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SYNTHESIS AND BRIDGE REVERSAL BARRIER OF 3,3-BIS(BROMOMETHYL)-1,5-DITHIA[5](1,1')FERROCENOPHANE

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Summary

3,3-Bis(bromomethyl)-1,5-dithia[5](1,1')ferrocenophane has been prepared by the reaction of ferrocene-1,1'-dithiol and pentaerythritol tetrabromide. The bridge reversal barrier and some other spectroscopic features are described.

Introduction

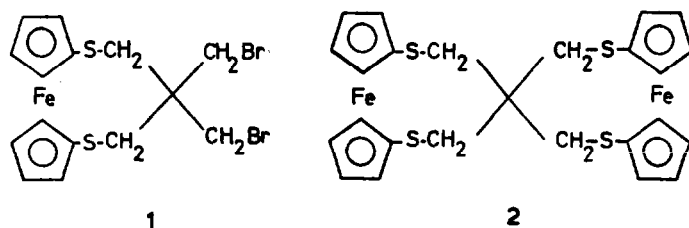
To date [1]- and [3]ferrocenophanes have been the subject of numerous dynamic NMR studies [1–7] while [5]ferrocenophanes have received very little attention [8]. In this paper we report the preparation of, and some spectroscopic data for a new [5]ferrocenophane containing two sulfur atoms in the bridge.

Results and discussion

Although the initial aim of this work was the synthesis of 3,3'-spirobi[1,5-dithia[5](1,1')ferrocenophane] (**2**), we have found that the reaction of ferrocene-1,1'-dithiol with pentaerythritol tetrabromide under conditions of high dilution gave 3,3-bis(bromomethyl)-1,5-dithia[5](1,1')ferrocenophane (**1**) in 12% yield as the only isolable product, together with a significant amount of an insoluble polymeric material. The spiroferrocenophane **2** was either not formed in this reaction (possibly due to steric strain which is induced in **1** after the first cyclization, thus preventing further reaction to produce **2**), or was formed but was not sufficiently soluble in

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typical organic solvents to permit its isolation from the reaction mixture.



The new [5]ferrocenophane **1**, bearing one ferrocene nucleus and two sulfur atoms in the bridge, exhibits some interesting spectroscopic properties (Table 1). Unexpectedly the ^1H NMR coalescent temperature for the ferrocenyl (Cp) and methylene protons (SCH_2) appears to be 25°C . At this temperature the ^1H NMR spectrum of **1** in nitrobenzene- d_5 shows a very broad signal for the CH_2S protons (δ 2.3–2.8 ppm), a sharp singlet for the CH_2Br protons (δ 3.56 ppm), and a broad signal for the Cp protons (δ 4.2–4.5 ppm). At 70°C all signals become singlets, while at -30.5°C a complex spectrum can be observed (Fig. 1). The latter “static” spectrum, which consists of four complex multiplets arising from the Cp protons and two approximate AB quartets, was used for DNMR analysis with spectral parameters extracted by simulation using LAOCOON computer program [9] (Table 2). The cyclopentadienyl protons were treated as an ABCD spin system and both types of methylene protons (CH_2S and CH_2Br) were considered as AB systems. By treatment of the kinetic data thus obtained values of 58.2 kJ mol^{-1} for the bridge reversal barrier ΔG^\ddagger (298 K) and 297.7 sec^{-1} for the rate constant (k_c) of this fluxional process were calculated. Although the conformational freedom of a 5-membered bridge is higher than that of a 3-membered bridge, a rough comparison of the ΔG^\ddagger value obtained for our [5]ferrocenophane (**1**) (total bridge length of 1000 pm) and the value reported [3] for the [3]ferrocenophane, $\text{Cp}_2\text{FeS}_2\text{Te}$ (ΔG^\ddagger 58.9 kJ mol^{-1} , 896 pm of the bridge length) can be made. This rough comparison demonstrates correlation of ΔG^\ddagger values and total bridge length.

The ^{13}C NMR spectrum of **1** obtained at 30°C in nitrobenzene- d_5 , shows two methylene carbon signals at 36.2 ppm (CH_2S) and 37.9 ppm (CH_2Br), two quaternary carbon signals at 47.7 ppm ($\text{BrCH}_2\text{CCH}_2\text{Br}$) and 89.3 ppm (Cp), and an unexpectedly broad signal of the cyclopentadienyl carbons at 69.3 ppm. These cyclopentadienyl carbon signals appear as separate peaks in case of 2-hetera[3](1,1')ferrocenophanes, reported previously [10,11].

TABLE I
THE DEPENDENCE OF ^1H NMR CHEMICAL SHIFTS IN **1** UPON TEMPERATURE

Type of Protons in 1	Chemical Shifts (δ , ppm) ^a	
	25°C	70°C
SCH_2	2.3–2.8, broad singlet	3.35, singlet
BrCH_2	3.56, singlet	3.56, sharp singlet
Cp (CD)	4.20, broad, singlet	4.20, singlet
Cp (AB)	4.2–4.5, broad, singlet	4.40, singlet

^a In nitrobenzene- d_5 from HMDS.

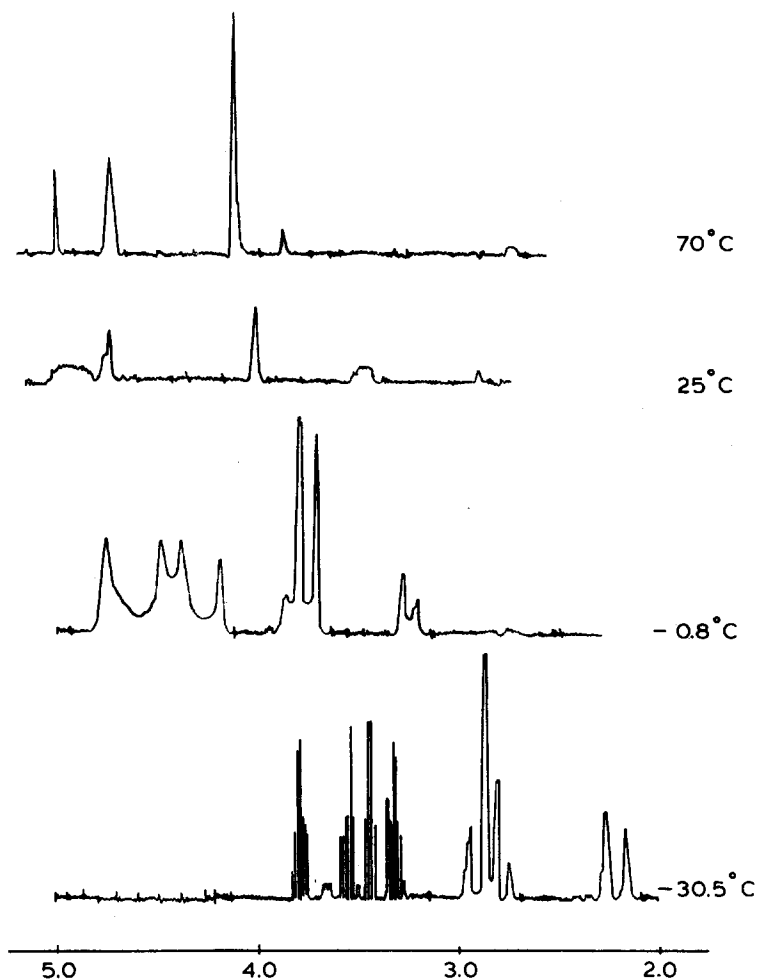


Fig. 1. Variable temperature ^1H NMR spectra of $\text{Cp}_2\text{FeS}_2\text{C}_3(\text{CH}_2\text{Br})_2$.

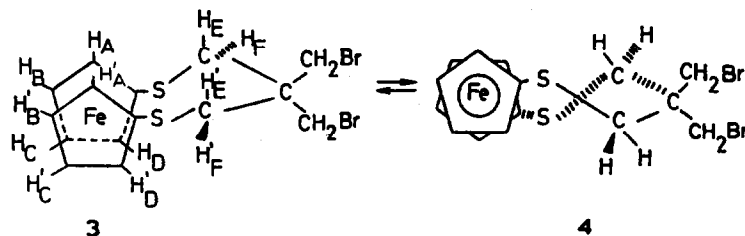
An examination of Dreiding models suggests two possible extreme conformational possibilities 3 and 4. The conformation 3 should be more rigidly constrained due to steric strain and the necessary tilting required for a dynamic change of conformation, while twisted conformation 4 should be capable of the "flipping" involving the three-carbon fragment required in the bridge reversal process. To establish the exact mechanism of the bridge reversal process, which probably

TABLE 2

SPIN-SPIN COUPLING CONSTANTS (Hz) FOR THE CYCLOPENTADIENYL AND METHYLENE HYDROGENS OF 1

$J(\text{AB})$	$J(\text{AC})$	$J(\text{AD})$	$J(\text{BC})$	$J(\text{BD})$	$J(\text{CD})$	$J(\text{EF})$	$J(\text{CH}_2\text{Br})$
1.3	1.3	2.6	2.6	2.6	1.3	13.4	11.0

involves both inversion of the bridge or its carbon fragment and rotation along the Cp-Fe bond, other compounds similar to 1 should be investigated.



The mass spectrum of 1 exhibits a molecular ion peak of m/e 476, which is also the most abundant peak. The peak for m/e 262 in the spectrum may be attributed to the bridged $\text{Cp}_2\text{FeS}_2\text{CH}_2$ ion, although a non-bridged form cannot be excluded. Some examples in the literature indicate that the formation of a bridged form is favoured [12,13]. In analogy, a $\text{Cp}_2\text{FeMe}_2\text{S}$ ion (bridged or non-bridged) was observed by mass spectrometry in the case of dithia[n](1,1')ferrocenophanes [14] and ferrocene paracyclophanes [15].

The IR spectrum of 1 shows a strong CH_2S deformation band at 1419 cm^{-1} and two weak but distinct C-S stretching bands at 635 and 610 cm^{-1} .

Experimental

^1H NMR spectra were recorded at 60 or 200 MHz using JEOL-C-60H and Varian XL-200 spectrometers. ^{13}C NMR spectra were obtained at 50 MHz employing the Varian XL-200 spectrometer. Variable temperature ^1H NMR spectra were examined in nitrobenzene- d_5 , CDCl_3 and $\text{CD}_2\text{Cl}_2/\text{CS}_2$ mixed solvent solutions. The IR spectrum was obtained on a Pye Unicam SP-200 spectrophotometer, and the MS spectrum was measured on an LKB-2021 instrument using a direct inlet system. The temperature measurements were made employing a thermocouple with $\pm 1^\circ\text{C}$ accuracy adopted for use in an NMR tube. Ferrocene-1,1'-dithiol and pentaerythritol tetrabromide were prepared by literature methods [6,16].

Preparation of 3,3'-di(bromomethyl)-1,5-dithia[5](1,1')ferrocenophane (1)

Solutions of ferrocene-1,1'-dithiol (2.00 g, 8.0 mmol) and pentaerythritol tetrabromide (1.60 g, 4.0 mmol) in 35 ml of ethyl alcohol/benzene (4/3) were added simultaneously dropwise during 2 h to vigorously stirred and refluxing ethyl alcohol (200 ml) containing 0.7 g (17.5 mmol) of sodium hydroxide. The reaction was carried out under nitrogen with stirring and reflux for 12 h. Then solvents were evaporated under reduced pressure and dry chromatography on a silica gel column using n-hexane and carbon disulfide as eluents afforded 0.45 g (12%) of an orange amorphous powder. The rest of the reaction product was a polymeric material insoluble in typical organic solvents. M.p. (dec) 215°C , elemental analysis: Found: C, 38.21; H, 3.65. $\text{C}_{15}\text{H}_{16}\text{Br}_2\text{FeS}_2$ (476.07) calcd.: C, 37.94; H, 3.39%. ^1H NMR (δ , CS_2): 3.17 (br s, 4H, CH_2S); 3.40 (s, 4H, CH_2Br); 4.03 and 4.15 ppm (two m, 8H, Fc). ^{13}C NMR (δ , $\text{C}_6\text{D}_5\text{NO}_2$): 36.2 and 37.9 (CH_2S and CH_2Br); 47.7 ($\text{C}(\text{CH}_2\text{Br})$); 69.3 (Cp); 89.3 ppm (Cp-quaternary). MS (m/e): 478 ($M+2$, 57), 477 ($M+1$, 23), 476 (parent ion and base peak), 474 (53), 262 (65), 184 (27), 152 (48), 135 (21), 126

(23), 115 (27), 100 (26), 67 (22), 56 (38), 53 (47), 41 (28), 39 (29). IR (cm^{-1} , KBr): 1419 (CH_2S), 635 and 610 (C-S).

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