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THE STRUCTURE AND CONFORMATION OF BRIDGED FERROCENES

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FERROCENES bridged by one or more polymethylene chains provide an interesting molecular framework for the study of conformational mobility and electronic interactions. In the course of our studies we have prepared several singly and doubly bridged ferrocenes and report herein conclusions regarding certain aspects of the structure of these substances derived in part from an examination of their n.m.r. spectra.

We consider first 1,1'-trimethyleneferrocene (Ia). In this substance a half cyclohexane conformation for the three carbon bridge is not possible since the distance separating the terminal carbon atoms of such a conformation (2.52 Å) is insufficient to span the distance between the rings (3.32 Å).[1] Appreciable compression of the metal-ring bond is not likely especially in view of the close proximity of the rings in ferrocene.[2] Moreover models suggest that unlike the parent molecule the rings in Ia are forced to adopt a more nearly prismatic configuration in which such interannular repulsions are increased. These geometrical requirements are readily accommodated by rotation of C_α valences about the C_α-C_β bond

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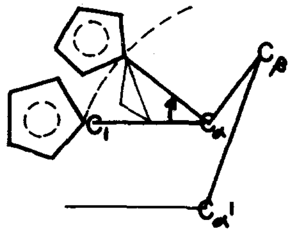
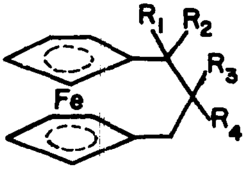
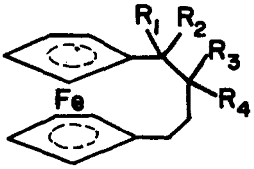
[1] J. D. Dunitz and L. E. Orgel, Nature 171, 121 (1953).

[2] Yu. T. Struchkov, Zhur. Obshchei Khim. 27, 2039 (1957).







Ia. $R_1, R_2, R_3, R_4 = H$

Ib. $R_1 = R_2 = O; R_3, R_4 = H$

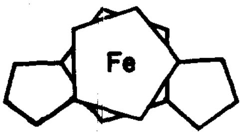
Ic. $R_1, R_3, R_4 = H; R_2 = OH$

Id. $R_1, R_2 = H; R_3, R_4 = CH_3$

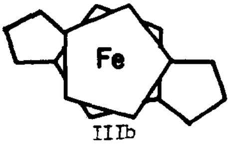
IIa. $R_1, R_2, R_3, R_4 = H$

IIb. $R_1 = R_2 = O; R_3, R_4 = H$

IIc. $R_1, R_2 = H; R_3 = R_4 = O$



IIIa



IIIb

axis or by a combination of such transformations and valence angle deformation at C_β. In the former circumstance, in which no angle strain is introduced in the bridge, a rotation of 23°55' suffices to accommodate the required minimum distance separating the rings and results in a tilting of each of the rings by an angle of 15°3' from their parallel orientation. The inclusion of angle deformation at C_β does not greatly diminish the extent of ring tilting. These metal-ring bond deformations are probably not attended by a prohibitive increase in potential energy[3,4] nor do they

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[3] C. J. Ballhausen and J. P. Dahl, Acta Chem. Scand. 15, 1333 (1961).

[4] E. R. Lippincot and R. D. Nelson, Spectrochimica Acta 10, 307 (1958).

introduce any detectable magnetic inequivalence in ring protons since these give rise to sharp singlet absorption (6.05τ)[5] in Ia[6] as they do in 1,1'-dimethylferrocene. By contrast the ring protons in $\alpha, \alpha, \alpha', \alpha'$-tetramethyl-1,1'-dimethyleneferrocene, in which ring tilting must be large are reported to exhibit pronounced differences in chemical shift.[5]

The apparent magnetic equivalency of methylene protons in Ia (8.05τ) is admissible only in terms of a rapid inversion of the chain which effectively averages the spatial orientations of these protons and their distances from the metal atom, and furthermore requires that the resulting average chemical shifts of α and β protons be very nearly identical. This inversion cannot involve a planar transition state for the bridge since the activation energy associated with such a state, estimated to be 20-30 Kcal/mole, would impose greater conformational rigidity than is observed. The considerable strain of such a configuration is evidenced by the failure of the ketone (Ib) to undergo base catalyzed deuterium exchange. By contrast, its homologue (IIa), the enol form of which is devoid of strain, readily undergoes deuterium exchange. Furthermore, pyrolysis of the acetate, benzoate, and p-nitrobenzoate, as well as the ethyl and methyl carbonates of the alcohol (Ic) does not afford any detectable amount of the expected olefin. The latter reactions yield the ethyl and methyl ethers of Ic instead.

Rapid conformational exchange in Ia is best accounted for in terms of transition states involving ring-metal bond bending and ring tilting modes. The importance of these vibrational modes for such interconversion is

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[5] Spectra were determined in $CDCl_3$ solution at a concentration of approximately 60 mg /cc and recorded at 60 mc with a Varian model V-4300 spectrophotometer. Peak positions, given in values of τ, were calibrated against tetramethylsilane as internal standard by sidebanding.

[6] K. L. Rinehart et al., J. Am. Chem. Soc. 82, 4111 (1960).

manifest in the spectrum of the doubly bridged derivative IIIa wherein such deformations are largely precluded owing to rigidity of the molecule. This substance has been assigned structure IIIb by Schlogl and Seiler,[7] but there are cogent grounds for rejecting this formulation in favor of its geometrical isomer IIIa (conformations not implied) which these authors apparently did not consider. Resonance absorption for the methylene protons in III appears as a broad band centered at 8.10 τ (width at half height, 14 cps) with two smaller, broad satellite bands approximately 17 cycles to either side of this peak, suggesting an intermediate rate of chain inversion. The small spin splitting observed for ring proton resonance in this substance (major peak 6.13τ) is also attributable to the rigid ring tilted conformation of this molecule, which brings one proton on each of the rings considerably closer to the metal atom than the other two.

The magnetic inequivalence of ring protons in Id, evidenced by the closely spaced pair of triplets at 5.93 and 6.05 τ ($J \sim 2$ cps), is very likely the consequence of an increase in the angle of ring tilt in this substance brought about in part by a contraction of the internal valence angle at C_β due to the gem dimethyl group.[8] The appearance of sharp singlet absorption for both methyl and methylene protons indicates rapid inversion of the bridge in this compound as in Ia and rules out long range spin-spin coupling as the cause of the observed ring proton splitting.

The rate of conformational exchange must be considerably diminished in 1,1'-tetramethyleneferrocene (IIa) since the α and β bridge proton resonances appear as two broad, well separated, structureless peaks centered at 8.17 and 7.58τ. Models suggest that the greater energy barrier

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[7] K. Schlogl and H. Seiler, Angew. Chem. 72, 38 (1960).

[8] P. Schleyer, J. Am. Chem. Soc. 83, 1368 (1961).

derives from the fact that chain inversion in this substance, unlike that in Ia or Id, requires passage of a methylene group through the inside of the bridge. Such transition states would undoubtedly involve considerable repulsion between the metal atom or the ring carbon atoms and the chain.

The preparation of these ferrocene derivatives and a detailed report of their chemistry will shortly be given.

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