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Preliminary communication

The mesomorphic anomaly of 4-[2-(4-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]phenyl *trans*-4-pentylcyclohexyl-1-carboxylates

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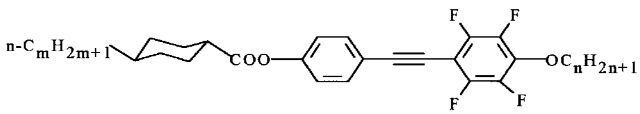
Four homologous series of 4-[2-[4-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]phenyl *trans*-4-alkylcyclohexyl-1-carboxylates have been prepared. Their liquid crystalline behaviour was investigated by optical polarizing microscopy and DSC. Series A, B and C exhibit the nematic phase. The phase transition behaviour of series D is anomalous. The compounds of series D with a short alkoxy chain exhibit enantiotropic smectic A and nematic phases, while those with a long alkoxy chain exhibit only the nematic phase.

Due to the growing interest of the electronics industry in liquid crystals for use in electro-optical display systems, worldwide research and development activities in the liquid crystal field have been remarkably enlarged in the last three decades.

Nematic compounds with low viscosity and high clearing points are required for display devices having a short response time and broad temperature range. It is well known that the introduction of a *trans*-1,4-disubstituted cyclohexane ring into liquid crystal molecules reduces birefringence and viscosity [1–3]. The molecules containing cyclohexylene usually exhibit nematic phases. Fluorination, it is also well known, has a dramatic effect on mesomorphic behaviour and alters certain physical properties of organic compounds, for example, giving increased chemical and thermal stability, and reduced viscosity. Thousands of liquid crystalline compounds with mono-, di-, or tri-fluorophenyl groups [4–8], or 2,3,5,6-tetrafluorophenylenes [9–13] have been reported. In addition, liquid crystals with acetylenic linkages in their cores (tolanes) are reported to possess high birefringence [14–17]. They are valuable as components of mixtures for some electro-optical applications, therefore considerable attention has been paid to the synthesis of tolane-based liquid crystals.

In order to meet the higher quality requirements for nematic compounds corresponding to more sophisticated application levels, we combined these three groups mentioned above and synthesized four new types of liquid crystals containing 2,3,5,6-tetrafluoro-1,4-phenylene and *trans*-1,4-cyclohexylene in the core (compounds A, B, C, D).



A $m = 2$, $n = 5$
B $m = 3$, $n = 5$
C $m = 4$, $n = 4$–8, 10
D $m = 5$, $n = 5$–9, 12

The mesomorphic properties of the new compounds were studied by thermal optical polarizing microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a temperature control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). The transition temperatures obtained by polarizing microscopy of the new compounds are given in the table.

The transition temperatures of compounds A, B, C and D for $n = 5$ versus the number of carbon atoms (m) of the alkyl chain are shown in figure 1. By increasing the length of the alkyl chain, the smectic character is enhanced.

The transition temperatures of C and D are plotted against the number of carbon atoms (n) in the alkoxy chain in figures 2 and 3, respectively. It can be seen that series C and D show enantiotropic nematic phases with

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Table. Transition temperatures by polarizing microscopy. Cr = crystal, SmA = smectic A phase, N = nematic phase, I = isotropic phase, Recr = recrystal.

Compounds	*m*	*n*	Transition temperatures/°C
A-5	2	5	Cr 77.8 N 172.7 I 172.5 N 41.4 Recr
B-5	3	5	Cr 65.0 N 196.4 I 196.1 N 32.5 Recr
C-4	4	4	Cr 76.4 N 203.6 I 202.7 N 44.6 Recr
C-5	4	5	Cr 70.4 N 191.6 I 191.2 N 48.8 Recr
C-6	4	6	Cr 65.1 N 186.9 I 186.3 N 39.5 Recr
C-7	4	7	Cr 57.9 N 179.8 I 179.5 N 40.5 Recr
C-8	4	8	Cr 61.3 N 178.6 I 177.6 N 43.1 Recr
C-10	4	10	Cr 54.3 N 164.4 I 163.5 N 44.1 Recr
D-5	5	5	Cr 60.5 SmA 81.0 N 192.8 I 192.1 N 74.2 SmA 34.7 Recr
D-6	5	6	Cr 53.0 SmA 63.2 N 188.3 I 186.7 N 63.2 SmA 30.8 Recr
D-7	5	7	Cr 57.3 SmA 69.1 N 181.6 I 181.1 N 67.6 SmA 31.3 Recr
D-8	5	8	Cr 52.9 N 177.9 I 177.6 N 40.4 Recr
D-9	5	9	Cr 51.6 N 171.5 I 169.8 N 38.5 Recr
D-12	5	12	Cr 63.4 N 157.2 I 156.1 N 43.5 Recr

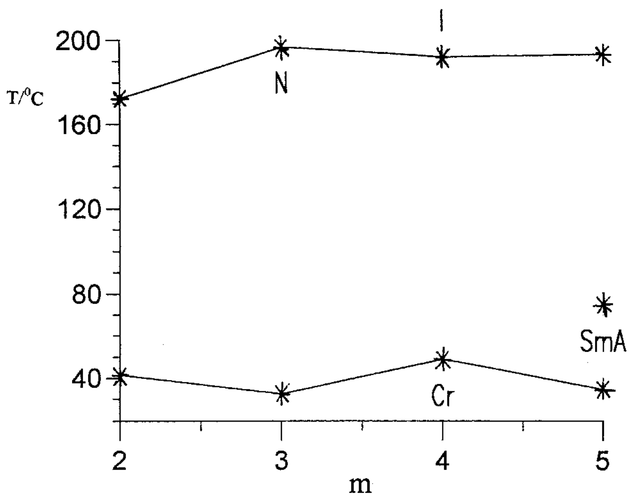

Figure 1. Transition temperature versus *m* for compounds A, B, C, D, when *n* = 5.

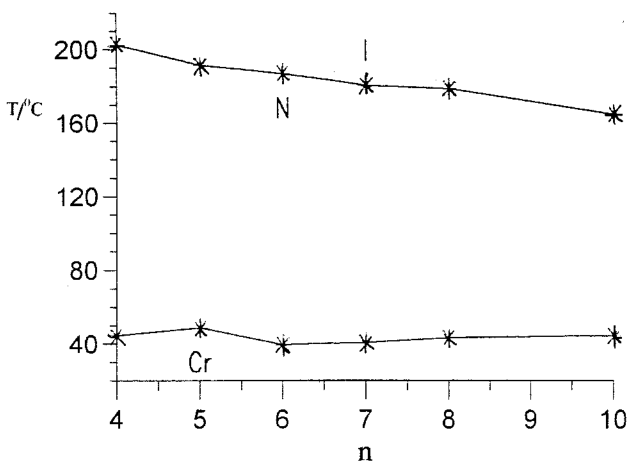

Figure 2. Transition temperature versus *n* for series C compounds.

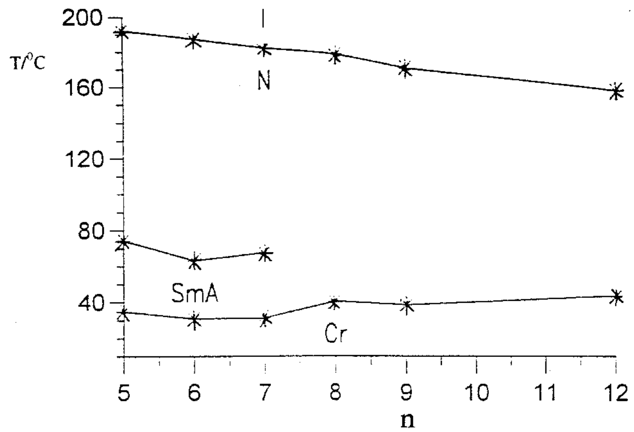

Figure 3. Transition temperatures versus *n* for series D compounds.

relatively high clearing points, which drop with increasing alkoxy chain length. Generally, as the alkyl chain length (*m*) increases, the tendency to form smectic phases increases at the expense of the nematic phase. This is due to increasing lateral intermolecular attractions and decreasing terminal intermolecular attractions.

However, compounds of series D with short alkoxy chains (*n* = 5, 6, 7) exhibit smectic A and nematic phases, whereas those with longer chains (*n* = 8, 9, 12) show only the nematic phase; see figures 4 and 5, respectively. Such anomalous behaviour has only been reported by Hasse and Paulus [18] for *trans*, *trans*-4′alkylbicyclohexyl-4-carbonitriles (cyclohexylcyclohexanes, CCHs). CCHs with short alkyl chains exhibit a smectic phase, whereas CCHs with longer chains only possess a nematic phase. The explanation, corroborated by X-ray investigation, is that, because of dipole–dipole interactions of cyano groups, CCHs with longer alkyl chains form dimers,

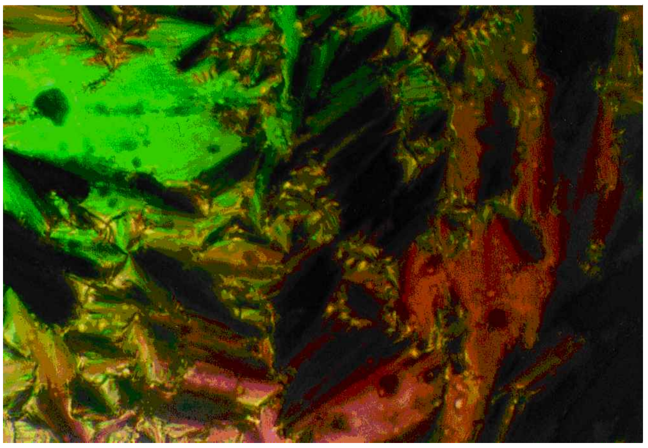

Figure 4. Optical texture of the smectic A phase of compound D-5 ($n = 5$) at 68.0°C.

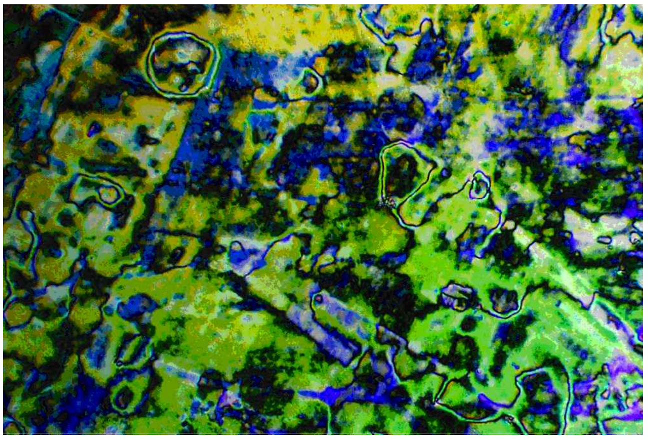

Figure 5. Optical texture of the nematic phase of compound D-12 ($n = 12$) at 139.0°C.

leading to larger molecular lengths in the nematic state as compared with the length of the monomers. However, series D compound show similar behaviour without cyano groups. In order to give a reasonable explanation, the molecular orientation of series D compounds is now being studied by X-ray diffraction.

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