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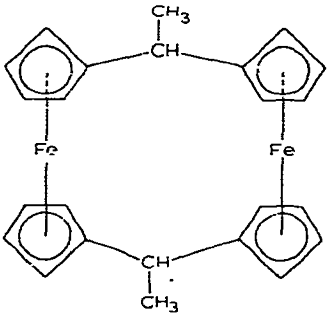
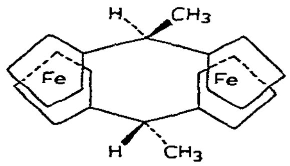
The molecular structure of a [1.1]ferrocenophane

1,12-Dimethyl[1.1]ferrocenophane (I) has recently been synthesized[1]. The PMR spectrum was interpreted in terms of an *exo*-methyl configuration and, on steric grounds, the *trans*-geometry (II) was preferred to the eclipsed *cis*-form (III)[1]. We have determined the molecular structure of I as part of a series of X-ray studies[2,3] on constrained ferrocene derivatives, and to confirm the specific proposals[1] advanced for this compound.



I



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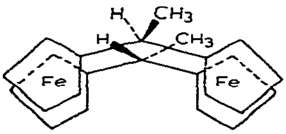

III

The following information was established from precession photographs with Mo K_α radiation ($\lambda = 0.7107$ Å.): $C_{24}H_{24}Fe_2$, $M = 424.2$, $a = 18.14 \pm 0.03$, $b = 6.10 \pm 0.02$, $c = 18.67 \pm 0.03$ Å, $\beta = 119°40' \pm 10'$, $\rho_m = 1.51$ g·cm^{-3}, $Z = 4$, $\rho_c = 1.57$ g·cm^{-3}. Space group: *Pc* or *P2/c*; the latter was established by the results of the analysis. A total of 1781 independent, non-zero structure amplitudes was measured visually from equi-inclination Weissenberg photographs using CoK_α radiation. The structure was solved by the heavy atom method, and the molecular configuration shown in Fig. 1 was established and confirmed by a full-matrix least squares refinement of the data. At the present stage of refinement, the crystallographic *R*-factor on 1781 reflexions is 0.12, with Fe–C distances ±0.02, C–C ±0.03 Å, and C–C–C angles ±1°.

The molecule is shown to exist in the *cis*-configuration (III) with the methyl groups *exo*. The ferrocenophane molecules lie on 2-fold rotation axes and the crystallographic asymmetric unit contains two independent "half-molecules", each comprising a bis(cyclopentadienyl)iron, or ferrocene unit, and a bridging methine carbon with attached methyl group. In the following discussion, the values for the molecular parameters are averaged over the two half-molecules.

The cyclopentadienyl rings of each ferrocene unit are staggered by an angle of 22.4° with respect to each other as compared to 36° in crystalline ferrocene[4]. These

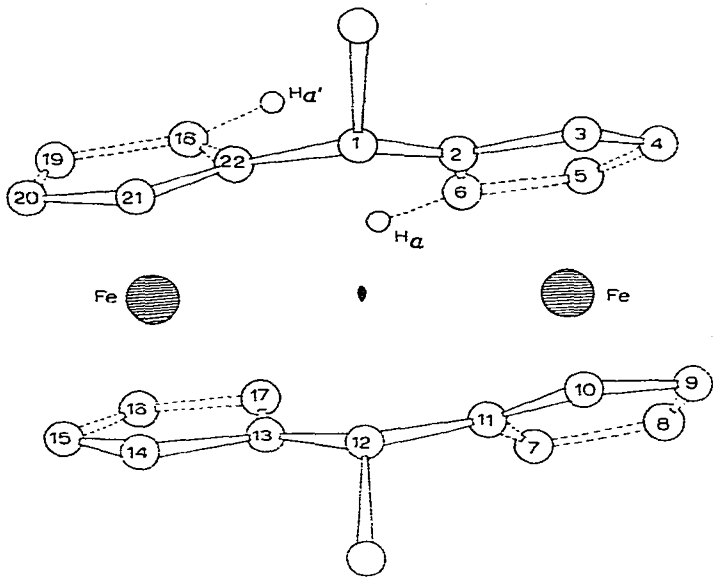

Fig. 1. Perspective view of one of the two crystallographically independent ferrocenophane molecules viewed down the *b*-axis. The two-fold axis relates one half of the molecule to the other [*e.g.* C(2) is related to C(13)]. The bond angle C(2)–C(1)–C(22) is 117°, the angles C(1)–C(2)–C(3) and C(1)–C(22)–C(21) are 121°, and the C(1)–C(2)–C(6) and C(1)–C(22)–C(18) angles are 130°.

rings are also tilted with respect to each other by 2.7° with the C(3)–C(10) distance being 3.29, compared to 3.39 Å for the C(6)–C(7) distance (see Fig. 1). The Fe-ring distance is 1.65 Å and the average Fe–C distance is 2.05 Å. The Fe–Fe distance in the ferrocenophane molecule is 4.60 Å and the cyclopentadienyl rings, linked through the bridging groups, are twisted by 31° to each other. The iron atom does not lie on a line joining the centers of mass of the two attached cyclopentadienyl rings, but is slightly displaced such that it is located equidistant (within the accuracy of the present analysis) from the five carbon atoms of each ring*.

The PMR spectrum of I in CS_2 solution indicates that four of the sixteen ring protons are deshielded with respect to the remaining twelve[1]. We do not consider that the Fe–H distances, as inferred from the measured Fe–C distances, can account for this effect in terms of the shielding influence of the metal atom on the ring protons[5]. Alternatively, it has been suggested[1] that the unique proximity of the H_α and $H_{\alpha'}$ atoms (see Fig. 1) to two cyclopentadienyl rings might cause them to be specifically deshielded, an effect which would be enhanced by any low-field shift arising from steric interaction between the H_α and $H_{\alpha'}$ atoms[6,7]. We have estimated** the separation of these protons in the crystal as 2.03 Å, a value which is considerably greater than

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* A similar effect has been observed in other ferrocene derivatives where the rings are tilted with respect to each other[3] (I. C. Paul, unpublished data).

** The criteria were, (a) the ring hydrogen atoms lie in the best plane of the ring to which they are attached[8], (b) the C–H bond bisects the external angle which the carbon atom makes with its two neighbouring carbon atoms, and (c) the C–H bond length is 1.12 Å. (A recent electron diffraction study on ferrocene in the vapour phase indicates that the hydrogen atoms may be displaced by 5° from the plane of the ring towards the iron atom.[8])

would be obtained from a model without the large angle of twist between the rings and without the distortion of several bond angles from normal values (see legend to Fig. 1). Although this separation is less than the sum of the accepted Van der Waals radii of two covalently bound hydrogen atoms (*i.e.* 2.4 Å[9]) and some measure of steric compression may be inferred, it is difficult to be certain of the magnitude of the contribution of this effect to a low-field shift in the resonance of these protons in the PMR spectrum of 1*.

Finally, we calculate that the *endo*-hydrogen atoms attached to C(1) and C(12) are separated by 2.54 Å, so it appears unlikely that the stability of the *cis*-isomer (III) would be significantly affected by non-bonded interaction between these atoms.

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* Coulson and Haigh[10] have discussed the effect of non-bonded hydrogen–hydrogen interactions on the geometry of some aromatic hydrocarbons, and have concluded that in these molecules hydrogen atoms can approach to within 1.97–2.04 Å of each other with very little increase in energy to the system.