

Preliminary communication

The Bridge Reversal Barrier for
1,2,3- Trithia-[3]-ferrocenophane

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SUMMARY

The application of accurate NMR band shape studies has enabled the barrier energy for the bridge reversal process to be determined for the first time in a [3]-ferrocenophane $[(\eta\text{-C}_5\text{H}_4)_2\text{FeS}_3]$.

In the course of our investigations of fluxional phenomena involving sulphur[1,2,3], and in particular the reversal energies of 6-membered heterocyclic rings [2,3], it became apparent to us that the chair-to-chair interconversions of such rings were closely analogical to the postulated [4] bridge reversal process of [3]-ferrocenophanes, which could be envisaged as containing the $\overbrace{\text{Fe-C-E-E-E-C}}$ six membered ring (Fig. 1). Whereas very extensive accurate data are available for 6-membered ring reversal barriers [5], there are no quantitative data published for bridge reversal barriers.

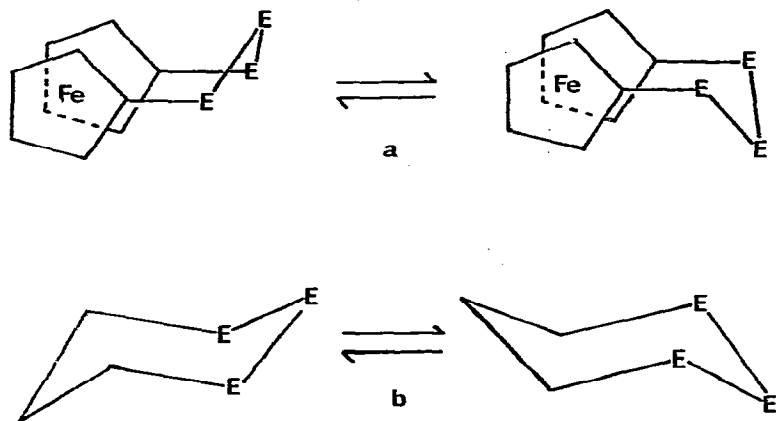


Fig. 1. (a) Bridge reversal of [3]-ferrocenophanes and
 (b) Inversion of six-membered rings.
 (E = CH₂, O, S, Se or Te)

Several examples of [3]-ferrocenophanes exhibiting temperature variable ¹H NMR spectra have been reported [6]. In order to complement our DNMR studies of sulphur containing six-membered rings [2,3,7], we have undertaken an accurate analysis of the variable temperature ¹H NMR spectrum of 1,2,3- trithia-[3]-ferrocenophane first reported by Davison and Smart [6].

Accordingly, a complete set of spectra between the slow (5°C) and the fast (200°C) exchange rates were recorded in d⁵-PhNO₂ solution, with hexamethyldisiloxane as an internal reference. (Fig. 2). Simulation of the "static" spectrum as an ABCD spin system was readily performed using the LAOCNR computer program (Fig. 3). The NMR parameters obtained from the "static" spectrum, were then utilised in the computer simulation of the dynamic spectra between +50°C and +170°C as an ABCD ⇌ BADC spin problem. Treatment of the kinetic data obtained yielded $\Delta G^\ddagger(298\text{K}) = 80.6(\pm 1.3) \text{ kJmol}^{-1}$ for the trisulphide bridge reversal energy barrier.

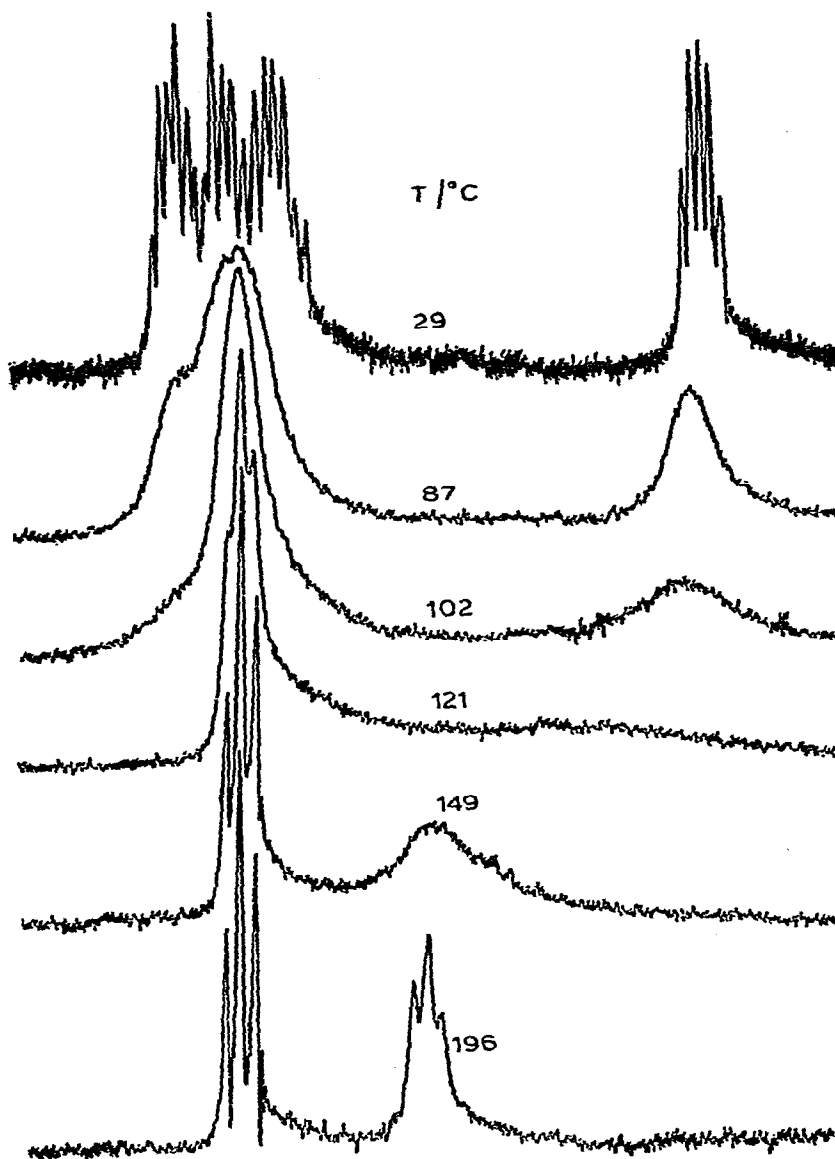


Fig. 2. ^1H NMR spectra of $[(\eta\text{-C}_5\text{H}_4)_2\text{FeS}_3]$ in $\text{d}^5\text{-PhNO}_2$ solution between 29°C and 196°C .

It is of interest to compare this barrier with that for the ring reversal energy in the analogous 1,2,3-trithiacyclohexane (Fig. 1(b), $E = S$). The literature value for this is 55.4 kJmol^{-1} [8], which is *ca.* 25 kJmol^{-1} less than the bridge reversal barrier reported herein. This strikingly large energy difference suggests a reversal

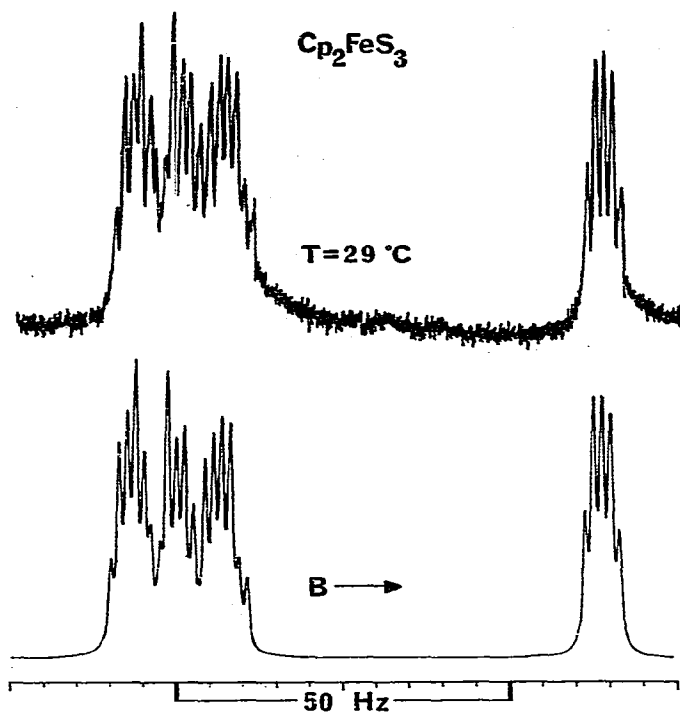


Fig. 3. Comparison of the "static" ^1H NMR spectrum of $[(\eta\text{-C}_5\text{H}_4)_2\text{FeS}_3]$ and the LAOCNR computer simulation

mechanism which involves either significant contributions from processes other than bond rotations and/or largish torsional barriers for the cyclopentadienyl-iron bonds.

We are currently analysing the DNMR spectra of a series of trichalcogen -[3]-ferrocenophanes $[(\eta\text{-C}_5\text{H}_4)_2\text{FeX}_2\text{Y}]$ ($\text{X} = \text{S}$ or Se , $\text{Y} = \text{S}$, Se and Te) [9] and the [3]-ferrocenophanes $[(\eta\text{-C}_5\text{H}_4)_2\text{Fe}(\text{CH}_2)_2\text{X}]$ ($\text{X} = \text{CH}_2$, O , S and Se). Preliminary results indicate a successful 'freezing-out' of the bridge reversal process for the first time in some of these complexes. It is expected that the energy barrier data which we shall obtain for these series, and their relationship to barriers for the corresponding six-membered ring reversals will provide greater insight into the mechanism and factors which govern bridge reversals in [3]-ferrocenophanes.

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