Paramagnetic Nematic Liquid Crystals

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Paramagnetic Nematic Liquid Crystals

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Abstract. Five nematogenic complexes, bis[1-(p-n-decyl-biphenyl) 3-(p-substituted phenyl) propane-1,3-dionato]-copper (II), have been prepared. The mesophase, which occurs monotropically in all of them, is of the usual nematic type, but has paramagnetic properties. Magnetic, dielectric and electron paramagnetic resonance measurements are presented. A preliminary analysis of the data indicates the existence of antiparallel correlations in the nematic phase.

Introduction

In a recent note,[1] we presented examples of new complexes that form paramagnetic nematic liquid crystals. We established by miscibility studies that the mesophases are of the usual nematic type, i.e., composed of rod-like molecules, and by magnetic susceptibility measurements that they are, in fact, paramagnetic. We now describe some further investigations on these materials.

The first copper containing (discotic) mesogens were prepared by Giroud-Godquin and Billard,[2,3] and since then other similar materials have been synthesized,[4-7] but none of them exhibit a nematic phase. We felt that it would be of interest to explore this possibility, and were able to prepare a few nematogenic copper complexes. After these studies had been completed,[1] we came across a report by Galyametdinov et al.[8] on bis(4-heptyloxy -2-hydroxy-N-4-phenyloxy (dodecyloxybenzoate) benzaldimi-

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nato) copper (II). However, as even the transition tempera-
tures of this complex are not given in their report,[8] we
shall not discuss their work any further in this paper.

Experimental

4-n-Decyl-4'-acetylbiphenyl was prepared following
the method described by Byron et al.[9] The ligands and
the corresponding copper complexes were prepared according
to the scheme shown in figure 1. All the complexes were
recrystallised several times from methyl ethyl ketone
and obtained as green needles. The transition tempera-
tures were determined with a polarizing microscope equi-
pped with a heating stage and a controller (Mettler
FP52 and FP5) and from thermograms recorded on a diffe-
rential scanning calorimeter (Perkin-Elmer, Model DSC2 or
DSC4). The calorimeter was calibrated using pure indium
as a standard. The enthalpies of transitions were also
calculated from the thermograms. The purity was checked
by analytical and spectral data. The elemental analysis
data are given in table 1. Infrared and electronic absorp-
tion spectra were recorded on Shimadzu IR-435 and Hitachi
U-3200 spectrophotometers. Typical values for complex 3
of table 2 are -

IR ν_{max} (nujol mull) 1588 cm^{-1} and 1608 cm^{-1}
UV-VIS $\lambda_{max}^{CHCl_3}$ (ϵ) 366 (84,000) 316 (57,000) and
                                240 (51,000).

Magnetic susceptibility measurements were made using
a Cahn RG balance, which was calibrated with $Hg[CO(SCN)_4]$.
EPR spectra were recorded on a Varian E109 spectrometer
operating at X-band frequency (9.05 GHz); the samples
were heated using a Varian variable temperature acce-
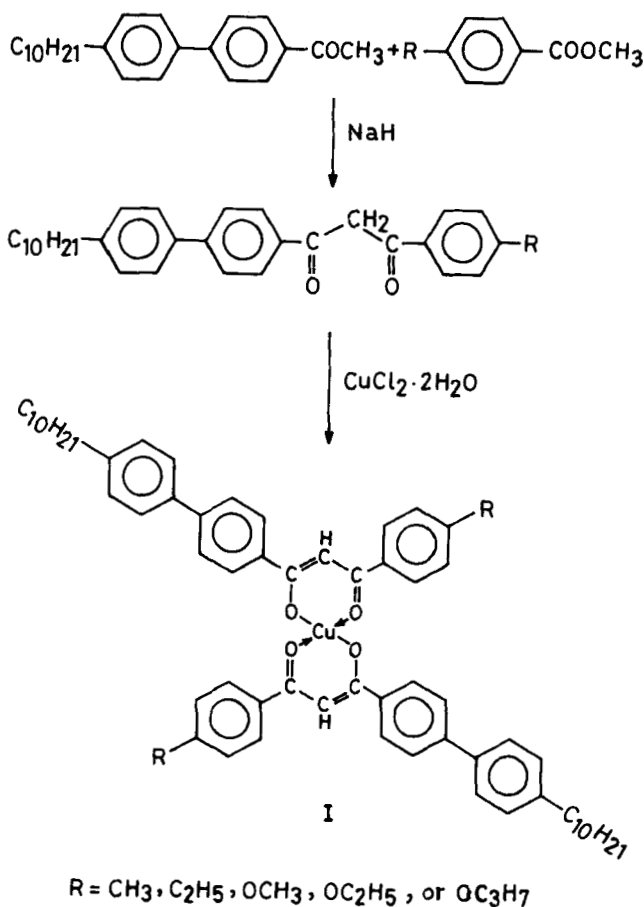
Fig. 1. Synthetic route for bis[1-(p-n-decylbiphenyl)
3-(p-substituted phenyl)propane 1,3-dionato]
copper (II) complexes.

Table 1. Elemental analysis data of the complexes I

Complex number	Calculated, %		Found, %	
	C	H	C	H
1	79.22	7.63	79.20	7.54
2	79.39	7.82	79.30	7.82
3	76.68	7.39	76.76	7.39
4	76.93	7.58	76.79	7.49
5	77.16	7.75	77.02	7.65

ssory (E257/WL-257) and the temperature was controlled by nitrogen gas flow. The dielectric constants were measured with a Wayne-Kerr bridge (Model B642) operating at 1592 Hz.

Thermodynamic data

The temperatures and heats of transition for the five complexes are given in table 2. The transition to the nematic phase is monotropic in all five cases. Complexes 1 and 2 show the nematic phase after considerable supercooling of the isotropic liquid, so that the crystallisation is more or less immediate. Hence

Table 2. Transition temperatures (°C) and
          heats of transition (kcals/mole)

Complex number	R	K		N		I
1	CH_3	.	224.0 12.68	.	$(169.5)^a$ —	.
2	C_2H_5	.	181.5 9.20	.	$(153.8)^a$ —	.
3	OCH_3	.	194.0 12.11	.	(179.0) 0.092	.
4	OC_2H_5	.	186.6 12.24	.	(166.5) 0.093	.
5	OC_3H_7	.	183.5 13.66	.	(153.5) 0.096	.

K : Crystal, N : Nematic and I : Isotropic liquid

[a]The heat of transition could not be accurately determined because of the onset of crystallisation

The temperature in parentheses indicates a monotropic transition.

the heat of N-I transition (ΔH_{NI}) could not be measured for these two cases. For complexes 3, 4 and 5, $\Delta H_{NI} = 0.092$, 0.093 and 0.096 kcals/mole respectively. These values are slightly lower than what is usually observed for this transition.[10] Complex 3 exhibits a metastable nematic phase which exists over an appreciable temperature range before crystallisation occurs. As such a number of physical measurements could be made on this complex.

Structure I (figure 1) can be looked upon as an elongated molecule with two lateral substituents: the two biphenyl moieties with the decyl chains form the long axis, while the two phenyl rings with R form the 'lateral' substituent. Consequently, the mesophases of these complexes may be expected to be of the usual nematic type composed of 'rod-like' molecules. This was confirmed[1] by studying the miscibility of complex 3 with the well known nematogen 4"-n-pentyl-4-cyano-p-terphenyl (5CT). For the sake of completeness, we reproduce the miscibility diagram in figure 2. It was also ascertained that the nematic phases of complexes 3 and 4 are continuously miscible.

Magnetic susceptibility measurements

The magnetic susceptibilities in the three phases of complex 3, uncorrected for diamagnetism, were found to be:

Polycrystal at 27°C $\chi_{mean} = 901.4$

Nematic at 175°C $\chi_{"} = 140.2$ $\times 10^{-6}$ emu/mole

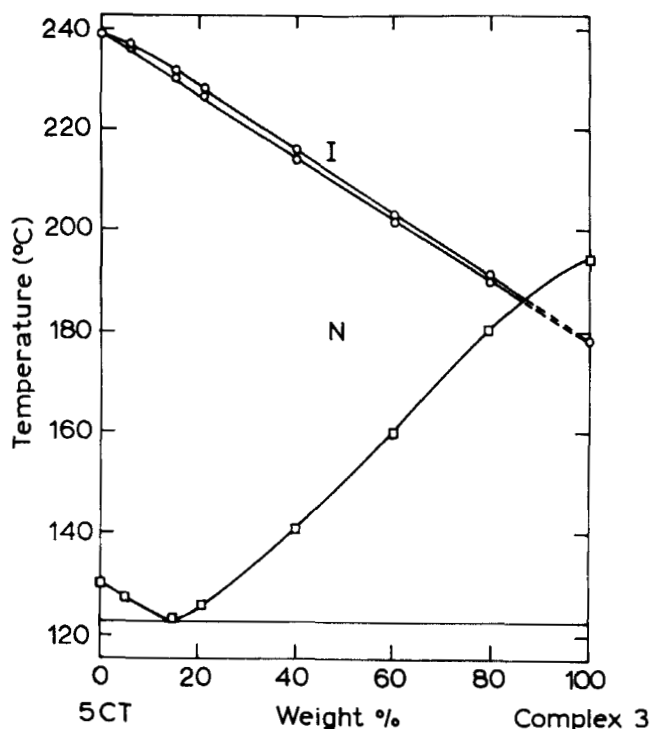Isotropic liquid at 200°C $\chi_{is} = 60.1$

Fig.2. Miscibility diagram of 5CT with complex 3. Squares represent the solid-nematic or solid-isotropic transitions determined in the heating mode, and circles the isotropic-nematic (I-N) transitions determined in the cooling mode. The dashed lines signify monotropic transitions.

It was verified that the anisotropy of magnetic susceptibility in the nematic phase is positive ($\Delta X = \Delta X_{para} + \Delta X_{dia} > 0$) by observing the Freedericksz transition in a homeotropically aligned sample (bend geometry); the threshold field was 6.6 kG for a sample of thickness 25 µm. Since the diameter of the sample container of the Cahn RG balance was about 5 mm and the magnetic field

used was 3 kG, it is clear that the measured susceptibi-
lity in the nematic phase represents $\chi_{\shortparallel}$ for an aligned
sample.

$\chi_{\shortparallel}$ and χ_{is} were also determined as functions of
temperature. The temperature stability was estimated
to be better than ±0.2°C. The observed molar susceptibi-
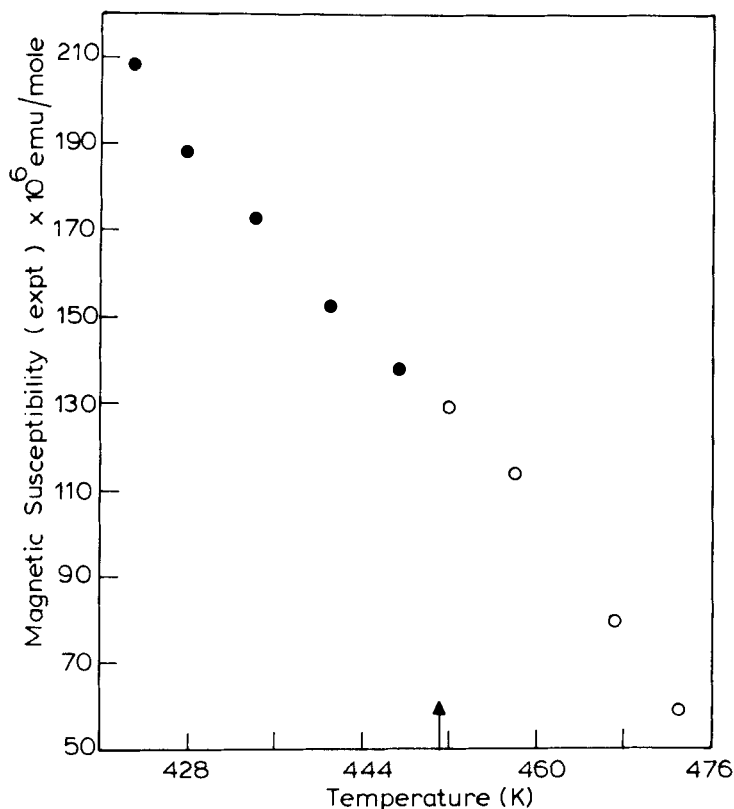lity is plotted against T in figure 3.

Fig.3. Experimental values of the magnetic susceptibility
(uncorrected for diamagnetism). Open circles repre-
sent $\chi_{isotropic}$ and closed circles $\chi_{\shortparallel}$ in the nematic
phase. The arrow represents the N-I transition
temperature.

χ_{is} was corrected for diamagnetism by the standard procedure.[11] The diamagnetic anisotropy in the nematic phase was calculated by Flygare's method,[12] which has proved to be quite successful in a number of cases.[13-15] The contribution of the alkyl chains to the anisotropy was taken to be negligible.[13-17] One then gets

$$[\chi_{\shortparallel}]_{dia} = \bar{\chi}_{dia} + \frac{2}{3} S\Delta\chi_{dia}$$

where S is the order parameter, which can be obtained from the Maier-Saupe theory. Although the absolute value of S derived from this theory may be in error, the predicted temperature variation of S tends to be reasonably accurate (except very close to the transition). As we shall see, it is the temperature variation that is probably more relevant to our discussion. The calculated suscepti- bilities in the isotropic and nematic phases are given in figure 4; the trend is in agreement with experimental curves for diamagnetic nematics.[17,18]

The paramagnetic susceptibility, after correcting for diamagnetism, versus 1/T is presented in figure 5. There is a Curie-Law type of variation in both phases, but the slope for χ_{is} is nearly twice that for $\chi_{\shortparallel}$ in the nematic. A plot of $1/\chi$ versus T also leads to essentially the same conclusion. The negative paramagnetic anisotropy of the molecule may account for a small part of the difference in the slopes, but even allowing for this, it appears that the effective magnetic moment per molecule is lower in the nematic, perhaps due to antiparallel correlations in this phase. However further studies are necessary before this result can be established conclusively.
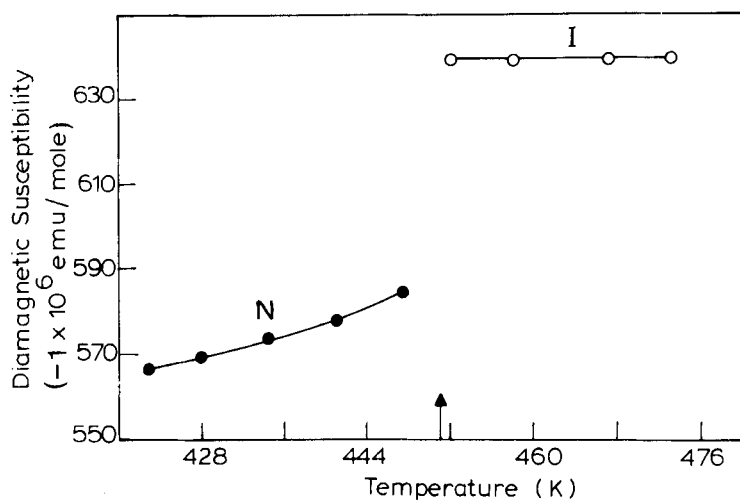
Fig.4. Calculated diamagnetic susceptibility. Open
circles represent $\chi_{isotropic}$ and closed circles
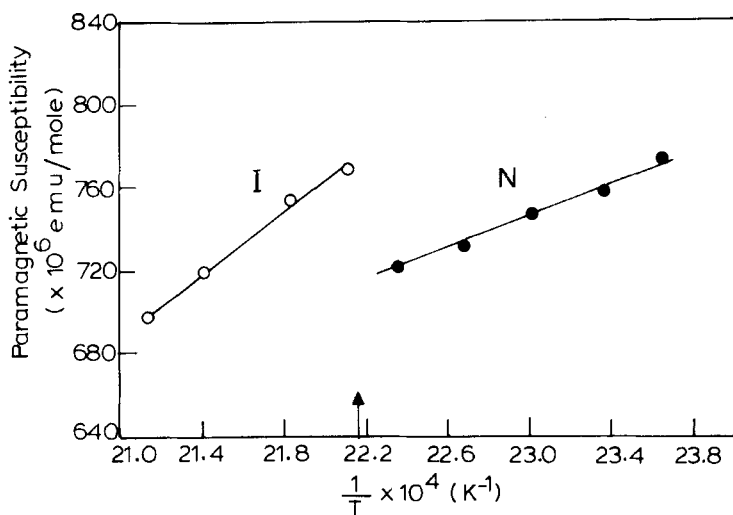$\chi_{\shortparallel}$ in the nematic phase.

Fig. 5. Paramagnetic susceptibility versus 1/T.

Electron paramagnetic resonance (EPR) studies

The EPR spectra were recorded in the polycrystalline, nematic and isotropic phases of complexes 3 and 4. Figure 6 gives the spectra for complex 3. The spectra were closely similar for complex 4 and $g_{\shortparallel}$ and $g_{\perp}$ in the nematic phase were calculated to be 2.261 and 2.062 for both complexes. These values agree well with those repor- ted for other copper complexes.[19] (Here $\shortparallel$ and $\perp$ are with reference to the unique axis of the complex.) From the magnitude of the hyperfine spacing, it would seem that the rate of molecular reorientation is slow, i.e., the rotational correlation time is greater than about 10^{-8} s. This implies that the viscosity is high or that there are molecular aggregates or, most probably, a combination of the two. Such aggregates appear to be present in the isotropic phase as well, for the spectra are essentially unchanged at the transition. A more detailed analysis of the data would evidently be of much interest. As we shall see presently, dielectric studies provide supporting evidence for the existence of strong near neighbour correlations.

On the other hand, the spectra of a dilute solution of complex 3 in 5CT (0.13 mole %) were of the standard type for a paramagnetic probe in a nematic.

Dielectric constant measurements

Dielectric constant measurements were made on complex 3. A 100 micron thick sample was taken between tin oxide coated glass plates and aligned in a 15 kG magnetic field. Both $\varepsilon_{\shortparallel}$ and $\varepsilon_{\perp}$ were measured on the same sample by rotating the cell to the appropriate configuration.
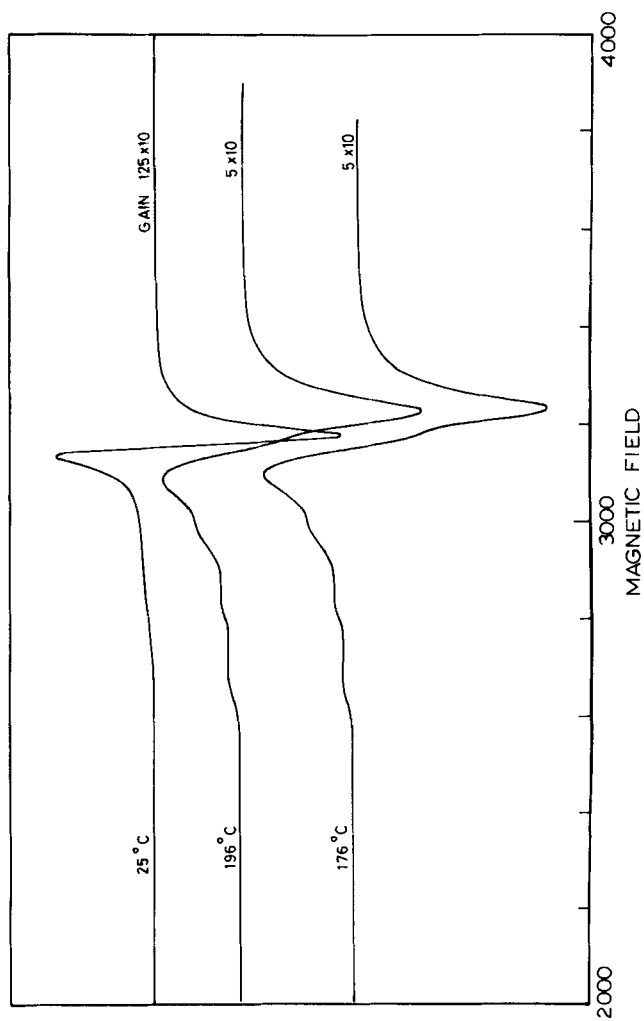
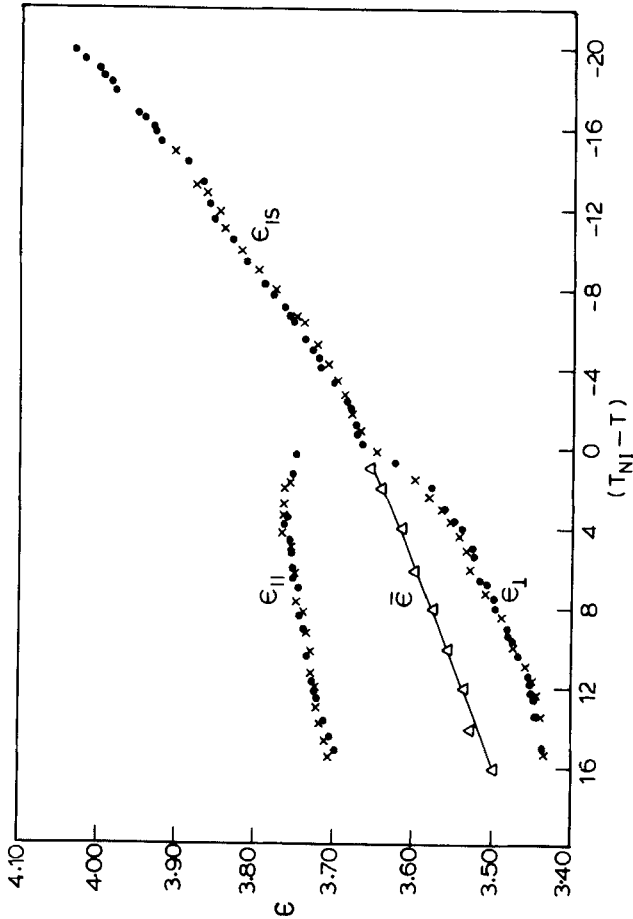Fig. 6. EPR spectra of complex 3 in the polycrystalline (25°C), isotropic (196°C) and nematic (176°C) phases.

Fig. 7. $\epsilon_{\parallel}$, $\epsilon_{\perp}$, ϵ_{is} and $\bar{\epsilon}$ versus T. Dots and crosses represent independent sets of measurements on two separate samples.

$\varepsilon_{\shortparallel}, \varepsilon_{\perp}, \; \bar{\varepsilon}$ and ε_{is} are plotted in figure 7, and the dielec-
tric anisotropy ($\Delta\varepsilon$) in figure 8.

The most striking feature about these results is
that $\bar{\varepsilon}$ as well as ε_{is} increase markedly with increase
of temperature, indicating a high degree of near neigh-
bour antiparallel correlation.[20] This behaviour is remark-
able in view of the fact that the dielectric anisotropy
is quite small, only about 0.27 at the lowest temperature
of measurement.

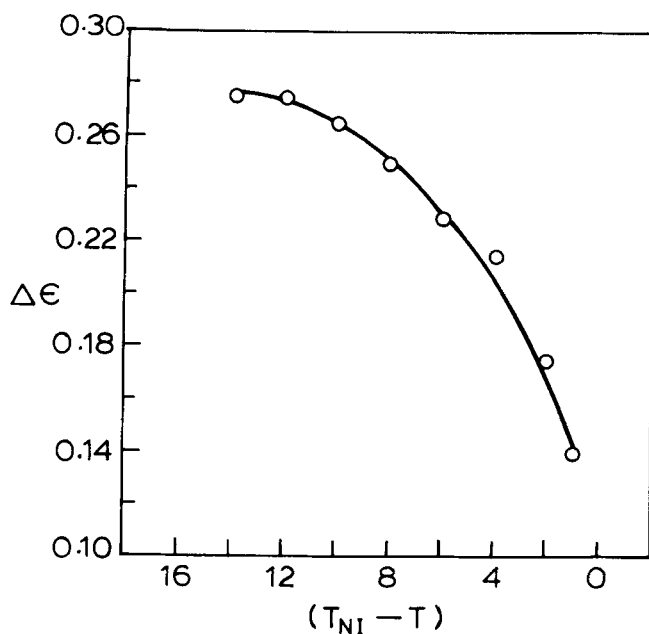The birefringence of the nematic was determined
to be 0.18 at $T_{NI} - T \simeq 10°$.

Fig. 8. Temperature variation of the dielectric anisotropy

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