Molecular-mechanics study of oligomeric models for poly(ferrocenylsilanes) using the ESFF forcefield

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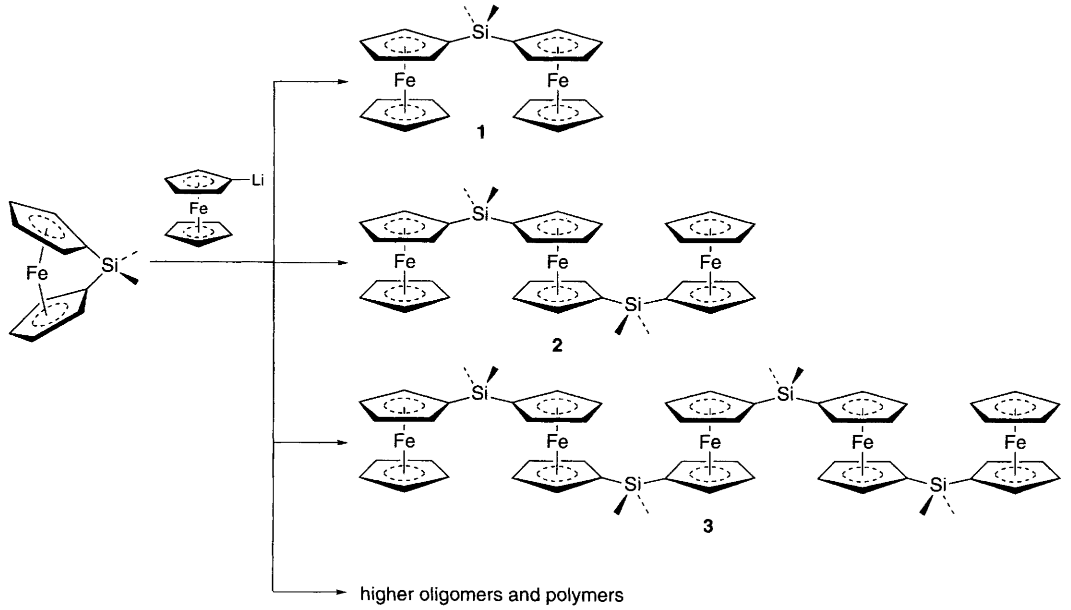
Molecular mechanics has been employed using the new generalised ESFF forcefield to study the conformations of the oligomeric metallocene species Fc[Fe$(C_5H_4)_2$SiMe$_2$]$_n$H [Fc = Fe(η-C_5H_5)(η-C_5H_4); *n* = 1 1, 2 2 or 4 3]; the calculations show that the isolated neutral molecules are conformationally flexible with the lowest energy configurations having close contacts between the positively charged iron atoms of the ferrocene units and the negatively charged cyclopentadienyl rings of their neighbours; the lowest energy conformations in the solid state are predicted to be very different due to the possibility of intermolecular iron···cyclopentadienyl contacts which is in excellent agreement with the crystal structure determinations.

Since the first thermal ring-opening polymerisation reactions of [1]silaferrocenophanes were reported in 1992,[1] high-molecular mass poly(ferrocenylsilanes) have attracted considerable interest as rare examples of polymers incorporating transition metals in the backbone.[2] The properties of the polymers may be varied by altering the substituents on the silicon bridge,[3–5] and by varying the degree of methylation of the cyclopentadienyl rings.[6] Poly(ferrocenylsilanes) are of interest due to their potentially interesting optical, electronic and magnetic behaviour. Doped materials have so far shown low conductivities, but modification of the bridging groups is anticipated to offer possible routes to electronically delocalised materials.[2] The reaction of low-molecular mass poly(ferrocenylsilanes) and tetracyanoethylene has been reported to yield a ferromagnetic material.[7] In addition, pyrolysis of certain poly(ferrocenylsilanes) has yielded novel iron–silicon–carbon ceramics.[8,9]

It is clear that metal–containing polymers will become increasingly important in many technological applications due to their multifunctional characteristics. Therefore it is vital that we develop the ability to understand and predict the physical and electronic properties of these materials both in solution and in the condensed phase. For example, it has already been demonstrated that the rheological properties, such as the glass-transition temperature (T_g), depend upon the nature of the substituents on the silicon bridges.[3,4] These materials also exhibit cooperative electronic interactions between the iron centres; in solution they all exhibit multiple reversible redox events, the degree of interaction between the iron centres varying with the nature of the substituents on the silicon bridge. Two possible explanations for this variation have been proposed: different inductive effects on the electronic structure of the bridge of different substituents, or differing Fe···Fe separations owing to different conformations of the polymers in solution.[10] Knowledge of the preferred conformations of both neutral and oxidised polymers may shed light on this problem. Recently short-chain oligomers have been studied as models for the conformational and electrochemical behaviour of high-molecular mass polyferrocenylsilane polymers. These can be prepared by the reaction of lithioferrocene and Fe(η-$C_5H_4)_2$SiMe$_2$ and typically yield oligomers comprising between two and eight ferrocene units bridged by SiMe$_2$ groups depending on the precise reaction conditions (Scheme 1).[11] The crystal structures of **2**[12,13] and **3**[11] have been determined.

In this communication we describe the application of the new ESFF (Extensible Systematic ForceField)[14,15] forcefield from Biosym Technologies to investigate the conformational space of these low-molecular mass oligoferrocensilanes both in solution and in the solid state, with the view to developing good



Scheme 1 Anionic polymerisation of a 1-[sila]ferrocenophane

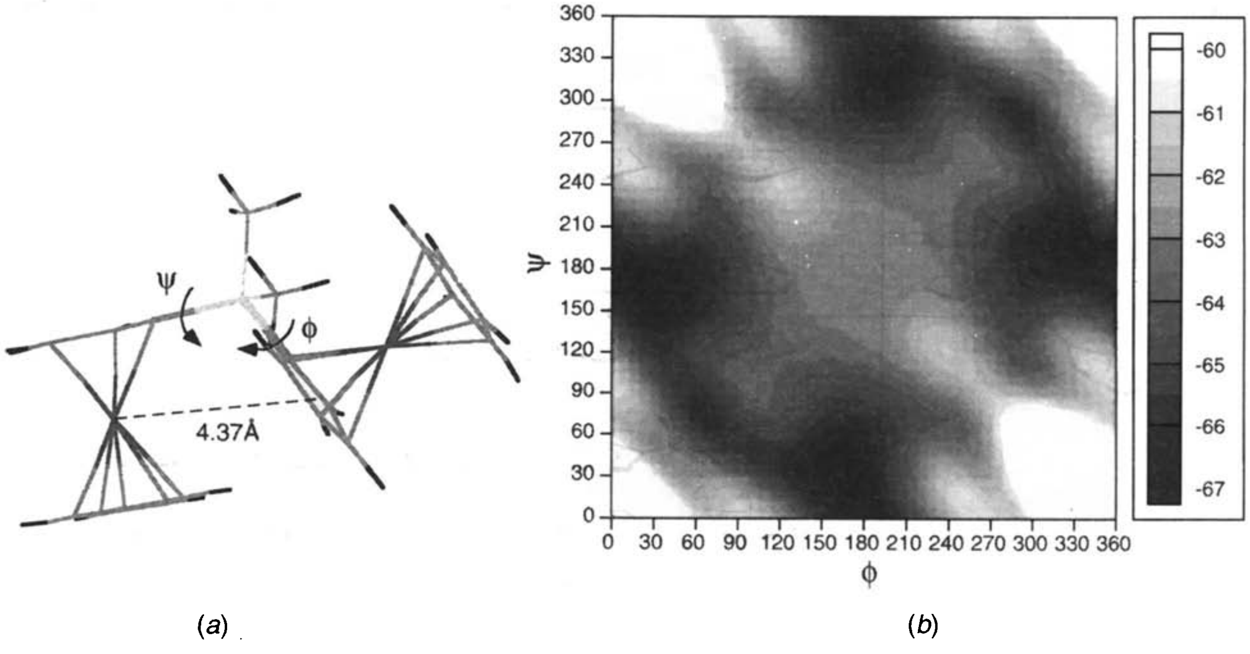
theoretical models for the higher molecular mass polymers. This forcefield has used an innovative approach to generating potential parameter sets. This approach relies on a minimal set of atomic parameters which is used to generate a much larger set of potential parameters through a series of empirical rules. The atomic parameters used to generate the potential parameters were determined by a procedure which involved density functional theory (DFT) calculations, fitting experimental data, and fitting crystal structures and their properties. The basic DFT calculated parameters are electronegativity, hardness and ionization potential. These parameters were determined for each atom type based on the hybridization of atoms and the distribution of valence electrons in the hybridized orbitals. Having calculated these basic atomic parameters, the non-bonded atomic parameters were generated by fitting the crystal lattice constants and their available properties (*e.g.* sublimation energies) with rigid molecular entities. The atomic force constant parameters were produced by fitting the available data for bond dissociation energies, spectroscopic data, and force-constant data. Remaining atomic reference parameters for bonds and angles were then optimized by minimizing the force on each atoms at a range of experimental crystal structures, selected for their varied bonding chemistries.

We began our study by investigating the conformational preferences of the isolated neutral ferrocenylsilanes **1**–**3**. We initially studied **1**, since its conformations are fully defined by only two torsion angles, ϕ and ψ [Fig. 1(*a*)]. Thus the entire range of conformers can be depicted in a single plot of ϕ *vs.* ψ [Fig. 1(*b*)] and the global minimum assigned unambiguously. The two-dimensional energy surface for **1** was obtained by varying ϕ and ψ in 10° increments from 0 to 360° and minimising the structure at each step with ϕ and ψ restrained. The high symmetry of the plot results from the indistinguishability of the two ferrocenes comprising the molecule, *i.e.* conformer ϕ/ψ is equivalent to ψ/ϕ. Furthermore, conformers ϕ/ψ and $-\phi - \psi$ are mirror images of one another and thus have the same energy. The four equi-energy minima in this plot correspond to $\phi = 35.7°$ and $\psi = 162.0°$; this arrangement allows close contact between the negatively charged substituted ring of one ferrocene and the iron atom of the other as shown in Fig. 1(*a*). For **2** and **3**, the global minima could not be defined on a simple energy surface as for **1**; instead they were found by sampling a wide range of conformational space by molecular dynamics. The molecule was 'heated' to 900 K for 5000 picoseconds to produce an essentially random conformation. The energy of the molecule was then minimised from this random starting point with no restraints. The procedure was repeated 100 times for **2** and 300 times for **3**.

A major finding from all these calculations is that the conformations of the isolated neutral molecules **1**–**3** are principally determined by the electrostatic attraction between the positively charged iron atoms of the ferrocene units and the negatively charged cyclopentadienyl rings of their neighbours. The atomic charges, which are centred on the atomic positions, are listed in Table 1. These interactions cause the molecules to curl up on themselves which leads to quite short interactions not only between the cyclopentadienyl rings and neighbouring Fe atoms but also between end members. These lowest energy conformations could possibly account for the interactions between the Fe centres observed in the electrochemical experiments.

However, the conformations observed in the experimental crystal structures of **2** and **3** do not correspond to the global minima we have found for the isolated molecules. We have therefore examined the crystal structures in more detail. Firstly, full relaxation of the atomic coordinates and cell parameters of the structures of **2** and **3** were performed with the same potentials used in the isolated conformer calculations and the calculated cell parameters are summarised in Table 2. For **2**, the root mean square deviation (rmsd) between the crystallographic and calculated bond lengths (of which there are 68 excluding bonds to hydrogen) is 0.08 Å. For the bond angles (of which there are 249) the rmsd is 5.8° which falls to 2.0° if the C–Fe–C angles are excluded (as these angles are extremely sensitive to the relative rotation of the rings which are better described in terms of torsional angles). For the torsional angles, only the ϕ, ψ and the ring-twist angles were calculated (seven in total) and found to have a rmsd of 16.5°. Similar results were obtained for **3**. Thus agreement between experiment and calculations is very good, especially considering that the potentials have not been fitted in any way to structures of this type.

The crystal structures of both **2** and **3** can be viewed in terms of layers. A layer of **3** is illustrated in Fig. 2 and shows that many close *inter*molecular iron···cyclopentadienyl approaches are present. The twist of each terminal group allows close approach of its iron atom to the rings of two chain ferrocenes in



(*a*) (*b*)

Fig. 1 (*a*) Definition of the torsion angles ϕ and ψ and (*b*) plot of energy (kcal mol^{-1}) as a function of ϕ and ψ for conformations of **1** (cal = 4.184 J). Note that the four equi-energy minima in (*b*) all correspond to the conformation in (*a*).

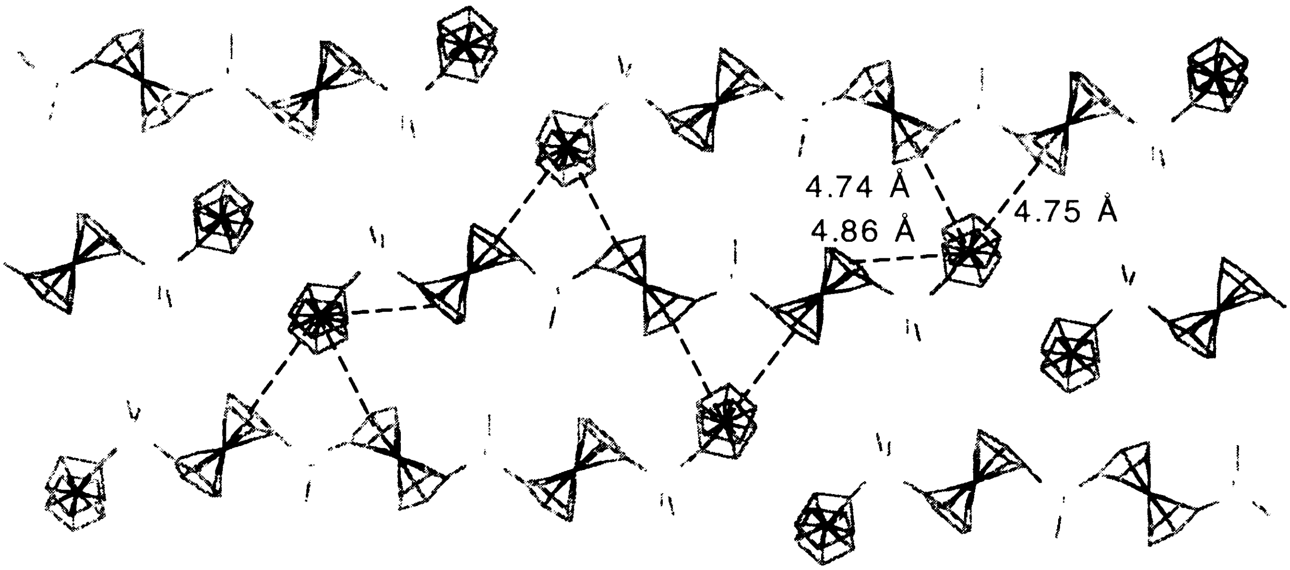


Fig. 2 A view of the crystal structure of **3** showing a layer of molecules and the close iron···cyclopentadienyl approaches around one of them

Table 1 Partial atomic charges used in the calculations

Atom[a]	Charge	Atom[a]	Charge
Fe	1.250	C_5H_4Si(3,4-C)	−0.180
Si	−0.182	Me(C)	−0.023
C_5H_5(C)	−0.180	C_5H_4/C_5H_5(H)	0.055
C_5H_4Si(1-C)	−0.083	Me(H)	0.030
C_5H_4Si(2,5-C)	−0.189		

[a] Atoms in parentheses are the particular atoms in the fragment which the values relate to.

Table 2 Calculated and experimental lattice constants of **2** and **3**

	2		**3**	
Parameter	Exptl.[12,13]	Calc.	Exptl.[11]	Calc.
a/Å	10.084	10.051	11.764	11.732
b/Å	14.958	14.835	11.85	12.016
c/Å	11.175	10.658	12.514	11.781
α/°	90	90.000	94.85	93.86
β/°	114.98	112.71	114.15	118.03
γ/°	90	90.000	117.66	114.23

an adjacent molecule. Since **3** has an odd number of ferrocene moieties, the terminal groups are oriented in opposite directions, allowing each molecule to have close iron···cyclopentadienyl approaches to two neighbours. Such good intermolecular interactions would not be possible for an even number of ferrocenes as the terminal ferrocenes would have the same orientation and therefore only be able to have close iron···cyclopentadienyl contacts with one neighbour. Interestingly, although the tetramer, hexamer and octamer have been isolated,[11] no crystal structures have yet been reported. Furthermore, in **2** it is not possible for the terminal groups to adopt this arrangement as each molecule has only one chain ferrocene; thus the terminal ferrocenes twist differently to allow favourable interactions with four neighbouring ferrocenes. Powder X-ray diffraction studies of **3** show a dominant peak at a *d*-spacing, indexed as the (011) reflection, corresponding to diffraction from the layers of molecules depicted in Fig. 2. The principal feature in the diffraction pattern of the polymer, $[Fe(C_5H_4)_2SiMe_2]_n$, is a broad peak centred around the same *d*-spacing.[5,16] This has been interpreted as evidence that the structures of the polymer and the pentamer are related.[16] Our calculations suggest that polymer molecules could adopt a similar layer structure to **3**, by some of the chain ferrocenes twisting approximately perpendicular to the layers in a similar fashion to the terminal ferrocenes of **3**. This would allow close iron···cyclopentadienyl interactions between adjacent polymer chains within a layer. The arrangement in the pentamer suggests that the polymer structure where every fifth ferrocene is twisted approximately perpendicular to the plane would allow a particularly good network of favourable iron···cyclopentadienyl interactions. Similarly, we would expect the nonameric species to crystallise into a layer structure with the first, fifth and ninth ferrocenes twisted perpendicular to the plane of the layer.

The ESFF forcefield has been shown to be a useful method for understanding and predicting the conformations of organometallic complexes both in the gas phase and in the solid state. The potentials are generated from atomistic parameters and appear to be readily transferable to organometallic complexes. The conformations of neutral oligo(ferrocenyl)-silanes are principally determined by iron···cyclopentadienyl electrostatic interactions. The possibility of intermolecular iron···cyclopentadienyl attractions in the solid state leads to different conformations being found in the crystal structures to those predicted for isolated molecules.

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