

The Effect of Bending Modes on the Intramolecular Electron-transfer Rates of Mixed-valence 1',3',1''',3'''-Tetraethyl- and 1',2',1''',2'''-Tetraethyl-biferrocenium Triiodides

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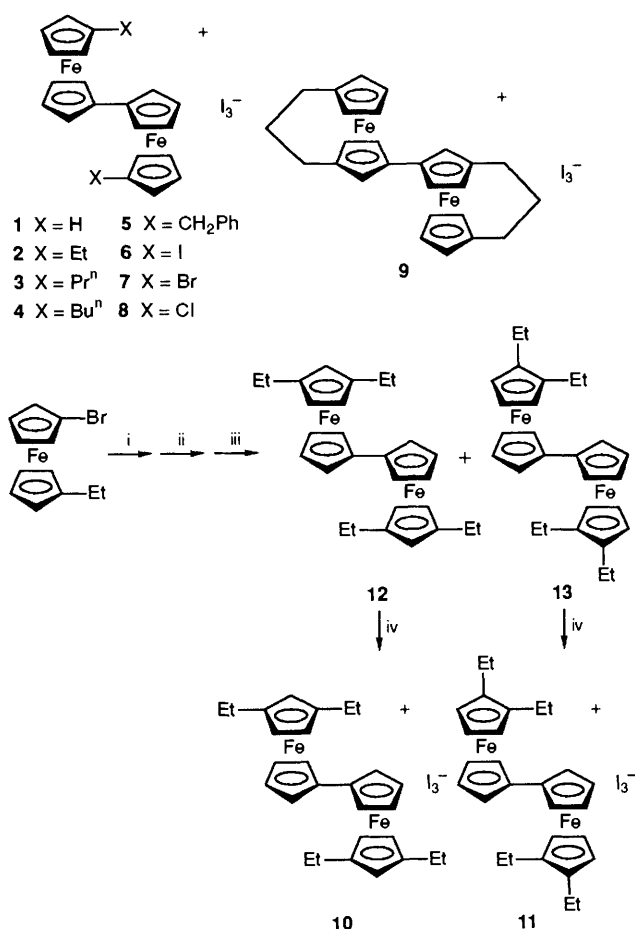
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The results of an X-ray structure determination of 1',3',1''',3'''-tetraethylbiferrocenium triiodide, the effects of changing the relative positions of ethyl substituents from 1',3',1''',3''' to 1',2',1''',2''' on the intramolecular electron-transfer rates of biferrocenium salts in the solid state, and a theoretical explanation of the influence of steric factors on the electron-transfer rates are reported.

The study of intramolecular electron transfer in mixed-valence complexes has enabled systematic and creative investigations to be carried out into the factors that affect rates of electron transfer in solution redox processes, solid-state materials, and biological electron-transport chains.¹⁻⁴ In the case of mixed-valence biferrocenium triiodide salts **1-8** (Scheme 1), considerable progress has been made in understanding the effects of the solid-state environment on the rate of electron transfer.⁵⁻¹¹ A recent interesting finding is that there is a significant influence on the electron-transfer rate in the mixed-valence biferrocenium salt **9** when the cyclopentadienyl (Cp) rings in each ferrocenyl moiety are linked by an interannular bridge.¹² Such a structural modification of the parallel relation between the two Cp rings around the Fe ion would lead to greater metal-ligand interactions as the rings tilt. To study why the substituents on the Cp rings of **1-8** and the tilting of the Cp rings in **9** play a significant role in the electron transfer, we have prepared the two new constitu-

tional isomers **10** and **11** in which the relative positions of the ethyl substituents are changed (Scheme 1), and determined the crystal structure of **10**.[†] We now show that there is a dramatic difference in electron-transfer rates between **10** and **11**. Furthermore, we have performed extended Hückel MO calculations on biferrocenium triiodide **1** for different dihedral angles between the two Cp rings to elucidate the geometric effect on the rate of intramolecular electron transfer in mixed-valence biferrocenium cations.

[†] All new compounds gave satisfactory spectroscopic and analytical data. *Selected physical data:* **12**, m.p. 46.7-47.5 °C; M⁺, *m/z* 482; ¹H NMR (200 MHz, CDCl₃) δ 1.03 (t, 12H, CH₃), 2.11 (q, 8H, CH₂), 3.73 (s, 6H, Cp), 4.05 (t, 4H, fulvalenide) and 4.14 (t, 4H, fulvalenide). **13**, m.p. 75.3-76.4 °C; M⁺, *m/z* 482; ¹H NMR (200 MHz, CDCl₃) δ 1.01 (t, 12H, CH₃), 2.08 (q, 8H, CH₂), 3.77 (d, 2H, Cp), 3.82 (d, 4H, Cp), 4.07 (d, 4H, fulvalenide) and 4.11 (d, 4H, fulvalenide).



Scheme 1 Reagents and conditions: i, AcCl, AlCl₃; ii, LiAlH₄, AlCl₃; iii, activated Cu; iv, I₂

As shown in Fig. 1, the mixed-valence cation **10** is located at a centre of symmetry with a centroid-to-centroid distance of 3.345(8) Å for each metallocene.† The Cp rings are not perfectly eclipsed, with an average staggering angle of 3.6(1)°, and the Fe–C distances range from 2.03(1) to 2.11(1) Å. The spread of distances arises because the Cp rings are not parallel; the angle between the two least-squares Cp rings of the ferrocenyl moiety is 5.9(7)°. The tilt angle in **2** is 4.7°.¹³ The average of these Fe–C distances, *i.e.*, 2.06(1) Å, lies midway between the 2.045 Å observed for ferrocene¹⁴ and the 2.075 Å observed for the ferrocenium cation.¹⁵ The I–I distance in the centrosymmetric I₃⁻ ion is 2.914(1) Å which is in accord with the accepted value of 2.92 Å proposed for the free I₃⁻ ion.¹⁶ The single-crystal X-ray determination of the structure of **10** indicates that this mixed-valence cation has a delocalized electronic state. This is also consistent with our Mössbauer results.

† Crystal data for **10**: C₂₈H₃₄Fe₂I₃, *M* = 862.98, triclinic, space group, *P*1̄, *a* = 8.457(2), *b* = 9.027(2), *c* = 10.918(1) Å, α = 105.78(1), β = 101.61(1), γ = 106.30(2)°, *U* = 734.3(2) Å³, *F*(000) = 413, *D*_c = 1.952 g cm⁻³, *Z* = 1, μ = 4.12 mm⁻¹, λ(Mo-Kα) = 0.70930 Å, *R* = 0.042, *R*_w = 0.042. Intensity data were collected to a 2θ limit of 44.9° on a Nonius CAD-4 diffractometer and corrected for absorption effects. Of the 2072 independent intensities, there were 999 with *F*_o² > 2.0 σ(*F*_o²), where σ(*F*_o²) was estimated from counting statistics. The structure was solved from Patterson and heavy-atom electron density maps and refined by full-matrix least-squares analysis. All non-hydrogen atoms were refined anisotropically. During the final cycles of refinement fixed hydrogen contributions with C–H bond lengths fixed at 1.08 Å were applied. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

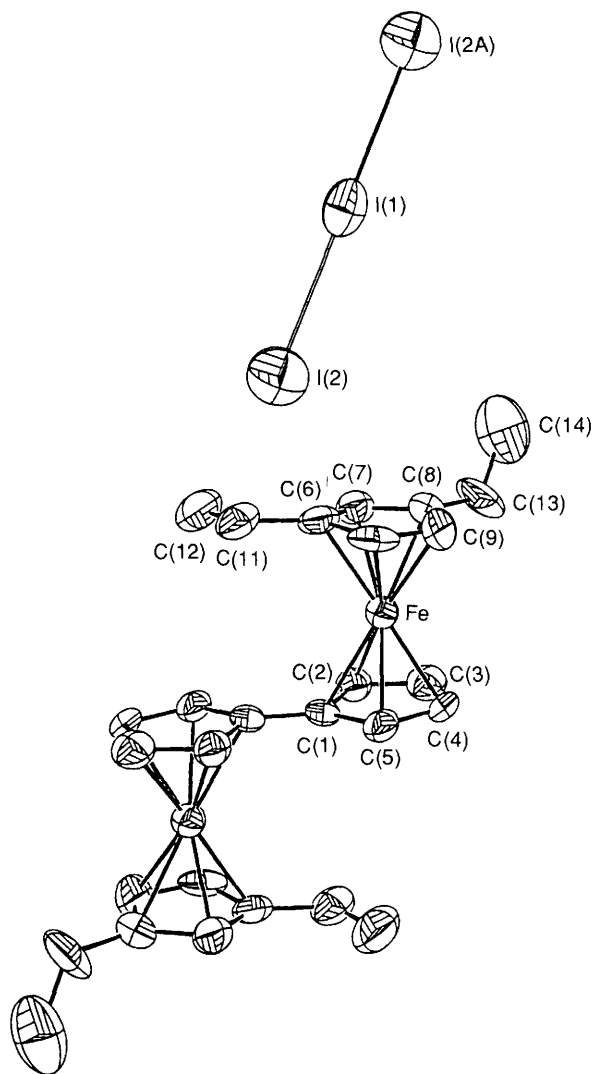


Fig. 1 Molecular structure of **10**. Important bond lengths (Å) and bond angles (°): I(1)–I(2) 2.914(1), Fe–C(1) 2.11(1), Fe–C(2) 2.05(1), Fe–C(3) 2.05(1), Fe–C(4) 2.04(1), Fe–C(5) 2.06(1), Fe–C(6) 2.11(1), Fe–C(7) 2.03(1), Fe–C(8) 2.06(1), Fe–C(9) 2.05(1), Fe–C(10) 2.06(1); I(2)–I(1)–I(2A) 180.0.

As shown in Fig. 2(A), the Mössbauer results indicate that compound **10** is delocalized on the Mössbauer time-scale (10⁷ s⁻¹) in the solid state above 130 K. At temperatures below 100 K, the cation of **10** shows two doublets in the variable-temperature Mössbauer spectra, one representing the Fe^{II} site and the other the Fe^{III} site. Increase of temperature causes the two doublets to move together, eventually to become a single ‘average-valence’ doublet at 130 K. On the other hand, there is a marked difference in the appearance of the variable-temperature Mössbauer spectra of **11**. Fig. 2(B) illustrates the spectra obtained for a microcrystalline sample of **11**. At 200 K and below two doublets can be seen; above this temperature there is only one average doublet (electron transfer rate > *ca.* 10⁷ s⁻¹). Thus, the change of the relative positions of the ethyl substituents from 1',3',1''',3''' in **10** to 1',2',1''',2''' in **11** leads to a reduction in the intramolecular electron-transfer rate.

X-Band EPR spectra in the solid state were run at 77 K for **10** and **11**. Compound **10** gives an axial-type EPR signal characterized by *g*_{||} = 2.91 and *g*_⊥ = 1.97. The *g*-tensor anisotropy, Δ*g* = *g*_{||} – *g*_⊥, is 0.94. In the case of **11**, *g*_{||}, *g*_⊥ and Δ*g* are 3.05, 1.95 and 1.10, respectively. The smaller *g*-tensor anisotropy in **10** indicates that the cation of **10** has a smaller thermal barrier for electron transfer in the solid state. An empirical correlation has been reported between the *g*-tensor

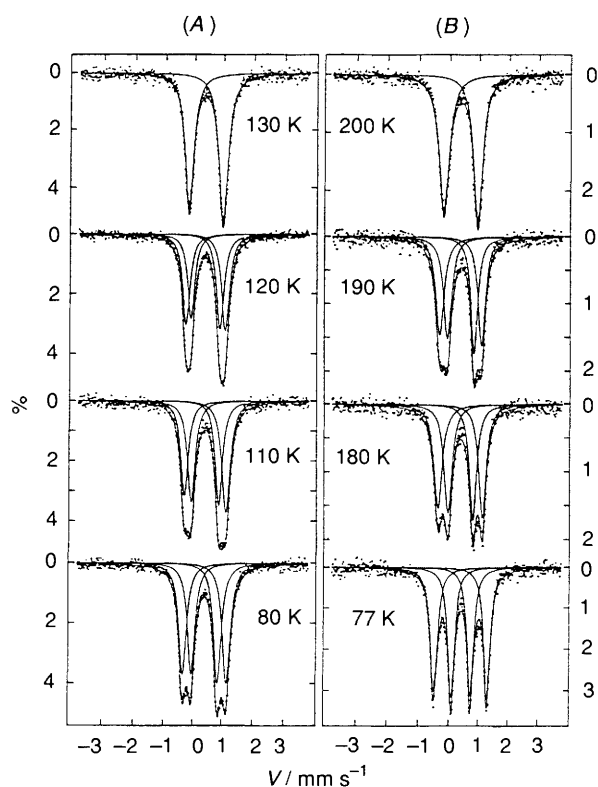


Fig. 2 ^{57}Fe variable-temperature Mössbauer spectra of (A) **10**; (B) **11**

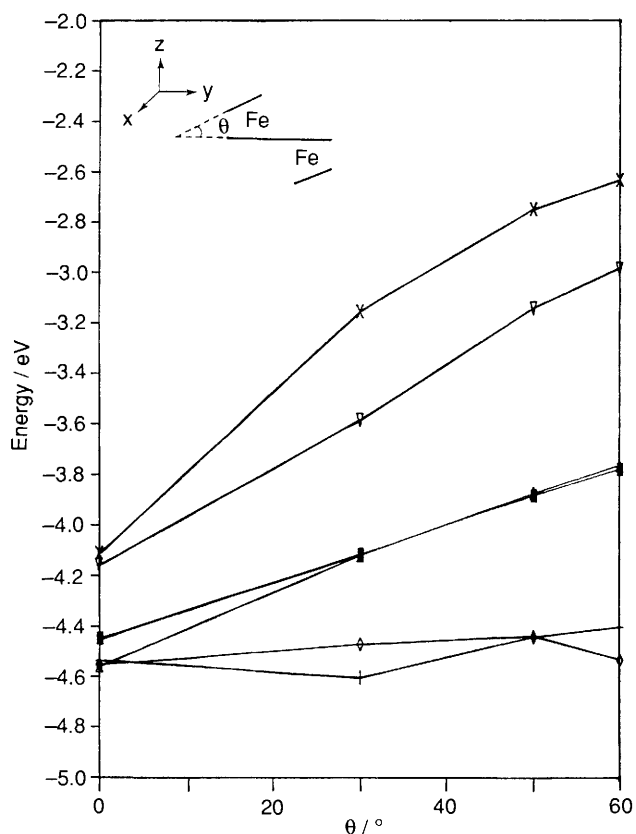


Fig. 3 Fragment orbitals for bending biferrocenium triiodide from parallel geometry: \times $d_{z^2} + d_{z^2}$; \blacktriangle $d_{xy} - d_{xy}$; ∇ $d_{z^2} - d_{z^2}$; \diamond $d_{x^2-y^2} - d_{x^2-y^2}$; \blacksquare $d_{xy} + d_{xy}$; $+$ $d_{x^2-y^2} + d_{x^2-y^2}$

anisotropies and the rates of electron transfer for biferrocenium salts.¹⁷

Finally, it is necessary to discuss why compounds **10** and **11** have lower transition temperatures for delocalization in comparison with that of **2**. We now propose a theoretical model to explain the difference in transition temperatures for delocalization in the mixed-valence cations **2**, **10** and **11**. We believe that the difference in transition temperatures is not due only to a difference in the electronic effect of ethyl substituents. First, it is clear that the electronic effect of the ethyl substituent is not additive by comparing the transition temperatures of **1**, **2**, **10** and **11**: 365, 275, 130 and 200 K, respectively. Secondly, further evidence can be gleaned from the electrochemical data of 1',1'''-diethylbiferrocene, **12** and **13**. 1',1'''-Diethylbiferrocene and compounds **12** and **13** show two one-electron oxidation waves, and the separation between the two oxidation waves is 0.36, 0.37 and 0.37 V, respectively. In other words, the magnitude of the interactions between the two Fe ions in **2**, **10** and **11** is equivalent in the solution state. Of course, this is not consistent with our solid-state variable-temperature ^{57}Fe Mössbauer results. We suggest that the difference in the rates of electron transfer of **2**, **10** and **11** is a result of differences in the degree of tilting of the Cp rings caused by the ethyl substituents. Fig. 3 illustrates the fragment orbitals for bending of biferrocenium triiodide **1** from parallel geometry. As can be seen in Fig. 3, the $d_{z^2} \pm d_{z^2}$ and $d_{xy} \pm d_{xy}$ orbitals rise rapidly in energy as the Cp rings are bent back. In other words, the metal nonbonding orbitals start to interact with the ligand π orbitals. Hence, bending back the Cp rings would lead to a larger extent of metal-ligand interactions which would eventually render the intramolecular electron transfer much more feasible. In comparison with **2**, compound **10** has a larger tilt angle, basically caused by the ethyl substituents on the Cp rings. Therefore, the ethyl substituents in **10** modify the local structure of the ferrocenyl moiety and lead to stronger metal-ligand interaction.

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