trans,trans-1,4-Bis(dicarbonyl-π-cyclopentadienyliron)buta-1,3-diene: Nuclear Magnetic Resonance Evidence for a Static Structure in Solution

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Summary The structure of the title compound has been shown by n.m.r. spectroscopy to be static in solution.

THE n.m.r. spectrum of *trans,trans*-1,4-bis(dicarbonyl-π-cyclopentadienyliron)buta-1,3-diene (I) determined in tetrahydrofuran, methylene chloride, or acetone solution shows only two sharp singlet resonances.[1] The low-field resonance, attributed to the four butadiene protons, was observed to broaden at low temperatures. It has been suggested that this broadening was caused by a slowing of a stereodynamic equilibration of the four protons *via* a cyclobutene intermediate.[2]

We now show that the degeneracy of the butadiene protons observed in tetrahydrofuran is removed when the n.m.r. spectrum of (I) is determined in either C_6D_6 or $CD_3{\cdot}C_6D_5$ solution. In C_6D_6 the n.m.r. spectrum (60MHz) had, in addition to the singlet assigned to the cyclopentadienyl protons, a symmetrical pattern with thirteen observable lines. At 100 MHz this spectrum was resolved into a recognisable AA′BB′ pattern with J_{AB} 15·5, $J_{AB'}$ −0·5, and $J_{BB'}$ 10·1 Hz (based on the assumption that J_{AA} is *ca.* 0). The observed coupling constants are comparable to those for other *trans,trans*-1,4-disubstituted butadienes.[3] The observance of the AA′BB′ pattern at ambient temperature is conclusive evidence that the structure of (I) is static in solution and the same as that observed in the crystal. The spectrum of (I) in toluene is virtually invariant up to 116°. Thus, there is no evidence for ring closure even at high temperatures.

In the absence of special effects due to the iron groups, the failure of (I) to undergo stereodynamic equilibration of the butadiene protons *via* ring closure to a cyclobutene followed by ring opening is consistent with the 19 and 24 kcal energies of activation observed for these processes in other butadienes.[4]

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