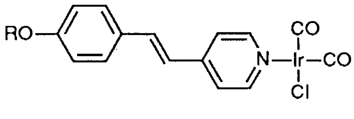
Greatly Enhanced Electronic Polarisabilities in Metal-containing Liquid Crystals

Clive Bertram, Duncan W. Bruce,* David A. Dunmur,* Susan E. Hunt, Peter M. Maitlis and Mark McCann
Department of Chemistry, The University, Sheffield S3 7HF, UK

The mean electronic polarisability ($\bar{\alpha}$) and the polarisability anisotropy ($\Delta\alpha$) are determined for two series of metal-containing liquid crystals; comparison of the values with those of the free ligands clearly shows the dramatic increase in these parameters consequent on complexation to a transition metal.

The inherent anisotropy of liquid crystal mesophases gives rise to an anisotropy of physical properties, such as refractive index and relative permittivity, and it is the exploitation of these anisotropic properties that has led to the widespread application of liquid crystalline materials. These applications are quite diverse and systematic synthetic studies of organic systems have allowed some 'molecular tuning' of these properties. For example, the 4′-alkyl-4-cyanobiphenyls have a birefringence, Δn *ca.* 0.18 while the related 4-alkylcyano-bicyclohexanes have $\Delta n \approx 0.06$. Similarly, the dielectric



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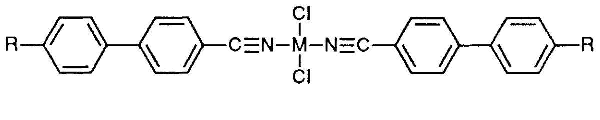

2a M = Pd
b M = Pt

anisotropy (Δε) of the 4′-alkyl-4-cyanobiphenyls is *ca.* 10, while their 2-fluoro analogues[1] have Δε *ca.* 45, probably owing to the breakdown of antiparallel correlations in the nematic phase.[2]

The introduction of metal centres into liquid-crystalline materials has the potential to affect many of the anisotropic properties associated with liquid crystals owing to the inclusion of a centre of electronic polarisability. We now report the results of physical measurements made on two series of metal-containing liquid crystals that show such effects.

We have recently synthesised mesomorphic complexes of iridium by complexation of 4′-alkyloxy-4-stilbazoles[3] to Ir(I) centres,[4] following the demonstration of mesomorphism in the related complexes containing 4-pyridylbenzylideneaniline ligands.[5] The complexes show liquid-crystal phases (pentyloxy → octyloxy, nematic; heptyloxy → dodecyloxy, S_A) at *ca.* 70–130 °C.

The mean polarisability ($\bar{\alpha}$) of the stilbazole ligands was determined for the butyloxy, pentyloxy, undecyloxy and dodecyloxy derivatives *via* the refractive indices and densities of solutions of the stilbazole dissolved in an isotropic host (*p*-xylene), and values of $35 \pm 4 \times 10^{-40}\ \mathrm{J^{-1}C^2m^2}$ were found (*e.g.* $\sim 31 \times 10^{-40}$ for pentyloxystilbazole and $\sim 39 \times 10^{-40}$ for dodecyloxystilbazole). These values are similar to those of, for example, the alkylcyanobiphenyls and alkylcyanobicyclohexyls[6] (see Table 1). However, the complexes formed when the ligands are attached to Ir(I) show a remarkable increase in polarisability. The values of $\bar{\alpha}$ for **1** are as shown in Table 2.

Determination of the polarisability anisotropy (Δα) of these complexes (obtained from measurement[†] of the principal refractive indices of solutions of the complexes in the commercial 'I-eutectic' nematic liquid-crystal mixture (BDH) show similarly large enhancement (Table 2) when compared to the Δα (28 ± 6) measured in a similar way for the stilbazoles themselves.

We have previously reported[7,8] the liquid-crystalline properties of the complexes **2** derived from complexation of alkyl- or alkyloxy-cyanobiphenyls to palladium or platinum. We have determined $\bar{\alpha}$ and Δα for some of these and related complexes; the values for the ligands themselves are included for comparison in Table 1. Again much higher values of both $\bar{\alpha}$ and Δα are found, and are more than twice the values for the component ligand, although in these materials the contribution from the metal's electrons would appear to be somewhat smaller. These results are consistent with the high birefringence (Δ*n*) of these materials,[9] which can exceed 0.4.

Table 1 Mean electronic polarisabilities and polarisabilitiy anisotropies for some nitrile liquid crystals and their metal complexes

Compound[a]	$\bar{\alpha} \times 10^{-40}/\ \mathrm{J^{-1}C^2m^2}$	$\Delta\alpha \times 10^{-40}/\ \mathrm{J^{-1}C^2m^2}$
$[\mathrm{PdCl_2(5CB)_2}]$	82 ± 8	45 ± 9
$[\mathrm{PdCl_2(CCH5)_2}]$	79 ± 8	30 ± 6
$[\mathrm{PdCl_2(PCH7)_2}]$	86 ± 9	39 ± 8
$[\mathrm{PtCl_2(5CB)_2}]$	90 ± 10	—
5CB	37.5	19.4
PCH5	36.2	16.0
CCH5	35.5	12.6

[a] 5CB is 4-pentyl-4′-cyanobiphenyl, CCH5 is *trans*,trans-4′-pentylbicyclohexyl-4-carbonitrile, PCH7 is 4-(4′-heptylcyclohexyl)phenylcarbonitrile, and PCH5 is 4-(4′-pentylcyclohexyl)phenylcarbonitrile.

Table 2 Mean electronic polarisabilities and polarisabilitiy anisotropies for iridium(I) complexes of stilbazoles

1	$\bar{\alpha} \times 10^{-40}/\ \mathrm{J^{-1}C^2m^2}$	$\Delta\alpha \times 10^{-40}/\ \mathrm{J^{-1}C^2m^2}$
R = $\mathrm{C_5H_{11}}$-	59 ± 6	54 ± 10
R = $\mathrm{C_7H_{15}}$-	62 ± 6	59 ± 12
R = $\mathrm{C_9H_{19}}$-	60 ± 6	49 ± 10

For the first series of materials **1**, one ligand complexed to a metal centre leads to a significant enhancement of both polarisability and polarisability anisotropy while for the second series **2** with two ligands, the polarisability and polarisability anisotropy are approximately twice the values for the component ligand. Thus, while we have been able to demonstrate the increase in polarisability on the inclusion of a metal into a liquid-crystalline system, there are obviously other structural effects that need to be taken into account. The nature of these effects will only become apparent with an increased study of the physical properties of these new materials.

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[†] Polarisability anisotropies were determined by assuming a linear relationship between $(n_e^2 - n_o^2)/(\bar{n}^2 - 1)$ and the mole fraction of the solute. Since only very dilute solutions were used, the extrapolation leads to large uncertainties in Δα.

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