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CONFORMATIONAL INTERCONVERSION OF [1.1]FERROCENOPHANE: A MOLECULAR MECHANICS STUDY

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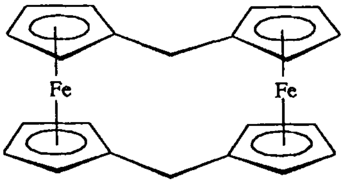
A molecular mechanics scheme developed for bridged ferrocene derivatives was applied to study the conformational energy surface of [1.1]ferrocenophane (1). The mechanism of the intramolecular interconversion of 1 is shown to be different from the mechanism of the *syn–syn* exchange proposed earlier for this 'molecular acrobat.'

INTRODUCTION

In [1.1]Ferrocenophane (**1**), two methylene bridges connect a pair of quasi-coplanar cyclopentadienyl rings of two different ferrocene units. Intuitively, such a system may exist in two forms: *syn* (**1a**) and *anti* (**1d**). Conformational features of **1** have been investigated by means of NMR spectroscopy[1,2] and, owing to its high flexibility on the NMR time scale, **1** was called a 'molecular gymnast'.[3] This flexibility was attributed to the low energy barrier of *syn–syn* exchange. A mechanism for this interconversion process between two *syn* conformations has been proposed by Mueller-Westerhoff[2] and it will be reviewed here, in terms of molecular mechanics calculations.

X-ray crystallographic studies of **1** revealed that the molecule exists in a *syn* conformation in the crystal.[4] The ferrocene units are skewed by about 13° to alleviate the steric repulsion. The space group is $P2_1/c$ with two enantiomorphous forms in the centrosymmetric lattice. The conformation in the crystal has nearly C_2 symmetry. These crystallographic facts and the NMR observations would indicate that the molecule exists practically as a *syn* C_2 enantiomeric pair, and that the *anti* conformer is higher in energy than the *syn* form.

In the course of our computational investigation of [4]superferrocenophane,[5] we have presented a molecular mechanics model which allows the computational interpretation of stereodynamics in some mononuclear ferrocenophanes.[6] In this paper, we describe the application of this model to binuclear [1.1]ferrocenophane (**1**) in order to gain more insight into its conformational behaviour.



[1.1]Ferrocenophane (**1**)

COMPUTATIONAL TECHNIQUE

Calculations were performed with the program BIGSTRN3,[7] incorporating changes due to the modified force field.[6] The technique and methodology used to locate, correlate and describe critical points on the potential energy surface have been described.[6]

CONFORMATIONAL ENERGY SURFACE

A search for stationary points on the MM2′[8] conformational energy surface of **1** located three energy

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minima, which could be correlated by means of three saddle points to form a closed circle. The surface is represented pictorially in Figure 1. ORTEP drawings of the conformations corresponding to unique stationary points on this energy surface are given in Figure 2, wherein structures are arranged in non-alphabetic order in order to help visualize structural changes between neighbouring stationary points on the surface. Structural and energetic features of the stationary points are summarized in Tables 1 and 2, respectively.

The global energy minimum (*syn* form) possesses C_2 symmetry and it appears as an enantiomeric pair, **1a** and **1a**′. The structure resembles that observed in the crystal, but there are some discrepancies (Table 1). The relative skew angle of two ferrocene units in **1a** is 34·4° whereas in the crystal it is only 13·3°. The relative twist angles of the cyclopentadienyl rings are also different: 25·7° calculated versus 9° observed, as these two structural parameters are interdependent. The calculated relative tilt angle of cyclopentadienyl planes within ferrocene moiety in **1a** (3·4°) is close to the observed value (2·7°). The calculated iron–iron distance in **1a** is smaller than that observed in the crystal by 0·17 Å. One would be tempted to attribute these discrepancies to the drawbacks in the force field applied, in particular to the iron–iron non-bonded parameters, since the force field was designed for mononuclear complexes and iron–iron distances were not included in the parameterization of the force field. It seems more likely, however, that the conformation of **1** in the crystal indeed differs to some extent from the conformation of an isolated molecule due to the packing force. When **1a** was reoptimized with the dihedral angles along the bridges fixed at their x-ray values, the relative skew, twist and tilt angles and the intramolecular distances were reproduced almost exactly (Table 1). In this fixed conformation the iron–iron distance differs from the crystal value only by 0·04 Å.

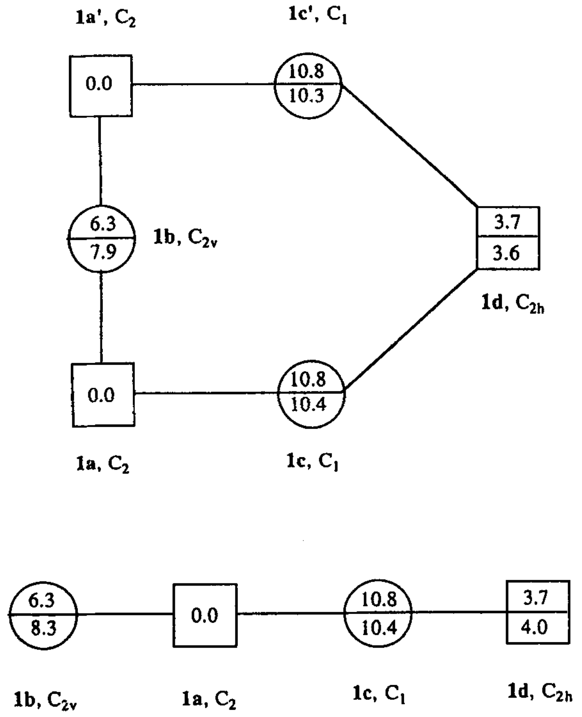

Figure 1. Conformational interconversion of [1.1]ferrocenophane (**1**). Squares and circles denote minima and saddle points, respectively. Relative potential energies (top) and free energies (bottom) of corresponding conformations are given inside squares and circles (compare with Table 1). The bottom graph represents a reduced surface wherein enantiomers are treated as indistinguishable species

The C_2 enantiomers, **1a** and **1a**′, interconvert into each other via a C_{2v} transition state **1b**, which is 6·29 kcal mol^{-1} (1 kcal = 4·184 kJ) higher in potential energy than the global minima (Figure 1). In this process, the 'inner' and 'outer' protons of the methylene bridges remain 'inner' and 'outer', respectively. The interconversion, in which the 'inner' protons become 'outer' and vice versa, is the path involving the *anti* intermediate conformer **1d**. The transition state **1c** connecting **1a** and **1d** minima possesses C_1 symmetry and is 10·81 kcal mol^{-1} higher in potential energy than **1a**. Conformer **1c** resembles that proposed by Mueller-Westerhoff[2] as a transition state for the *syn–syn* exchange. Nevertheless, in **1c** only one bridge undergoes flipping, whereas in the process proposed by Mueller-Westerhoff both bridges flip simultaneously. The skew angle of ferrocene units in **1c** is 62·8° (cross angle of two arrows in Figure 3).

The top part of Figure 1 might appear sufficient to represent the energy surface of **1**, where enantiomers are distinguishable species and homomeric forms of any stationary point are shown by single points. Although such a scheme is sufficient to understand conformational changes of a molecule, it does not always reflect the complexity of a surface. The surface of **1** is such a case. Thus, the same surface in the form of a 'full graph', where all enantiomeric and homomeric forms of each stationary point are indicated as distinguishable species, is shown in Figure 4. This detailed graph shows how labyrinthine and degenerate the conformational interconversion processes can be for a molecular system such as **1**.

There are two extra points, **1e** and **1e**′, in Figure 4, which did not appear in Figure 1. These D_2 enantiomeric forms are two-dimensional partial maxima corresponding to the would-be transition state of *syn–syn* exchange proposed by Mueller-Westerhoff.[2] The dashed line correlating two **1a** points via **1e** shows the would-be process in which both methylene bridges flip simultaneously, the 'inner' protons becoming 'outer' and vice versa. In such a process, however, **1a** would interconvert into itself. Strictly, it would be a reaction path between permutational isomers of the **1a** conformer. The fact that the earlier proposed process[2] involves the structure which appears on MM2′ energy surface as two-dimensional partial maximum, much higher in energy than the saddle points **1b**, **1c** and **1c′**, makes the Mueller-Westerhoff mechanism unlikely for the *syn*–*syn* exchange.

The bottom part of Figure 1 shows the reduced energy surface wherein even enantiomers appear as indistinguishable species. The free energies appearing therein are the final energies, which can be compared with the observed values.

The *anti* form (**1d**) is nearly 4 kcal mol^{-1} higher in energy than the *syn* form (**1a** and **1a′**). Hence, in the equilibrium at room temperature, **1** should exist practically in the *syn* form, as a racemic mixture of the two chiral species. The relative free energy of **1c** is only 2 kcal mol^{-1} higher than that of **1b**. On the potential energy scale, **1c** is only 4·5 kcal mol^{-1} higher than **1b**. However, the absolute values for barrier heights

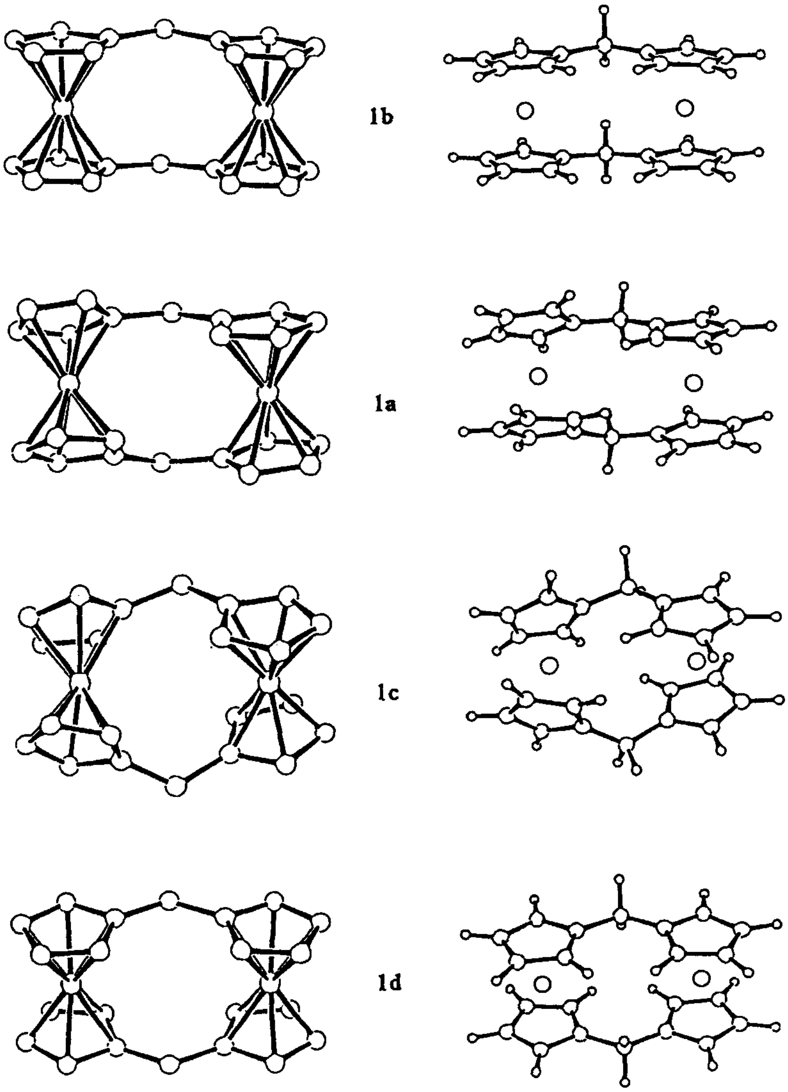

Figure 2. ORTEP drawings of conformations corresponding to the stationary points on the MM2′ energy surface of **1**. On the left-hand side drawings hydrogen atoms are omitted and on the right-hand side Fe—C bonds are omitted for clarity

Table 1. Salient MM2′-calculated and observed structural features of [1.1]ferrocenophane[a]

	1b	**1a**	X-ray[b]	**1a**[c]	**1c**	**1d**	**1e**
Point group	C_{2v}	C_2	C_1[d]	C_1[d]	C_1	C_{2h}	D_2
Skew[e]	0·0	34·4	13·3	16·2	62·8	0·0	65·5
Twist[f]	0·0	−25·7	−9·0[g]	−12·0[g]	(−73·0, −37·5)	(−46·2, 46·2)	−58·5
Tilt	3·2	3·4	2·7[g]	3·9[g]	(6·8, 15·5)	0·8	11·9
Bridge 1[h]	9·4	34·0	23·1	23·1	123·5	178·4	123·5
	−9·4	3·9	−7·2	−7·2	−69·4	−178·4	−67·1
Bridge 2	−9·4	3·9	−8·9	−8·9	−17·1	−2·8	−67·1
	9·4	34·0	24·2	24·2	75·5	2·8	123·5
$C_r{-}C_\alpha{-}C_r$	123·7	120·1	121·5[g]	122·7[g]	(125·0, 120·7)	123·8	125·0
D[i]	3·295	3·287	3·283[g]	3·290[g]	(3·296, 3·338)	3·279	3·309
$C_r{-}C_r$[j]	1·431	1·431	1·430	1·431	1·429	1·432	1·429
$C_r{-}C_\alpha$	1·502	1·500	1·494	1·500	(1·496, 1·498)	1·501	1·497
		1·501	1·509	1·501	(1·490, 1·503)		
Fe−Fe[k]	4·849	4·645	4·815	4·778	4·396	4·898	4·386

[a] Distances in Å, angles in degrees.
[b] Ref. 4.
[c] Optimized with fixed dihedral angles along the bridges at x-ray values.
[d] Nearly C_2 symmetry.
[e] Relative skew angle of two ferrocene units.
[f] Twist angle between cyclopentadienyl rings in ferrocene units.
[g] Average of two values.
[h] Dihedral angles along the bridges.
[i] Inter-ring distances in ferrocene units.
[j] Average C—C distance within cyclopentadienyl rings.
[k] Iron–iron distance.

Table 2. Total steric energy and other energetic features of MM2′-calculated conformations of [1.1]ferrocenophane[a]

	1b	**1a**	**1a**[b]	**1c**	**1d**	**1e**
Total steric energy	20·67	14·38	19·17	25·19	18·12	26·94
SE[c]	6·29	0·00		10·81	3·74	12·56
ν[d]	48·7i (C_2) 122·4 (C_s)	52·8 (C_2)		47·0i (C_1) 40·2 (C_1)	23·0 (C_2)	43·8i (C_2) 19·9i (C_2) 78·4 (D_2)
ΔG[e]	8·30	0·00		10·35	3·98	14·50

[a] Energies in kcal mol^{-1}.
[b] Optimized with fixed dihedral angles along the bridges at x-ray values.
[c] Relative steric energy.
[d] Imaginary (i) (saddle points and partial maxima only) and lowest real vibrational frequency (cm^{-1}). Symmetries of modes are given in parentheses.
[e] Relative free energies at 298 K. Compare with conformational energy surfaces in Figure 1.

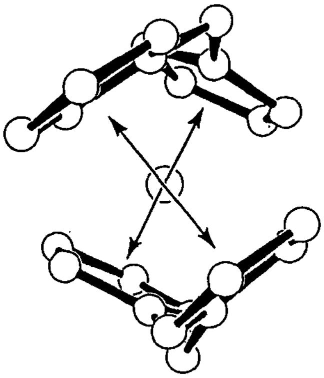

Figure 3. Side view of **1c**. The relative skew angle of the two ferrocene units is 62·8°

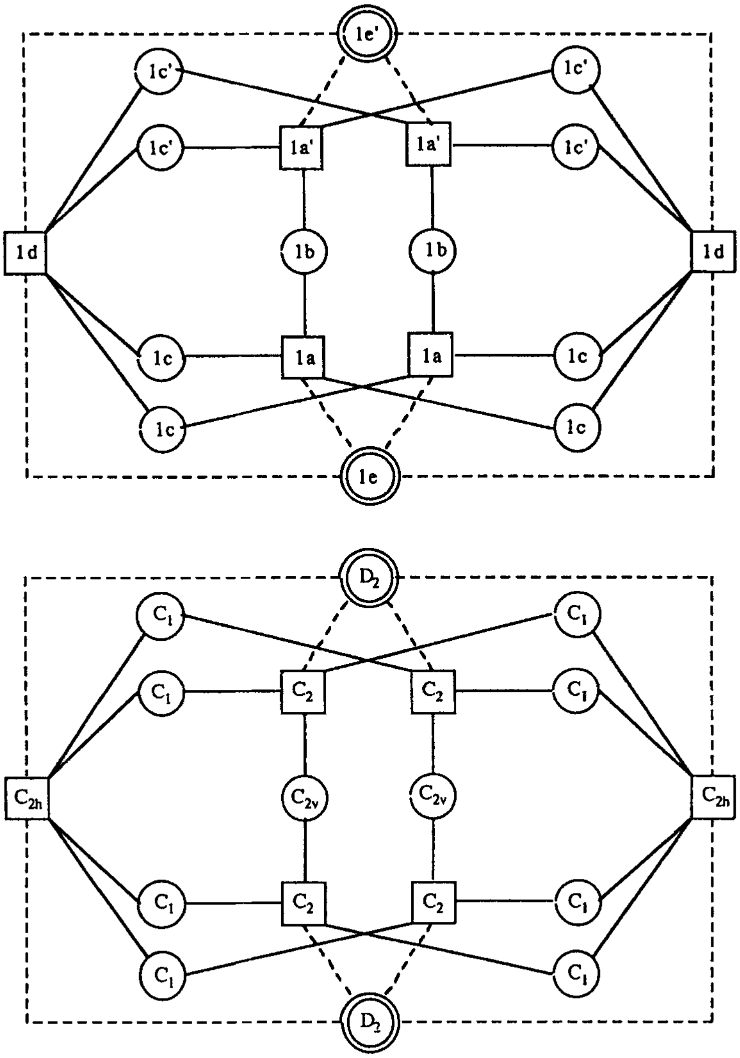

Figure 4. Graphs of conformational interconversion of **1**. Squares, circles, and double circles denote minima, saddle points and two-dimensional partial maxima, respectively. Enantiomers and all permutational isomers of each stationary point are treated as distinguishable species. Entries inside squares and circles in the top and bottom graphs denote stationary points (compare with Figure 1) and molecular symmetries, respectively

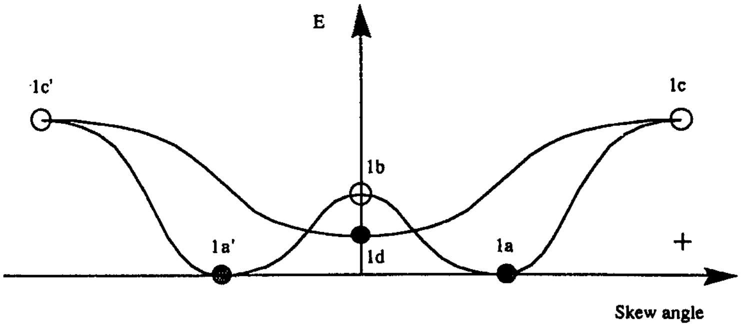

Figure 5. Conformational energy surface of **1** where the relative skew angle of the two ferrocene units was chosen as a reaction coordinate

(8·3 kcal mol^{-1} for **1b** and 10·35 kcal mol^{-1} for **1c**) are higher than those expected from NMR studies.[1,2]

The conformational energy surface of **1** can also be illustrated in another form wherein the relative skew angle of two ferrocene units serves as the reaction coordinate. Figure 5 shows such a surface which allows changes in energy with changes in the skew angle to be traced. This illustration shows how well the molecule deserves to be named a 'molecular acrobat.'[3]

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