

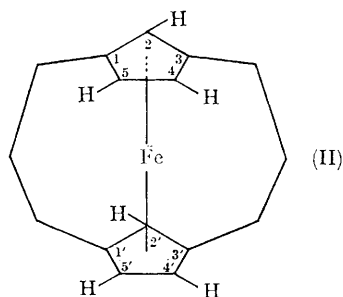
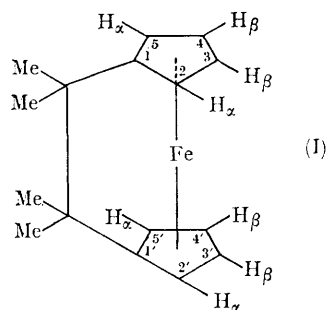
The Degree of Inclination between the Two Cyclopentadienyl Rings in a Dibridged Ferrocene

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THE prediction¹ that the chemical shift between the α - and β -protons (τ 6.01 and 5.46 in benzene) in 1,1'-(tetramethylethylene)ferrocene (I) is a consequence of the non-parallelism of the cyclopentadienyl rings has been given additional substance by the results of a crystal structure analysis of (I), where it is shown that the rings are tilted by 23.2° with respect to each other.² The protons at the high-field position were considered to correspond to the H_α atoms due to their greater proximity to the iron atom.¹ In 1,1'; 3,3'-bis(trimethylene)ferrocene (II), the ring proton signals occur at τ 6.43 and 6.14 in benzene, with the high-field protons attached to C-2 and C-2'.³ As this implies that these hydrogen atoms are probably closer to the iron nucleus, it would appear that there is a tilt of the two cyclopentadienyl rings with respect to each other despite the constraints placed on the system by the two 3-carbon bridges. This is probably achieved by rotation of the two rings about the C-1-C-3 and C-1'-C-3' axes respectively. A crystal structure analysis has been carried out on (II) to determine the extent of the tilt between the rings and the other structural features of the dibridged system.

1,1';3,3'-Bis(trimethylene)ferrocene crystallises in the monoclinic system with $a = 23.91 \pm 0.02$, $b = 9.07 \pm 0.01$, $c = 23.22 \pm 0.02$ Å, and $\beta = 94^\circ 41' \pm 15'$, as determined by precession methods using Mo- K_α radiation ($\lambda = 0.7107$ Å). The space group is $C2/c$ with sixteen molecules in the unit



cell. The structure analysis, therefore, requires the determination of the positions of two crystallographically independent molecules. The intensities were estimated visually from equi-inclination Weissenberg photographs taken with Co- K_α

radiation ($\lambda = 1.792 \text{ \AA}$). At the present stage of refinement, the crystallographic R -factor is 0.13 on a total of 1961 independent reflexions. The accuracy of the results has been reduced by the difficulty of taking full account of positional disorder involving the central methylene carbon atom in two of the bridges. In the absence of the constraints of crystal packing forces, there would be two energetically equivalent positions for these carbon atoms. No attempt has been made to include hydrogen atoms in the analysis. The average standard deviation of an Fe-C bond is 0.016 \AA , and of a C-C bond is 0.025 \AA . Crystallographic details will be published in full at a later date.

The important structural features are common to the two crystallographically independent molecules and in the following discussion, distances and angles are averaged over both molecules. The average C-2-C-2' distance is 3.01 \AA , the average among the C-1-C-1' and C-3-C-3' distances is 3.09 \AA , and the

average among the C-4-C-4' and C-5-C-5' distances is 3.36 \AA . The angle of tilt between the rings is 9° . The two cyclopentadienyl rings are eclipsed within the accuracy of the analysis. The carbon atoms of the eight independent methylene groups attached to cyclopentadienyl rings have an average displacement of 0.21 \AA from the plane of the ring to which they are bonded. The average of the twenty independent Fe-C distances is 2.01 \AA which is probably significantly shorter than the values of 2.04–2.06 \AA reported in most other ferrocene structures.^{2,4}

The present investigation provides evidence that in methylene-bridged ferrocene structures there is a correlation between the difference in the chemical shift due to the ring protons and the tilt of the cyclopentadienyl rings with respect to each other. Further structural studies are in progress which may help to produce a more unified theory for this correlation.

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¹ K. L. Rinehart, Jr., A. K. Frerichs, P. A. Kittle, L. F. Westman, D. H. Gustafson, R. L. Pruett, and J. E. McMahon, *J. Amer. Chem. Soc.*, 1960, **82**, 4111.

² M. Burke Laing and K. N. Trueblood, *Acta Cryst.*, 1965, **19**, 373.

³ K. L. Rinehart, Jr., D. E. Bublitz, and D. H. Gustafson, *J. Amer. Chem. Soc.*, 1963, **85**, 970.

⁴ N. D. Jones, R. E. Marsh, and J. H. Richards, *Acta Cryst.*, 1965, **19**, 330; J. D. Dunitz, L. E. Orgel, and A. Rich, *ibid.*, 1956, **9**, 373; Yu. T. Struchkov and T. L. Khotsyanova, *Kristallografiya*, 1957, **2**, 382; Z. L. Kaluskii, Yu. T. Struchkov, and R. L. Avoyan, *Zhur. strukt. Khim.*, 1964, **5**, 743; A. C. MacDonald and J. Trotter, *Acta Cryst.*, 1964, **17**, 872.