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SHORT COMMUNICATION

[1.1]FERROCENOPHANES IN SOLUTION—*ANTI* OR *SYN* ISOMERS?

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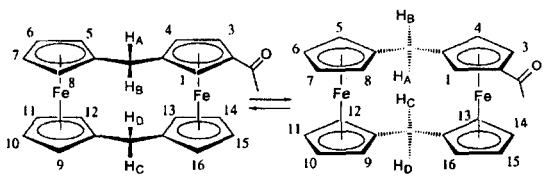
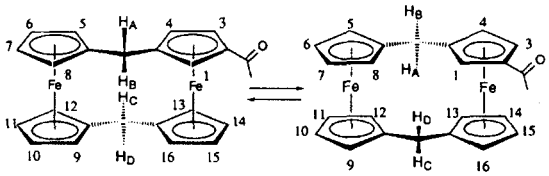
Carbon-bridged [1.1]ferrocenophanes have generally been assumed to have *syn* structures, since *anti* isomers have been considered to be too strained. The recent discovery that such compounds may crystallize as *anti* isomers raises the question of whether the compounds prefer *anti* or *syn* conformations in solution. The synthesis of β-acetyl-[1.1]ferrocenophane (1) and its investigation by ^{1}H,^{1}H-NOESY are reported. Compound 1 was found to be a rapidly equilibrating mixture of *syn* isomers in $CDCl_3$ at 22 °C.

INTRODUCTION

β-Acetyl-[1.1]ferrocenophane(**1**) has been shown, using 2D NMR spectroscopy (^{1}H,^{1}H-NOESY), to be a rapidly equilibrating mixture of *syn* conformers (Scheme 1) rather than *anti* conformers (Scheme 2) in $CDCl_3$ at 22 °C.

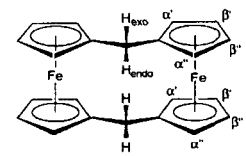


Scheme 1

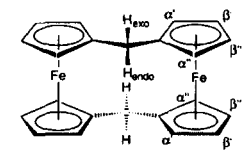


Scheme 2

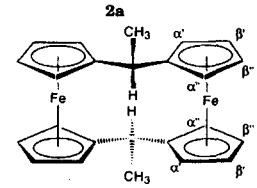
The parent [1.1]ferrocenophane (**2**) and its derivatives have generally been assumed to have *syn* structures (cf. **2a**) rather than *anti* structures (cf. **2b**), since *anti* conformers have been considered to be too strained.[1] However, recently the crystal structure of the first *anti* isomer (**3a**) of a carbon bridged [1.1]ferrocenophane, i.e. of 1,12-dimethyl[1.1]ferrocenophane (**3**) was reported.[2] Besides **3a**, which is an *exo, exo, anti* isomer, two other isomers of **3** have been isolated and characterized, i.e. *exo, exo, syn*-**3** (**3b**)[3] and *exo, endo, syn*-**3** (**3c**).[4]



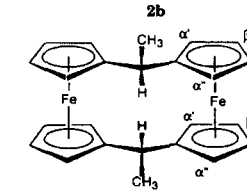
2a



2b



3a



3b

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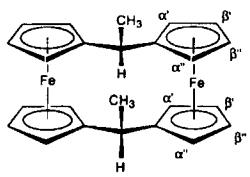
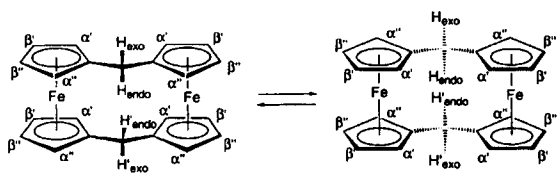


3c

The discovery of these isomers of **3** in the solid state raises questions about the structure of [1.1]ferrocenophanes in general and in particular their structure and dynamics in solution, e.g. are they present as *anti* or *syn* isomers and are these isomers interconverting.

Compound **2**, which crystallizes as *syn* conformers, exhibits an unusually simple ^{1}H NMR spectrum in solution, i.e. only three bands are observed. This has been shown to be due to a fast degenerate rearrangement.[5]



Scheme 3

Assuming a *syn* structure for **2** in the initial state, this rearrangement exchanges the *exo*- and *endo*-methylene hydrogens, α'- and α''-hydrogens and β' and β''-hydrogens, respectively (Scheme 3).

The barrier for this identity reaction has been determined to be 28 ± 4 kJ mol^{-1} and its mechanism has been suggested to be a pseudo-rotation analogous to the twist boat–twist boat interconversion in cyclohexane.[5]

Owing to the apparent symmetry of **2**, it has not been possible to use 2D NMR spectroscopy (NOESY) to determine whether **2** has *anti* or *syn* structure in solution.

RESULTS AND DISCUSSION

With the aim of obtaining a [1.1]ferrocenophane with suitable NMR spectroscopic properties for structure determination, compound **2** was acetylated. Acetylation of **2** has previously been reported to yield both α- and β-acetyl-[1.1]ferrocenophanes.[6] In our hands, only one monoacetylated compound, i.e. the β-isomer was isolated together with a diacetylated [1.1]ferrocenophane.

The ^{1}H,^{1}H-NOESY spectrum of **1** in $CDCl_3$ was obtained at 22 °C. Assigned ^{1}H chemical shifts and observed NOEs are given in Table 1. Obviously the acetyl substitution caused the wanted separation of the NMR signals. At a first glance, the number of the signals suggests the presence of only a single β-isomer. However, the fast degenerate rearrangement of **2** suggests the presence of a similar but non-degenerate rearrangement of **1** (Scheme 1). This is confirmed by

Table 1. Chemical shifts, assignments and observed nuclear overhauser enhancements (NOEs) for β-acetyl-[1.1]ferrocenophane (**1**)[a]

Proton No.	δ/ppm	NOEs of signals from these protons[h]
1	5·05[b]	CH_3, 8, H_A, H_B
3	4·78[c]	CH_3, 4, 14*w*
4	4·70[d]	3, 5, H_A, H_B
5	4·29	4, 6, H_A, H_B
6, 7, 10, 11	4·20[e]	5, 8, 9, 12
8, 9	4·40	1, 7, 10, 16, H_A, H_B, H_C, H_D
12, 14	4·34	CH_3, 3*w*, 4*ω*, 5, 11, 13, 15, H_C, H_D
13	4·25	4*w*, 12, 14, H_C, H_D
15	4·03	CH_3, 1*w*, 3*w*, 14, 16
16	4·53	CH_3, 1*w*, 9, 15, H_C, H_D
H_A, H_B	3·58, 3·53[f]	1, 4, 5, 8, H_C, H_D
H_C, H_D	3·47, 3·40[g]	9, 12, 13, 16, H_A, H_B
CH_3	2·44	1, 3, 14*w*, 15, 16*w*

[a] The ^{1}H was referenced to $CDCl_3$ at δ7·27.
[b] $J_{1,4} = 2{\cdot}0$ Hz, $J_{1,3} = 1{\cdot}5$ Hz.
[c] $J_{3,4} = 2{\cdot}6$ Hz, $J_{1,3} = 1{\cdot}5$ Hz.
[d] $J_{3,4} = 2{\cdot}6$ Hz, $J_{1,4} = 2{\cdot}0$ Hz.
[e] Broad signal.
[f,g] AB quartets, chemical shifts obtained from 1D NMR simulations, $J_{HA,HB} = 18{\cdot}9$ Hz and $J_{HC,HD} = 18{\cdot}9$ Hz.
[h] *w* indicates weak NOEs.

band broadening and band splitting observed for **1** at low temperatures.

The NOEs in Table 1 are fully consistent with **1** being a mixture of rapidly equilibrating β'- and β''-isomers (Scheme 1). Thus H_A and H_B exhibit NOEs with H_1, H_4, H_5 and H_8. The other two methylene protons, H_C and H_D, show NOEs to H_9, H_{12} H_{13} and H_{16}. It has not been possible to make definitive assignment of the signals of the AB spectra of H_A, H_B and H_C,H_D groups, respectively. However, each of the protons in the pair H_A,H_B shows NOE to only one of the protons in the pair H_C,H_D.

The results in Table 1 are not consistent with **1** being an *anti* isomer or equilibrating *anti* isomers (Scheme 2), since H_A and H_B do not show any expected NOE to H_9, H_{12} H_{13} and H_{16}. Furthermore, H_C and H_D do not exhibit any observable NOE to H_1, H_4, H_5 and H_8.

Thus, our conclusion is that **1** under the present conditions consists mainly of *syn* isomers which are rapidly equilibrating, as shown in Scheme 1.

EXPERIMENTAL

Procedure for acetylation of [1.1]ferrocenophane. A modified procedure described by Kansal *et al.*[6] was used. A Perrier complex was prepared from acetyl chloride (33 mg, 0·42 mmol) and a large excess of aluminium chloride (330 mg, 2·5 mmol) in dry methylene chloride (10 cm^3). The mixture was stirred for 0·5 h and the solid material was separated by filtration. The residue was washed with dry methylene chloride (6 cm^3) and the combined filtrates were added dropwise during 0·5 h to a solution of **2** (130 mg, 0.33 mmol) in dry methylene chloride (10 cm^3) at 0 °C. The reaction mixture turned blue–violet and was stirred for another 40 min at room temperature. Then the mixture was washed several times with water. After drying over $MgSO_4$, the solvent was evaporated. The residue was flash chromatographed on silica gel (0·032–0·063 mm) using an eluent consisting of light petroleum (b.p. 40–60 °C) and diethyl ether (2:3, v/v).

The first-eluted compound was starting material then the β-acetyl compound **1** (49 mg, 30%) was eluted before diacetylated [1.1]ferrocenophane (25 mg, 16%). The products were further purified by crystallization from light petroleum (b.p. 40–60 °C). The mass spectrum of **1** showed a molecular peak at m/z 438 (found, 438·0407; calculated for $C_{24}H_{22}Fe_2O$, 438·0369). NMR: δ_H ($CDCl_3$), 5·05 (1H, ring H_1), 4·78 (1H, ring H_3), 4·70 (1H, ring H_4), 4·53 (1H, ring H_{16}) 4·40 (2H, ring H_8, H_9), 4·34 (2H, ring H_{12} H_{14}), 4·29 (1H, ring H_5), 4·25 (1H, ring H_{13}), 4·20 (4H, ring H_6, H_7, H_{10}, H_{11}), 4.03 (1H, ring H_{15}), 3.58 and 3.53 (AB quartet, 2H, methylene bridge- H_A, H_B), 3·47 and 3·40 (AB quartet, 2H, methylene bridge H_C, H_D), 2·44 (3H, CH_3). The mass spectrum of diacetylated [1.1]ferrocenophane showed a molecular peak at m/z 480 found, 480·0381; calculated for $C_{26}H_{24}Fe_2O_2$, 480·0475) NMR: δ_H ($CDCl_3$), 5·12 (2H, ring H), 4·82 (2H, ring H), 4·62 (2H, ring H), 4·57 (2H, ring H), 4·37 (2H, ring H), 4·27 (2H, ring H), 4·07 (2H, ring H), 3·56 and 3·49 (AB quartet, 4H, methylene bridge H), 2·48 (6H, CH_3). The number of signals indicates symmetrically positioned acetyl groups in two different rings in β-positions.

NMR spectroscopy. The spectra were recorded using a Varian Unity 500 instrument operating at 499·92 MHz and equipped with a 5 mm ID500-5 indirect detection probe from Nalorac. Deuteriochloroform (>99·95 atom% ^2H) was used as solvent and ^1H chemical shifts were referenced to $CDCl_3$ ($\delta = 7{\cdot}27$). The spectra were obtained at 22 °C. One-dimensional proton spectra were recorded with standard parameters, and for 1D NMR simulations the Varian VNMR-S program on a SUN platform was used.

The 2D NMR spectra were acquired using non-spinning 5 mm samples with deuterium field-frequency locking. For the ^1H,^1H- NOESY spectra the following parameters were used: spectral width, 4711·4 Hz (f_2) and 4711·4 Hz (f_1); 256 increments and 16 scans per increment in t_1; one-time zero filling in f_1 and f_2; mixing times, 0·8, 1·6 and 3·0 s. Spectra were processed in the phase- sensitive mode with shifted square sine-bell weighting in both f_1 and f_2.

Mass-spectrometry. All mass-spectra were recorded on a high-resolution Zab Spec FPD instrument from VG Instruments (electron impact ionization, 70 eV).

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