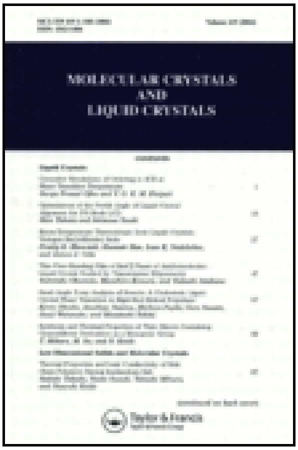

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An Amplified Odd-even Effect in Metal-Containing Siamese Twin Liquid Crystals

Duncan W. Bruce [a] [b] & Martin D. Hall [a]

[a] Centre for Molecular Materials and Department of Chemistry, The University, Sheffield, S3 7HF, UK

[b] DWB is the Sir Edward Frankland Fellow of the Royal Society of Chemistry, 1994/95

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An Amplified Odd–even Effect in Metal-Containing Siamese Twin Liquid Crystals

DUNCAN W. BRUCE*[†] and MARTIN D. HALL

Centre for Molecular Materials and Department of Chemistry, The University, Sheffield S3 7HF, UK

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Iridium complexes of dimeric stilbazoles have been synthesised and a very large odd-even effect in the melting behaviour has been observed. This is attributed to the presence or absence of stacking interactions in the solid state.

Keywords: Metal-containing liquid crystal; iridium; stilbazole; Siamese twins

The first dimeric liquid crystal systems were synthesised many years ago by Vorländer,[1] but more recent interest derives from the work of Griffin[2] and Luckhurst[3] who made examples of so-called "Siamese Twin" molecules (Figure 1).

Dimeric liquid crystals can be regarded as two mesogenic cores linked by a flexible spacer and one of the interesting features of these materials comes from the prounced odd-even effect in certain physical properties[4,5] as well as in the melting and particularly clearing behaviour.

This communication describes what we believe to be the first examples of metal-containing Siamese twin liquid crystals.[6] These materials show a very large odd-even effect in their melting behaviour which is explained on the basis of the solid state packing determined by metal–metal interactions.

We have been studying liquid crystal derivatives of stilbazoles[7] for several years and have examined mesomorphic complexes of Ag(I)[8], Rh(I), Ir(I)[9], Pd(II) and Pt(II)[10]. We wished to extend this work by using dimeric stilbazoles which would lead to dimeric liquid crystals in the case of Rh(I) and Ir(I) complexes, and to semi-flexible main-chain polymers for Ag(I), Pd(II) and Pt(II). The dimeric stilbazoles (n-(OPhVPy)$_2$, where n is the number of methylene groups in the linking chain) themselves were obtained in moderate yield *via* a Heck coupling between 4-vinylpyridine and an *α,ω-bis* (4-bromophenoxy)alkane (Figure 2). These new compounds, none of which was mesomorphic, gave satisfactory microanalytical and ^{1}H NMR data.

Reaction of these stilbazoles with [IrCl(COD)]$_2$ in CH$_2$Cl$_2$ under an atmosphere of CO[10] led to the dimeric iridium carbonyl complexes which were characterised by elemental analysis and ^{1}H NMR spectroscopy.

In common with its monomeric counterpart, *cis*-[IrCl(CO)$_2$(n-OPhVPy)], the dimeric complex *cis,cis*-[8-(OPhVPy)$_2${IrCl(CO)$_2$}$_2$][11] was burgundy in the solid

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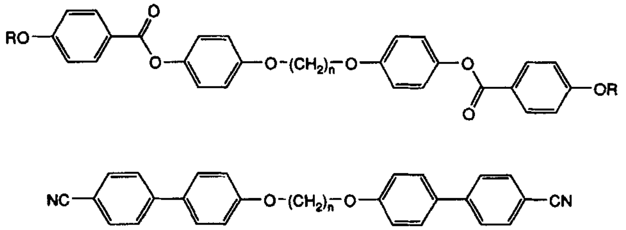

FIGURE 1 Examples of Siamese twin molecules.

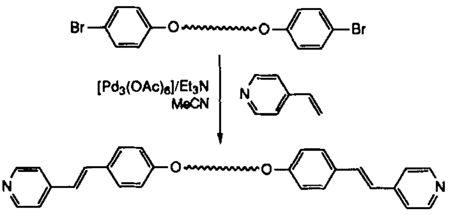

FIGURE 2 Synthesis of dimeric stilbazoles.

state showing four infrared bands in the carbonyl region, while in solution it was yellow showing two ν_{CO} stretches. In the complexes *cis*-[IrCl(CO)$_2$(*n*-OPhVPy)], this difference between the solid state and solution infrared spectra was attributed[9] to a stacking interaction in the solid state (as found in *cis*-[IrCl(CO)$_2$(pyridine)][12]), which disappears (as evidenced by a change in colour and by a change in the infrared spectrum) at the melting point.

The complex *cis,cis*-[9-(OPhVPy)$_2$\{IrCl(CO)$_2$\}$_2$] had similar infrared spectral characteristics in solution, but in the solid state spectrum differed from that of *cis,cis*-[8-(OPhVPy)$_2$\{IrCl(CO)$_2$\}$_2$], having only two bands with shoulders; it was also brown as opposed to the burgundy colour of *cis,cis*-[9-(OPhVPy)$_2$\{IrCl(CO)$_2$\}$_2$]. The same colour and spectrum were previously found[9] for a single preparation of *cis*-[IrCl(CO)$_2$(9-OPhVPy)] which was found to convert to the burgundy form on heating. The difference in colour and spectral features were attributed to a crystalline form where stacking did not occur.

On heating *cis,cis*-[9-(OPhVPy)$_2$\{IrCl(CO)$_2$\}$_2$] no change to a burgundy solid phase was observed and the complex melted into a SmC phase at 155°C which cleared with decomposition at 178°C. However *cis,cis*-[8-(OPhVPy)$_2$\{IrCl(CO)$_2$\}$_2$] did not melt on heating and simply decomposed at 320°C.

The extreme difference in the behaviour of the two complexes is therefore explained on the basis of the solid state structure. Thus, in *cis,cis*-[8-(OPhVPy)$_2$\{IrCl(CO)$_2$\}$_2$], it would be possible to form parallel stacks of Ir(I) units in an extended manner (Figure 3) and the even parity of the linking methylene chain would leave the two iridium units in parallel planes.

However in the case of *cis,cis*-[9-(OPhVPy)$_2$\{IrCl(CO)$_2$\}$_2$], attempts to form parallel stacks would quickly lead to a frustrated structure as the odd parity of the methylene linking chain ensures that the iridium units cannot be coparallel.

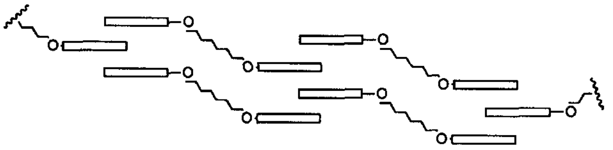

FIGURE 3 Proposed solid-state structure of *cis,cis*-[8-(OPhVPy)$_2$ {IrCl(CO)$_2$}$_2$] showing that stacking is still possible.

Thus, *cis,cis*-[8-(OPhVPy)$_2$ {IrCl(CO)$_2$}$_2$] is packed much more efficiently than *cis, cis*-[9-(OPhVPy)$_2$ {IrCl(CO)$_2$}$_2$], so much so that the latter will melt to give a mesophase while the former decomposes without melting. Thus, the odd-even effect expected for these complexes is greatly amplified by the solid state structure imposed by metal–metal interactions. These results are also of relevance to the debate[6] concerning the importance of metal/metal or metal/ligand interactions in determining the mesomorphism in metal-containing liquid crystal systems, and provide one example which implies that when coupled to solid-state packing constraints, such interactions can be unfavourable.

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