Effect of the end-groups upon delocalisation in polymethines: the first crystallographically characterised bond-alternated cyanine

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The reorganisation energy associated with the end groups may be used to influence the localisation behaviour of cyanines; thus, the 1,3-bis(ruthenocenyl)allylium cation is markedly unsymmetrical in the crystal structure of its hexafluorophosphate salt, with the positive charge localised on one ruthenium, whereas the analogous iron species is delocalised and has approximate C_5 symmetry.

Concepts of resonance lead to the expectation that typical polymethine cations or anions (cyanines) should have symmetrical structures, intermediate between two unsymmetrical extreme resonance structures [Figure 1(a)]. Numerous reported crystal structures[1] confirm that typical cyanines are indeed symmetrical delocalised systems with equalised C–C bond lengths. However, extrapolation of the properties of a typical cyanine to infinite chain length[2] affords a one-dimensional zero-band-gap material, which should be subject to a Peierls distortion.[3] If the end groups can stabilise the overall positive or negative charge, this distortion is predicted to result in a bond-alternated structure resembling *one* of the extreme structures in Fig. 1(a); the two structures are now related by an equilibrium arrow.[4–7] To date the only experimental evidence for a Peierls-distorted cyanine is for the compound shown in Fig. 1(b); the solution structure was shown to be unsymmetrical by comparison of its IR and UV–VIS–NIR spectra with those of symmetrical delocalized shorter chain homologues.[8]

Although previous studies have distinguished between end groups which stabilise the overall charge and those which do not,[7] the possibility of different charge-stabilising end groups controlling the length at which localisation occurs does not seem to have been discussed in detail. It has been noted[8,9] that Peierls-distorted cyanines are analogous to class II mixed-valence compounds, whilst typical cyanines are analogous to class III species. The placement of a compound in the Robin and Day classification[10] depends on the interplay of the electronic coupling between the two extreme localised structures, *V*, and the vertical reorganisation energy of Marcus theory, λ.[11] In a polymethine, *V* will be influenced by the length and planarity of the polymethine chain, whilst λ will have contributions from interconverting the end groups (for example: the $Me_2N^+=$ and $Me_2N–$ geometries in a cyanine such as that in Fig. 1(a);

analogous to the Ru^{II} and Ru^{III} coordination geometries in the mixed-valence Creutz–Taube ion[11]), as well as from the polymethine bridge itself, where the sense of the bond-length alternation must be inverted. In a typical cyanine, the end group effect is limited to changing a few bond lengths. We chose to investigate the Group 8 metallocenes as end groups with potentially different reorganisation energy characteristics: a carbocation α to a metallocene is stabilised through resonance contributions from the [(η^6-fulvene)(η^5-cyclopentadienyl)-metal] cation,[12] which has significantly different geometry from the parent metallocene,[13] especially when the metal is ruthenium[14] or osmium.[15]

We synthesised a range of 1,3-bis(metallocenyl)allylium salts, [Mc(CH₃)Mc′]⁺[X]⁻ {Mc = Mc′ = ferrocenyl (Fc), **1**; Mc = Mc′ = 2,3,4,5,1,2,3,4-octamethyl-1-ferrocen-1-yl (Fc″), **2**; Mc = Mc′ = ruthenocenyl (Rc), **3**; Mc = Fc, Mc′ = Rc, **4**; X = PF₆, **a**; X = BF₄, **b**}. Single crystal X-ray diffraction showed the cations in **1a**‡ and **2a**[16] to be essentially symmetrical with equalised C–C bonds in the allylium bridges, as might be expected by analogy with the previously described structure of closely related cyclopentadienyl(1,3-diferrocenyl-1-ylium-pentalenyl)iron tetrafluoroborate.[17] In contrast, we found the structure of **3a**‡ to be much less symmetrical (Fig. 2), although the packing diagrams for **1a** and **3a** are rather similar. The structural parameters for the Ru1 ruthenocene are similar to those for previously reported examples of ruthenocene-stabilised carbocations; *i.e.* it is essentially fully distorted to an [(η^6-fulvene)(η^5-cyclopentadienyl)ruthenium] cation structure. Thus, the Ru1–C11 bond length of 2.381(3) Å may be compared with 2.270(3) Å for the corresponding distance in [Cp*Ru(η^6-C₅Me₄CH₂)]⁺[BPh₄]⁻·CH₂Cl₂ **5**;[14] similarly the Ru1–C_{ring} distances fall in the range 2.089(2)–2.234(2) Å, whilst those for **5** fall in the range 2.066(3)–2.274(3) Å. In the [Rc(CH₃)Rc]⁺ cation of **3a**, the α-carbon C11 is bent towards Ru1 such that the C10–C11 bond makes an angle of 38.2° with the C6–10 plane; the corresponding angle in **5** is 40.4°. The dimensions of the Ru2 ruthenocene are typical for a 'normal' ruthenocene; thus, the Ru2–C_{ring} distances for **3a** fall in the range 2.167(2)–2.194(3) Å, whilst those for *E*-1,2-dimethyl-1,2-diruthenocenylethylene[18] and ruthenocene itself[19] fall in the
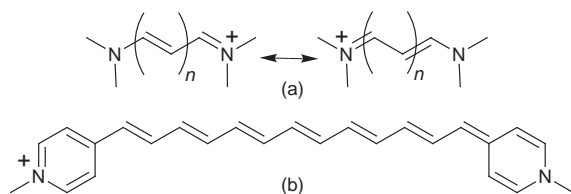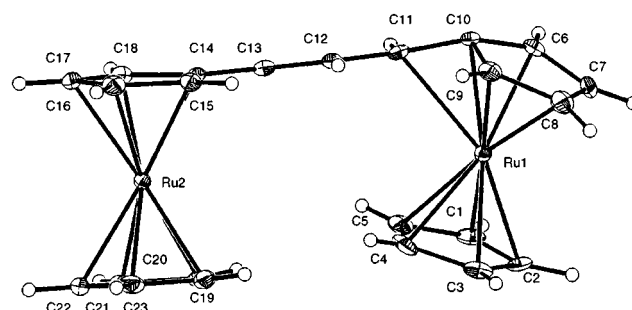

Fig. 1 Representations of (a) the extreme unsymmetrical resonance structures for a typical cyanine and (b) the Peierls-distorted cyanine reported by Tolbert and Zhao.[8]

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Fig. 2 View of the [Rc(CH₃)Rc]⁺ cation in the crystal structure of its hexafluorophosphate salt, **3a**, showing the atomic numbering scheme; non-hydrogen atoms are represented by 50% thermal ellipsoids, whilst hydrogen atoms are shown as spheres of arbitrary radius.

ranges 2.171(3)–2.216(3) and 2.181(2)–2.188(2) Å respectively. The α-carbon, C13, is *not* bent towards Ru2 and the Ru2–C13 distance is 3.237(3) Å. The structure of **3a** also shows considerable bond length alternation in the allylium bridge; the C(11)–C(12) bond length is 1.443(4) Å, whilst the C(12)–C(13) bond length is 1.343(4) Å.[20]

The structure of **3a** is the first crystal structure of a nominally symmetrical cyanine adopting an unsymmetrical bond-alternated structure. Indeed, the only previously reported Peierls-distorted cyanine is the much longer species shown in Fig. 1(b). One question that now arises is whether the unsymmetrical structure of the cation in **3a** is due to solid-state (crystal-packing) effects. However, *all* previous cyanine structures *are* symmetrical, despite a great variety of counterions and packing motifs. Moreover, the similarity in the packing of **1a** and **3a** suggests the differences in molecular structure are due to internal electronic, rather than external crystal-packing, effects.[21] We believe that the origin of these electronic effects is the larger reorganisation energy of the ruthenium system; the structural differences between ruthenocene and [(η⁶-fulvene)-(η⁵-cyclopentadienyl)ruthenium] cation are much greater than for the analogous iron species. To further investigate this question we studied the **3** cation in solution.[22] Symmetrical and unsymmetrical forms of cyanines are expected to have vibrational modes of different energies; calculations support this expectation for $[NH_2(CH)_nNH_2]^+$ ($n = 19, 25$).[23] The differences should be most readily detected in the stretches associated with the multiple bonding of the polymethine bridge. **3a** (1609 cm⁻¹ in KBr, 1598 cm⁻¹ in CH_2Cl_2) and **3b** (1603 cm⁻¹ in KBr, 1603 cm⁻¹ in CH_2Cl_2) both show a strong IR band which we assign to the multiple bond stretch; neither ruthenocene nor [(η⁶-fulvene)(η⁵-cyclopentadienyl)ruthenium] cations[24] show absorptions in the same region. The same band is also present in Raman spectra (1609 and 1601 cm⁻¹ for **3a** in KBr and CH_2Cl_2, respectively). The insensitivity of the band to the counter ion, or the medium, implies that the structure of the **3** cation is the same in crystals of both its tetrafluoroborate and hexafluorophosphate salts, and in CH_2Cl_2 solution. Moreover, the IR evidence implies that the structure of the **3** cation most closely resembles that of the **4** cation (1598 cm⁻¹ in KBr for **4a**), which is unsymmetrical both formally and electronically (according to ¹H–¹H coupling constants), and is somewhat different from those of the **1** (1558 and 1558 cm⁻¹ for **1a** in KBr and CH_2Cl_2 respectively) and **2** (1538 and 1542 cm⁻¹ for **2a** in KBr and CH_2Cl_2 respectively) cations (which have been shown to be symmetrical in the crystal structures of their hexafluorophosphate salts).

In conclusion, we believe that the large reorganisation energy associated with the ruthenocene / [(η⁶-fulvene)(η⁵-cyclopenta-dienyl)ruthenium] system has enabled us to characterise a bond-alternated cyanine at an unprecedentedly short chain length. We have presented the first crystal structure of a Peierls-distorted bond-alternated cyanine; vibrational spectroscopy suggests the cyanine is also unsymmetrical in solution. Control of the reorganisation energy in this way may be a useful design principle for the synthesis of other charge-localised cyanines, which have potential optical and electronic applications.

Notes and references

‡ Single crystals of **1a** and **3a** were grown by layering dichloromethane solutions with diethyl ether. Diffraction data were acquired at 85 K using an Enraf-Nonius CAD-4 diffractometer, employing Mo-Kα radiation (0.71073 Å). Structures were solved by direct methods using SHELXS97;[25] full-matrix least-squares refinement on F^2 against all reflections was carried out using SHELXL97.[25]

Crystal data: for **1a**, $C_{23}H_{21}F_6Fe_2P$, $M = 554.07$, orthorhombic, $a = 14.420(3)$, $b = 12.267(2)$, $c = 24.062(5)$ Å, $V = 4256.3(14)$ Å³, space group $Pbcn$, $Z = 8$, $\mu = 1.499$ mm⁻¹, 9150 reflections measured, 3752 unique ($R_{int} = 0.034$); the final R indices (for all data) were $R1 = 0.101$ and $wR2 = 0.1327$. Fourier maps revealed disorder, whereby there is a minor alternative orientation of the cation related to the major orienation by rotation about an axis perpendicular to the plane of the bridging group and passing through the central atom of the bridge. However, this could not be satisfactorily modelled and is, therefore, not included in the reported structure.

For **3a**; $C_{23}H_{21}F_6PRu_2$, $M = 644.51$, monoclinic, $a = 26.409(6)$, $b = 15.004(3)$, $c = 11.970(3)$ Å, $\beta = 113.83(2)°$, $V = 4338.6(17)$ Å³, space group $C2/c$, $Z = 4$, $\mu = 1.526$ mm⁻¹, 10256 reflections measured, 3818 unique ($R_{int} = 0.014$); the final R indices (for all data) were $R1 = 0.0238$ and $wR2 = 0.0491$.

CCDC 182/1296. See http://www.rsc.org/suppdata/cc/1999/1567/ for crystallographic files in .cif format.

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20 The bond length alternation in **1a** is insignificant, although the large values for the appropriate bond lengths [1.469(10) and 1.461(10) Å] are artefacts of unmodelled disorder in the structure.
21 The inherently unsymmetrical **4a** is isomorphous with **3a**.[16]
22 The **3** cation appears symmetrical on the NMR timescale at room temperature [as does the cation shown in Fig. 1(b)]; low temperature studies (to –85 °C, 500 MHz for ¹H and 125 MHz for ¹³C) also give no unambiguous evidence for localisation. UV–VIS solvatochromism studies are also inconclusive; symmetrical **1** and **2**, and unsymmetrical **4** all show similar behaviour to **3**.
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