Wide Range Nematic Mixtures Incorporating 4″-n-Alkyl-4-Cyano-*p*-Terphenyls

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Summary The 4″-n-alkyl-4-cyano-*p*-terphenyls permit the formulation of colourless, stable, wide range nematic mixtures of simple eutectic compositions, valuable for electro-optic displays, and the readily prepared 4″-bromo-4-n-heptanoyl-*p*-terphenyl provides a rare example of a direct smectic B to nematic transition.

RECENTLY,[1,2] we reported on the liquid crystalline behaviour of the 4′-n-alkyl- and 4′-n-alkoxy-4-cyanobiphenyls. The n-alkyl compounds are particularly low melting, and a number are nematic (or smectic) at room temperature. As a result of their large positive dielectric anisotropies, the materials perform well[3] in electro-optic displays based on the twisted nematic effect. Furthermore, the compounds are colourless, and chemically and photochemically stable. Using eutectic mixtures,[4] the nematic ranges may be widened to 0—60 °C making the materials attractive for electro-optic displays.

The desire for even wider range nematic materials necessitates the incorporation of other compounds of much higher nematic thermal stabilities. We have therefore synthesised new colourless 4″-n-alkyl-4-cyano-*p*-terphenyls (Table 1) exhibiting high nematic thermal stabilities, allied with chemical–photochemical stability.

The compounds were examined by microscopy and differential thermal analysis. A number exhibit solid polymorphism and enthalpies for the different transitions were determined.

The importance of these new materials lies in their mixtures with the low melting biphenyls. Eutectic mixtures have low melting points and high N–I temperatures (Table 2).

TABLE 1. Transition temperatures for the compounds 4″-R·C_6H_4·C_6H_4·C_6H_4·CN-4

R	K–N or S_E Temp. (*t*/°C)	S_A–N Temp (*t*/°C)	N–I Temp. (*t*/°C)
n-C_3H_7	182	—	257·5
n-C_5H_{11}	130	—	239
n-C_6H_{13}	125	—	228
n-C_7H_{15}	134	(125·5)	222
n-C_8H_{17}[a]	127	197	216

[a] Microscopic and miscibility studies have confirmed smectic polymorphism in this compound: S_E–S_B, 128 °C and S_B–S_A, 133 °C.

K = crystal; S = smectic; N = nematic; I = isotropic liquid. Temperature in parentheses is for a monotropic transition (S_A–N).

Ternary mixture (2) provides a nematic range equivalent to the best achievable for a *quinary* mixture of biphenyls.[4] Crystallisation occurs only slowly at −15 °C when the mixture is seeded. The low melting mixture (3) has an N–I temperature 30 °C higher than that attainable using biphenyls alone.[4] As with the biphenyls,[3] the predicted and observed eutectic temperatures (m.p. and N–I) are in good agreement. Furthermore, introducing a terphenyl does not adversely affect the electrical properties of the mixtures or their performance in electro-optic displays.

The 4″-n-alkyl-4-cyano-*p*-terphenyls were synthesised from 4-bromo-*p*-terphenyl by a method[2] analogous to that for the biphenyl analogues. The intermediate 4″-n-alkanoyl-4-bromo-*p*-terphenyls are liquid crystalline (Table 3).

TABLE 2. Some predicted eutectic mixtures of 4″-n-pentyl-4-cyano-*p*-terphenyl (5CT)[a] and 4′-substituted (R) 4-cyanobiphenyls and the actual temperature ranges

Mixture	Composition R/5CT	Molar %	Predicted K–N Temp.	Predicted N–I (*t*/°C)	Actual K–N Temp.	Actual N–I (*t*/°C)
(1)	n-C_5H_{11}	86·7	17	64	14	66
	5CT	13·3				
(2)	n-C_5H_{11}	52·6	0·4	63·5	0	62·5
	n-C_7H_{15}	35·4				
	5CT	12·0				
(3)	n-C_3H_7O	23·1	9	91	5	91
	n-$C_5H_{11}O$	22·9				
	n-$C_7H_{15}O$	18·8				
	n-$C_8H_{17}O$	23·9				
	5CT	11·3				

[a] Enthalpy of melting (ΔH) for 5CT = 4·06 kcal mol^{-1}.
K = crystal; N = nematic; I = isotropic liquid.

TABLE 3. Transition temperatures for the compounds 4″-R·CO·C_6H_4·C_6H_4·C_6H_4·Br-4

R	K–N or S_E Temp. (*t*/°C)	S_E–S_B Temp. (*t*/°C)	S_B–S_A Temp. (*t*/°C)	S_B or S_A–N Temp. (*t*/°C)	N–I Temp. (*t*/°C)
C_2H_5	224	—	—	—	282·5
n-C_4H_9	204	—	—	—	250
n-C_5H_{11}	205·5	—	—	—	241
n-C_6H_{13}	178	203·5	—	212	239
n-C_7H_{15}	175	204	211·5	218	233·5

K = crystal; S_E = smectic E; S_B = smectic B; S_A = smectic A; N = nematic; I = isotropic liquid.

The n-heptanoyl compound exhibits a direct S_B–N transition previously reported[5] for only two compounds.

As a result of the usefulness of the new cyano-*p*-terphenyls in mixtures for displays and the interesting smectic polymorphism of the ketones, other homologues of the series are being investigated.

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