# Some Novel Nematic 4-Cyanophenyl Esters Incorporating a Lateral Substituent

**Stephen M. Kelly**
*Brown Boveri Research Centre, CH–5405 Baden, Switzerland*

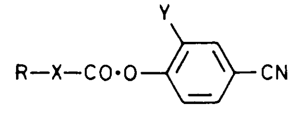
Ester derivatives of a novel phenol, 4-cyano-2-fluorophenol, have been prepared and found to exhibit wide-range nematic phases; many of these esters exhibit higher clearing points than those of the corresponding esters containing a hydrogen atom in place of the fluorine atom.

The existence of smectic phases below the nematic phase of a liquid crystal mixture for display devices can limit the amount of 'supercooling' of the nematic phase below the melting point. This is of serious disadvantage for mixtures intended for wide temperature-range display applications, *e.g.*, outdoor appliances.

The introduction of lateral substituents into liquid crystal systems is well known to depress, often drastically, their liquid crystal transition temperatures.[1] Moreover, smectic–nematic transitions are often more suppressed than nematic–isotropic liquid transitions. This fact has been utilised to produce novel series of enantiotropic nematic liquid crystals with very low smectic–nematic transition temperatures, by the incorporation of a fluorine atom in a lateral position of known nematic compounds.[2,3] Most of these materials are of low negative dielectric anisotropy ($\Delta\epsilon = \epsilon_1 - \epsilon_2 = ca. -1$) in the nematic phase.[2,3]

However, most commercial liquid crystal displays require nematic materials of positive dielectric anisotropy. In order to produce nematic compounds of positive dielectric anisotropy and very low smectic–nematic transition temperatures, it was decided to introduce a fluorine atom into 4-cyanophenol, from which a variety of esters[4,5] could be made *via* reaction with various acid chlorides. The lateral dipole of the fluorine atom should also advantageously lower the dielectric ratio $\Delta\epsilon/\epsilon_1$, which is of importance for multiplexed twisted nematic displays.

The novel esters were prepared by the reaction of known acyl chlorides with 4-cyano-2-fluorophenol in the normal way. The phenol was produced *via* demethylation of the corresponding anisole, which was prepared by cyanation of the known 4-bromo-2-fluoroanisole.[6] The esters were purified by column chromatography and subsequent crystallisation, and their structures were determined by analysis of their $^1$H n.m.r., i.r., and mass spectra. Their purity as determined by t.l.c. and g.l.c., was ≥99.8%.


**(A)**

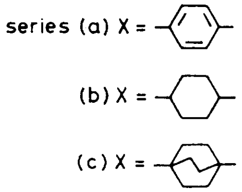


**Table 1.** Transition temperatures (in °C) for compounds (A).

| R | Y | Crystal–nematic/isotropic (a) | (b) | (c) | Nematic–isotropic (a) | (b) | (c) |
|---|---|---|---|---|---|---|---|
| n-Propyl | F | 55.5 | 84 | 112 | (51)[a] | 87.5 | 129 |
| n-Butyl | F | 46.5 | — | 91.5 | (42) | — | 125 |
| n-Pentyl | F | 53.5 | 75.5 | 84 | 55 | 93.5 | 133 |
| n-Hexyl | F | 46 | — | 82 | 46.5 | — | 123.5 |
| n-Heptyl | F | 47 | 76 | 81 | 54 | 92 | 125.5 |
| n-Propyl | H | 103.5 | 54.5 | 86.5 | (51.5) | 69.5 | 100 |
| n-Butyl | H | 67 | 56 | 99 | (42.5) | 68 | (96) |
| n-Pentyl | H | 64.5 | 47 | 89 | [58][b] | 79 | 109 |
| n-Hexyl | H | 44.5 | 49.5 | 77 | 47 | 71 | 102 |
| n-Heptyl | H | 44 | 54 | 54 | 57 | 82.5 | 106 |

[a] The figures in parentheses represent a monotropic transition temperature. [b] The figure in square brackets represents a 'virtual' monotropic transition temperature.

The fluoro-benzoate esters (series a) generally exhibit significantly lower m.p.s. ($\Delta T_{av.} = ca. -26$ °C) and slightly lower clearing points ($\Delta T_{av.} = ca. -1.6$ °C) than the analogous unsubstituted benzoate esters[7] (see Table 1). However, the fluoro-cyclohexane esters (series b) possess both higher m.p.s. ($\Delta T_{av.}$ = *ca.* +16 °C) and clearing points ($\Delta T_{av.}$ = *ca.* +14 °C) than the corresponding unsubstituted esters.[8] The m.p.s of the fluoro-bicyclo-octane esters (series c) are sometimes lower and sometimes higher ($\Delta T_{av.}$ = *ca.* +9 °C) than those of the unsubstituted esters,[9] but the clearing points are consistently higher ($\Delta T_{av.}$ = *ca.* +25 °C).

However, despite significant supercooling (to room temperature) below the m.p. of many of the esters no smectic phases could be observed. The analogous three-ring esters (*e.g.*, R = heptyl, X = bicyclohexyl; C–N, 112 °C; N–I, 222 °C; N–C, *ca.* 75 °C) also exhibit much lower smectic–nematic transition temperatures than the corresponding non-substituted esters (R = heptyl; C–S, 90 °C; S–N, 118 °C; N–I, 222 °C).[10]

The increases observed in the clearing points on the incorporation of a lateral fluorine atom in the cyano-substituted esters[7,8] to produce the esters (series a, b, and c) is in contrast to the decreases observed for the corresponding esters with an alkyl group in place of the cyano-group[2,3] and X = benzene or cyclohexane. When X = bicyclo-octane, certain homologues of the dialkyl series may show a slight increase in clearing point, but the average situation does correspond to a decrease of 1 or 2 °C. It is feasible that, in the case of the cyano-esters, the expected decrease in the clearing points due to the steric effect of the lateral fluorine atom[2,3] can be compensated by a more extended degree of association of the molecules.[11] In this case the terminal cyano-groups could be strongly associated in a dimer-arrangement as postulated for the all *trans*-4-(4-n-alkylcyclohexyl)-1-cyanocyclohexanes.[12] The 'shielding effect' of the cyclohexane and bicyclo-octane rings can be invoked to rationalise the higher clearing points of the esters (series b and c) relative to the benzoate esters (series a).[3] However, elucidation of the structure of the nematic phases of the esters (series a, b, and c) must await detailed *X*-ray studies.

Preliminary investigations of the physical properties of several of the esters reveal that they are of positive dielectric anistropy ($\Delta\epsilon$ = 4.0, $T_{red.}$ = 0.96) and exhibit advantageous combinations of elastic constants ($k_{33}/k_{11}$ = *ca.* 1) for multiplexed twisted nematic displays.[11]

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