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Preliminary communication

A novel fluxional molecule: 1,2,3-trithia-[3]-ferrocenophane

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Our studies[1] have shown diverse behavior of fluxional[2] organometallic complexes. Rosenblum has recognized[3] that the relatively simple room temperature NMR spectra of [3]- and [4]-ferrocenophanes results from rapid ring inversion. In contrast to that for C–C bonds, the barrier to rotation about S–S bonds is relatively high[4,5] (8–14 kcal·mole^{-1}). Thus, it is reasonable to expect that there would be a less rapid intramolecular inversion for 1,2,3-trithia-[3]-ferrocenophane than that occurring in [3]- and [4]-ferrocenophanes. Accordingly, we have synthesized this complex as the major product from the reaction of 1,1′-dilithioferrocene[6] with sulfur and we have demonstrated that it is a fluxional molecule. The ferrocenophane is an orange, air stable, sublimable solid (m.p. 149.5–150.5°) readily soluble in both polar and non-polar organic solvents (*Anal.:* Found: C, 42.48; H, 2.86. $C_{10}H_8FeS_3$ calcd.: C, 42.70; H, 2.75%.) In agreement with this formulation the mass spectrum shows strong peaks corresponding to the ions $C_{10}H_8FeS_n^+$, $n = 3$–0. At room temperature the NMR spectrum is markedly solvent dependent and shows four absorbtions of equal intensity in the range τ 5.6–7.2. Homonuclear spin decoupling of the room temperature spectrum, in C_6D_6 at 100 MHz., confirms that this is an ABCD pattern arising from the four non-equivalent cyclopentadienyl ring protons. Further, the decoupling is consistent with the assignment of the resonances at the lowest and highest fields to the protons adjacent to the bridge and those at intermediate fields to the non-adjacent pair. The two possible limiting structures I and II both have four non-equivalent ring protons. At 60 MHz., in deuterotoluene, increasing the temperature clearly shows that the low and high field resonances at τ 5.85 and 6.49 are averaged, with a concomitant change taking place for the intermediate pair. The resulting spectrum, at +190°, is a closely spaced AA′BB′ pattern centered at τ 6.11 which is similar to that found[3] for the ring protons in 2,2-dimethyl-[3]-ferrocenophane. The suggestion[3] that an eclipsed structure is favored over the alternate antiprismatic structure has been recently confirmed[7] for the doubly bridged bis(1,1′:3,3′-trimethylene)ferrocene. But α-keto-1,1′-trimethyleneferrocene[8], which has an sp^2 hybridized carbon atom in the bridge, has a structure in which the rings are not quite eclipsed★★. However, we wish to point

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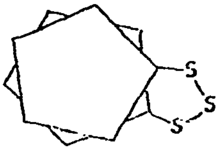
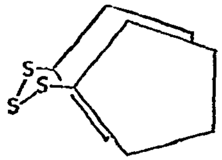
★Alfred P. Sloan Foundation Fellow 1967–1969.
★★The relative rotational orientation is 11.8° while for I and II it is 36° and 0° respectively.



(I)



(II)

out that as the sizes of the atoms in the bridge are increased, the staggered structure will be preferred. Though, while we favor II as the limiting structure in solution, we cannot conclusively rule out the alternate structure.

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