1.418	1.433	1.427	1.437	1.428		1.490– 1.503	0.005	*hh*
37	1,1′-($C_6H_2Me_3$-2″,4″,6″)$_2$-3,3′,4,4′-Me_4	1.431	1.414	1.415	1.411	1.432	1.421		1.506	0.003	1
38	2,2′,3,3′,4,4′,5,5′-Ph_8	1.423	1.438	1.429	1.435	1.421	1.429		1.481	0.004	*ii*
(F)	Ferrocenyl carbocations										
39	$\overset{+}{C}Ph_2(fc)$[e]	1.438	1.413	1.425	1.402	1.445	1.425	1.408	1.416	0.012	24
40		1.453	1.418	1.442	1.423	1.453	1.440	1.408	1.445	0.008	*jj*
41	$\overset{+}{C}H(fc)_2$[e]	1.46 1.46	1.42 1.43	1.40 1.40	1.42 1.41	1.46 1.43	1.43 1.43	1.43 1.40	1.30 1.42	0.01	*kk*
(G)	Monophosphaferrocene Substituents										
42	1-$Fe(CO)_4$, 3,4-Me_2							1.355		0.006	*ll*

[a] Average of 1,2; 5,1 bonds is 1.436 Å. Average of 2,3; 4,5 bonds is 1.408 Å. [b] Two molecules per unit cell. [c] Q. Lin, Y. Hu, F. Li, and J. Huang, *Wuli Huaxue Xuebao*, 1986, **2**, 68. [d] M. F. Daniel, A. J. Leadbetter, and M. A. Mazid, *J. Chem. Soc., Faraday Trans. 2*, 1981, 1837. [e] fc = $-C_5H_4FeC_5H_5$, fc′ = $-C_5H_4FeC_5H_4-$. [f] J. Trotter and A. C. McDonald, *Acta Crystallogr.*, 1966, **21**, 359. [g] Tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)dicopper(II). [h] M. R. Churchill, Y.-J. Li, D. Nalewajek, P. M. Schaber, and J. Dorfman, *Inorg. Chem.*, 1985, **24**, 2684. [i] This work. [j] E. Skrzypszak-Jankun, A. Hoser, E. Grzesiak, and Z. Kaluski, *Acta Crystallogr., Sect. B*, 1980, **36**, 934. [k] C. J. Cardin, W. Crawford, W. E. Watts, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1979, 971. [l] A. P. Krukonis, J. Silverman, and N. F. Yannoni, *Acta Crystallogr., Sect. B*, 1972, **28**, 987. [m] J. R. Doyle, N. C. Baenziger, and R. L. Davis, *Inorg. Chem.*, 1974, **13**, 101. [n] L. H. Hall and G. M. Brown, *Acta Crystallogr., Sect. B*, 1971, **27**, 81. [o] R. D. Rogers, W. J. Cook, and J. L. Atwood, *Inorg. Chem.*, 1979, **18**, 279. [p] W. F. Paton, E. R. Corey, J. Y. Corey, M. D. Glick, and K. Mislow, *Acta Crystallogr., Sect. B*, 1977, **33**, 268. [q] $C_{10}H_6$ = Naphthalene-1,8-diyl. [r] F. W. B. Einstein and A. C. Willis, *Acta Crystallogr., Sect. B*, 1980, **36**, 39. [s] A. N. Nesmeyanov, N. N. Sedova, Yu. T. Struchkov, V. G. Andrianov, E. N. Stakheeva, and V. A. Jazonova, *J. Organomet. Chem.*, 1978, **153**, 115. [t] A. N. Nesmeyanov, Yu. T. Struchkov, N. N. Sedova, V. G. Andrianov, Yu. V. Volgin, and V. A. Sazonova, *J. Organomet. Chem.*, 1977, **137**, 217. [u] G. J. Palenik, *Inorg. Chem.*, 1970, **9**, 2424. [v] G. J. Palenik, *Inorg. Chem.*, 1969, **8**, 2744. [w] C_5H_8 = cyclopentane-1,3-diyl. [x] P. Batail, D. Grandjean, D. Astruc, and R. Dabard, *J. Organomet. Chem.*, 1975, **102**, 79. [y] H. Stoeckli-Evans, A. G. Osborne, and R. H. Whiteley, *J. Organomet. Chem.*, 1980, **194**, 91. [z] A. G. Osborne, R. E. Hollands, R. F. Bryan, and S. Lockhart, *J. Organomet. Chem.*, 1985, **288**, 207. [aa] H. Stoeckli-Evans, A. G. Osborne, and R. H. Whiteley, *Helv. Chim. Acta*, 1976, **59**, 2402. [bb] A. G. Osborne, A. J. Blake, R. E. Hollands, R. F. Bryan, and S. Lockhart, *J. Organomet. Chem.*, 1985, **287**, 39. [cc] A. G. Osborne, R. E. Hollands, R. F. Bryan, and S. Lockhart, *J. Organomet. Chem.*, 1982, **224**, 129. [dd] M. B. Laing and K. N. Trueblood, *Acta Crystallogr.*, 1965, **19**, 373. [ee] D. P. Freyberg, J. L. Robbins, K. N. Raymond, and J. C. Smart, *J. Am. Chem. Soc.*, 1979, **101**, 892. [ff] From gas-phase electron diffraction studies. [gg] A. Almenningen, A. Haaland, S. Samdal, J. Bronvoll, J. L. Robbins, and J. C. Smart, *J. Organomet. Chem.*, 1979, **173**, 293. [hh] Yu. T. Struchkov, V. G. Andrianov, T. N. Salnikova, I. R. Lyatifov, and K. H. Materikova, *J. Organomet. Chem.*, 1978, **145**, 213. [ii] M. P. Castellani, J. M. Wright, S. J. Geib, A. L. Rheingold, and W. C. Trogler, *Organometallics*, 1986, **5**, 1116. [jj] R. L. Sime and R. J. Sime, *J. Am. Chem. Soc.*, 1974, **86**, 892. [kk] M. Cais, S. Dani, F. H. Herbstein, and M. Kapon, *J. Am. Chem. Soc.*, 1978, **100**, 5554. [ll] J. Fischer, A. Mitschler, L. Ricard, and F. Mathey, *J. Chem. Soc., Dalton Trans.*, 1980, 2522.

in the bond angles (*cf.* ranges of 1.405—1.432 Å and 1.414—1.437 Å for the *meta* and *para* isomers respectively). The unsubstituted ring shows similar distortion [1.325—1.410, 1.378—1.406, and 1.365—1.418 Å for (**1**), (**2**), and (**3**) respectively]. Particularly noticeable are the very short bonds [C(4)–C(5) 1.325(20), C(11)–C(12) 1.337(17) Å] present in *both* rings of the *ortho* derivative.

Shortening of the exocyclic C(cp)–C(substituent) bond has often been cited as evidence for conjugation of the substituent with the cp ring. Since the ferrocenyl group is electron-releasing (σ_R = −0.26),[13] one would expect the maximum shortening for conjugated electron-withdrawing substituents such as NO_2. The interannular C–C distances [C(15)–C(21)] for the nitrophenylferrocenes clearly refute this postulate. The C(15)–C(21) distances for the *ortho*, *meta*, and *para* derivatives are 1.456(16), 1.463(10), and 1.455(15) Å respectively, identical within experimental error. These distances are all short compared with that of biphenyl [1.496(3) Å][14] which is perhaps to be expected in view of the reduced steric interaction of a five- *versus* six-membered ring system compared with a six- *versus* six-

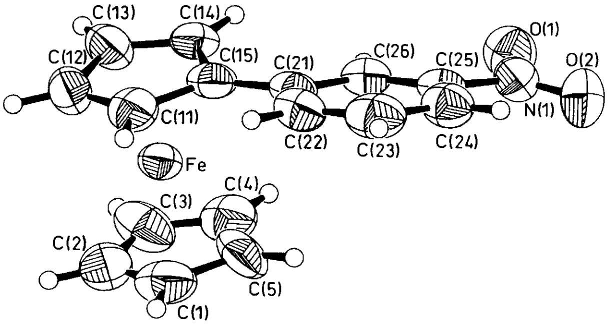


Figure 2. Molecular geometry and numbering scheme for (**2**)

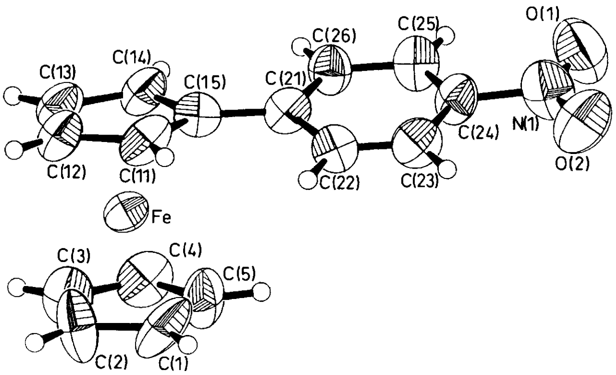


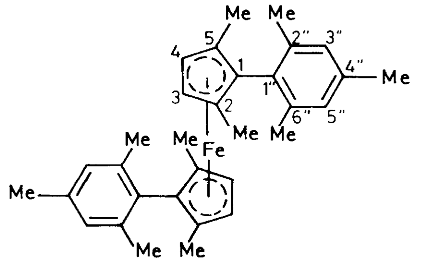
Figure 3. Molecular geometry and numbering scheme for (**3**)

membered ring system. The expected bond length for two sp^2 linked carbons is approximately 1.48 Å;[15] the larger values found for the biphenyls are said to be due to steric repulsion by the *o*-H atoms on the rings.

A case where strong π overlap is known to occur between two sp^2 carbons in adjacent ring systems is in porphyrin dications.[16] Here the interannular distance is 1.45(3) Å and the phenyl rings lie near to the mean porphyrin plane. The porphyrin plane itself is saddle shaped allowing the phenyl rings to adopt the near coplanar arrangement and alleviate steric repulsions. For the *m*- and *p*-nitrophenylferrocenes the interannular bonds are identical (within experimental error) to those of the porphyrin dications which is in keeping with the reduced steric interactions in the former two molecules. The fact that very similar bond lengths are found for all three derivatives renders the *ortho* value anomalous. For the *o*-nitro complex, interplanar angles of 43.6° (cp–arene) and 42.3° (NO_2–arene) mean that resonance effects will be reduced to about 25% of those for a coplanar structure and thus the C(15)–C(21) bond length would be expected to be greater than that of the *para* isomer. The NO_2 group in the *meta* position is not conjugate with the cp ring, yet this compound still shows shortening of the interannular bond. Examination of the literature reveals other such discrepancies.

The very crowded bis-mesityl complex (**4**)[1] has an almost identical interannular bond length [1.506(3) Å] to that of biphenyl itself. The dihedral angle in (**4**) is almost 90° which completely rules out any conjugative effects *via* the cp ring, whereas an angle close to 0° has been reported for biphenyl.[14] This contrasts with the very long interannular bond [1.55(2) Å] in 4-biphenylylferrocene,[9] where again the rings appear to be almost coplanar. [However, the crystallographic data are, by the authors' own admission, "not good" (R = 0.115).]

Table 7. Carbon-13 n.m.r. data[a] for compound (**4**)



cp	C^1	$C^{2,5}$	$C^{3,4}$			
	90.68	82.37	71.63			
Arene	$C^{1''}$	$C^{2''}$	$C^{3''}$	$C^{4''}$	$C^{5''}$	$C^{6''}$
	130.87 (138.9)	136.56 (137.5)	128.53 (127.2)	140.03 (136.0)	128.15 (127.2)	135.72 (137.5)
Methyls at	C^2, C^5	$C^{2''}$	$C^{4''}$	$C^{6''}$		
	12.77	22.44	20.80[b]	20.53[b]		

[a] In $CDCl_3$, δ in p.p.m. relative to $SiMe_4$; calculated values in parentheses. [b] Assignment arbitrary.

An interesting feature of structures (**1**)—(**3**) is the comparative shortness of the C–C bonds in the free cp ring [averaging 1.366(21), 1.391(12), and 1.389(12) Å respectively]. This compares with average values of 1.389—1.407 Å for ferrocene itself over a range of temperatures.[17] This suggests that, particularly for the *ortho* isomers, Fe–cp bonding is weaker making the ligand more like the cyclopentadienide anion. As a comparison, the C–C bond distances for the ionic complex $Na(C_5H_5){\cdot}Me_2NCH_2CH_2NMe_2$ were found to have an average value of 1.38(1) Å.[18]

The Fe–C bond distances are longer for the *ortho* derivative [average values for the *ortho*, *meta*, and *para* structures for bonds to unsubstituted cp are 2.050(14), 2.026(9), and 2.025(12) Å, respectively]. Closer examination of the *ortho* derivative (**1**) also reveals a slightly 'ring-slipped' structure. In all three structures the C–C bond distances in the unsubstituted cp ring were significantly smaller than those of the substituted cp. This finding led us to a survey of most of the known structures of ferrocenes, the results of which are listed in Table 6 and will be discussed at the end of the paper.

Carbon-13 *N.M.R. Spectroscopy*.—The assignments of the chemical shifts observed for (**4**) (Table 7) were made with reference to the known anisotropy of the ferrocene nucleus,[19,20] the known orthogonality of the arene rings,[14] and the lower intensities of the ring-linking quaternary carbons of biphenyls compared with other quaternary carbons in the structure. Estimates of the dihedral angles, Θ, were obtained using published procedures[21,22] and assuming that Θ for phenylferrocene is similar to that found for biphenyl itself in solution (26°). The following values were calculated for *o*-substituted phenylferrocenes: Me, 39; OMe, 21; NO_2, 46°. These values appear entirely reasonable, in the light of the crystal structures described above.

The barrier to rotation about the interannular bond in (**4**) must be considerable, since variable-temperature ^1H and ^{13}C n.m.r. experiments revealed no coalescence of the magnetically non-equivalent nuclei C(2″) and C(6″), and C(3″) and C(5″), even at 90 °C (solvent hexachlorobutadiene).

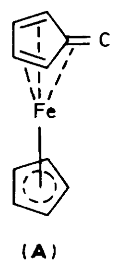
Mössbauer Spectroscopy.—We have previously measured Mössbauer data of phenylferrocenes,[6] including compounds (**1**)—(**3**), and now report the ^{57}Fe Mössbauer parameters of (**4**). The compound has an unusually high quadrupole splitting (Δ) of 2.51(1) mm s^{-1} and also a rather large isomer shift (δ = 0.56 mm s^{-1}). Phenylferrocene has Δ = 2.30(2) mm s^{-1} [δ = 0.52(2) mm s^{-1}] and the *o*-, *m*-, and *p*-methyl analogues have values of 2.42, 2.38, and 2.36 mm s^{-1} respectively.

The value for the *o*-methyl derivative is close to that for ferrocene itself (2.40 mm s^{-1}). This is the expected result for disruption of the hyperconjugative effect by the large interplanar angle predicted. However, in all three methylated phenylferrocenes the dominant effect of the substituent is one of electron release compared with phenylferrocene itself, as seen from the relative Δ values. This argument is reinforced by the data for complex (**4**) where both phenyl rings are heavily methylated and orthogonal to the cp rings thus eliminating any conjugate electron withdrawal. The observed Δ = 2.51 mm s^{-1} is therefore interpreted as an inductive release of electron density to the cp ring from both phenyl moieties and the cp methyl substituents. This is supported by the evidence from ^{13}C n.m.r. spectroscopy (see above).

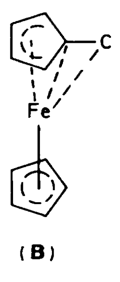
We have also obtained Mössbauer parameters for ferrocenyldiphenylcarbenium tetrafluoroborate (Table 6, entry 39) and its precursor alcohol [$Fe(\eta-C_5H_5)(\eta-C_5H_4CPh_2OH)$]. The latter showed parameters close to those of ferrocene [δ = 0.55(1), Δ = 2.38(1) mm s^{-1}], whereas the carbonium ion showed a marked decrease in quadrupole splitting [δ = 0.54(1), Δ = 2.30(1) mm s^{-1}]. Such ions normally show enhanced Δ values relative to their parent alcohols, *viz.* [$Fe(\eta-C_5H_5)(\eta-C_5H_4CH_2)$]$^+$$HSO_4^-$ and [$Fe(\eta-C_5H_5)(\eta-C_5H_4CH_2OH)$] have splittings of 2.70(2) and 2.40(1) mm s^{-1} respectively.[23] This enhancement has been attributed to overlap of iron-based orbitals, e_2, with the empty '*para* orbital' on the exocyclic carbon. The presence of two phenyl groups causes a major change in the mode of stabilisation of the carbocation. The reduction in Δ strongly suggests that stabilisation occurs *via* ligand-based orbitals, e_1, giving an η^6-fulvenoid type of structure (**A**) which is confirmed by *X*-ray data.[24]

General Comments on Ferrocene Structures.—It is significant that where electron-donating groups are present (*e.g.* Me; entries 35 and 36 of Table 6), the average C–C bond length in both cp rings is larger (1.42—1.44 Å) than that found in ferrocene itself, as are the Fe–C distances. Such electron-rich ferrocenes are characterised by Δ values which are greater than that of ferrocene.

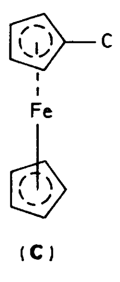
It is apparent from Table 6 that monosubstituted ferrocenes with electron-withdrawing substituents [including (**1**)—(**3**)] show longer C–C bonds in the substituted compared with unsubstituted cp rings. This phenomenon is quite general and suggests that if delocalisation of the cp ring charge over the substituent atom is occurring, then this effect is not transmitted to the free ring in the solid state. Such a transmission would be expected to lengthen the C–C distances of the free cp ring.



(**A**)



(**B**)



(**C**)

Another notable feature of these structures is that for electron-withdrawing groups, the bonds adjacent to the substituted carbon [C(1)–C(2), C(5)–C(1)] are generally significantly longer (average 1.436 Å) than the C(2)–C(3) and C(4)–C(5) bonds (average 1.408 Å). A more detailed examination of the data reveals three structural types including two extremes: those with a fulvenoid (η^6) structure (**A**) (exocyclic conjugate C–C bond lengths < 1.45 Å), those containing three contiguous short bonds of equal length, (**B**) (exocyclic conjugate bond lengths > 1.48 Å), and the intermediate cases where all bonds are approximately equal within experimental error, (**C**). Structures (**C**) have conjugate exocyclic C–C bond distances in the range 1.45—1.48 Å.

From Table 6, structures of type (**A**) include entries 12, 39, 40, 41. Compound 39 has already been assigned as a fulvenoid structure by Behrens.[24] Structures of type (**B**) are found for entries 11, 14, 37. Compounds falling into an intermediate category (**C**) are entries 2, 7, 10, 11, 24, 25. Of the remaining structures, entries 3, 4, 5, 6, 8, 9, 16, 21, 22, 23, 26 have large errors on the bond lengths ($\geqslant$ 0.01 Å). Others have no exocyclic carbon bonds (17—19, 27—32) or multiple substituents and/or steric interactions (20, 33, 35, 36, 38). Entries 13 and 15 do not appear to fit any particular structure type. Structures of type (**B**) differ from η^4-ligated complexes[25] in two ways: (*i*) the latter are characterised by a long–short–long bond sequence; (*ii*) the former still has a Fe–C(1) bond.

Triferrocenylamine (entry 19) shows some interesting features. It is the only structure available of a monosubstituted ferrocene containing an unambiguous electron-donor substituent ($+M$, mesomeric effect). The arrangement of bonds about the central N atom is almost planar, but the three ferrocenyl substituents are orientated differently. One is coplanar with the N plane, whilst the other two lie out of plane and have very similar C–C and C–N bond distances. The coplanar ring has however a significantly shorter (1.402 Å as opposed to 1.429 Å) C–N bond length commensurate with resonance of the nitrogen lone pair with the cp ring of the ferrocene moiety. Supporting this is the greatly reduced basicity of the compound.[26] The bond lengths of the conjugated cp ring are seen to be all equal within experimental error [average 1.431(7) Å]. This is in striking contrast to all the structures of monosubstituted ferrocenes where the substituents are electron withdrawing ($-M$). The cp ring coplanar with the N atom is therefore an almost perfect η^5 ligand.

Returning to the size of the free cp ring, Table 6 gives data for 42 complexes including ferrocene itself. Sixteen of these structures do not contain an unsubstituted ring. Of the remainder, 11 show an average C–C bond length less than that in the substituted ring (outside of experimental error). Amongst the remaining 15, all but one (entry 16) show a similar trend but the values lie within experimental error of those of the corresponding substituted ring. The data for entry 16 are old[27] and the four rings were not well resolved.

It has been previously suggested[28] that the apparent shrinkage of the unsubstituted cp ring is simply due to larger thermal vibrations around the Fe–cp axis. However, we wish to point out that recent data on ferrocene itself[17a,b] recorded at two different temperatures (298 and 173 K) show little evidence for such a shrinkage at the higher temperature (average C–C distances from neutron diffraction: 1.407 Å at 298 K, 1.396 Å at 173 K; averages from *X*-ray data: 1.389 Å at 298 K, 1.395 Å at 173 K), although at the lower temperature it is stated[17a] that there is a noticeable decrease in mean-square amplitudes perpendicular to the ring plane. The vibrational ellipsoid patterns found in ferrocene are said to be incompatible with pure rotational disorder.[17a] Whatever the nature of this disorder, it appears from our survey to be a feature of all monosubstituted ferrocenes for the free cp ring. It may well transpire that in all these structures there is rotation of this ring which has not been allowed for in the crystal structure analysis.

The vibration ellipsoids found in ferrocene are said to be incompatible with pure rotational disorder,[17a] but some type of disorder is likely to be present. Such disorder may well be a feature of the unsubstituted cp ring in the monosubstituted ferrocenes and thus complicate the analysis presented here. However, we feel that the trends observed in these data are valid despite the possibility of disorder in the rings which is difficult to account for in refinement.

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References

1 U. Eberhardt, B. Deppisch, and H. Musso, *Chem. Ber.*, 1983, **116**, 119.
2 S. Toma, E. Solcaniova, A. Maholanyiova, and J. Lesco, *Collect. Czech. Chem. Commun.*, 1975, **40**, 1629.
3 J. G. Mason and M. Rosenblum, *J. Org. Chem.*, 1960, **20**, 82.
4 G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 1953, 367.
5 W. F. Little and A. K. Clark, *J. Org. Chem.*, 1960, **25**, 1979.
6 R. M. G. Roberts, J. Silver, and B. Yamin, *J. Organomet. Chem.*, 1984, **270**, 221.
7 G. M. Sheldrick, SHELX 76, Package for Crystal Structure Determination, University of Cambridge, 1976.
8 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
9 F. H. Allen, J. Trotter, and C. S. Williston, *J. Chem. Soc. A*, 1970, 907.
10 J. Trotter and C. S. Williston, *J. Chem. Soc. A*, 1967, 1379.
11 M-T. Lee, B. M. Foxman, and M. Rosenblum, *Organometallics*, 1985, **4**, 539.
12 K. Yasufuki, K. Aoki, and H. Yamazaki, *Inorg. Chem.*, 1977, **16**, 624.
13 R. M. G. Roberts, J. Silver, A. S. Wells, and S. P. Wilkinson, *J. Organomet. Chem.*, 1987, **327**, 247.
14 G-P. Charbonneau and Y. Delugeard, *Acta Crystallogr., Sect. B*, 1976, **32**, 1420.
15 O. Bastiansen and M. Tratleberg, *Tetrahedron*, 1962, **17**, 147.
16 A. Stone and E. B. Fleischer, *J. Am. Chem. Soc.*, 1968, **90**, 2735.
17 (*a*) P. Seiler and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1979, **35**, 1068; (*b*) F. Takusagawa and T. F. Koetzle, *ibid.*, p. 1074; (*c*) G. Clec'h, G. Calvarin, J. F. Bérar, and R. Kahn, *C. R. Seances Acad. Sci., Ser. C*, 1978, **286**, 315.
18 T. Aoyagi, H. M. M. Shearer, and K. Wade, *J. Chem. Soc., Chem. Commun.*, 1976, 164.
19 R. R. McGuire, R. E. Cochoy, and J. A. Winstead, *J. Organomet. Chem.*, 1975, **84**, 269.
20 T. D. Turbitt and W. E. Watts, *Tetrahedron*, 1972, **28**, 1227.
21 R. M. G. Roberts, *Mag. Res. Chem.*, 1985, **23**, 52.
22 K. S. Dhami and J. B. Stothers, *Tetrahedron Lett.*, 1964, 631.
23 G. Neshvad, R. M. G. Roberts, and J. Silver, *J. Organomet. Chem.*, 1981, **221**, 85.
24 U. Behrens, *J. Organomet. Chem.*, 1979, **182**, 89.
25 F. A. Cotton and J. M. Troup, *J. Organomet. Chem.*, 1974, **77**, 83, 369; R. E. Ireland, G. G. Brown, jun., R. H. Stanford, jun., and T. C. McKenzie, *J. Org. Chem.*, 1979, **39**, 51; R. M. Moriarty, K. N. Chen, M. R. Churchill, and S. W.-Y. Chang, *J. Am. Chem. Soc.*, 1974, **96**, 3661.
26 M. Herberhold, M. Ellinger, U. Thewalt, and F. Stollmaier, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 74.
27 A. C. McDonald and J. Trotter, *Acta Crystallogr.*, 1964, **17**, 872.
28 H. Patin, G. Mignani, C. Make, J-Y. Le Marouille, A. Benoit, and D. Grandjean, *J. Organomet. Chem.*, 1980, **193**, 93.

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