Eutectic Mixtures of Nematic 4′-Substituted 4-Cyanobiphenyls

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Summary A numerical technique has been used to predict eutectic compositions of some liquid crystal mixtures; good agreement was found with experimental results on mixtures of 4′-n-alkyl- and 4′-n-alkoxy-4-cyanobiphenyls some of which are nematic over the range 0—60 °C.

GRAY, HARRISON, and NASH have recently reported the discovery[1] of a family of stable nematic liquid crystals derived from 4′-n-alkyl- and 4′-n-alkoxy-4-cyanobiphenyls. Electro-optic liquid-crystal devices[2] require materials that are nematic over the range 0—60 °C, and eutectic mixtures have to be used to cover this temperature range. The production of suitable eutectic mixtures by experiments alone is an extremely lengthy procedure. This task has been considerably simplified by a simple calculation.

Schröder and Johnson[3] have reported that the Schröder–van Laar equation[4] is a valid description of binary mixtures of liquid crystals chosen from a single family. This equation (1) relates the melting point (T) of a mixture to the mole fraction (X_A) of component A, where ΔH_A and T_A are the

$$\ln X_A = \Delta H_A(1/T_A - 1/T)/R \quad (1)$$

latent heat of melting and the m.p. of pure component A, and R is the gas constant. For a mixture with N components there will be N such equations, which can be solved simultaneously with $\sum_{i=A}^{N} X_I = 1$ to give the values of X_I and T corresponding to the eutectic mixture. However we have found a simple method of solution which can be carried out on a Hewlett Packard 9820A calculator. A value for T is chosen and the mole fractions (X_A, $X_B \cdots X_N$) are evaluated. When the sum $\sum_{i=A}^{N} X_I$ equals unity, the

value of T is the eutectic temperature and the mole fractions describe the eutectic composition. When the sum is greater than unity the value chosen for T is too high, and when less than unity, it is too low. Successive approximations enable the eutectic temperature to be found at the fifth attempt on average. Estimates of the nematic–isotropic transition temperature, T_{N-I}, of the mixtures were made using a linear extrapolation of the individual T_{N-I} values weighted by the eutectic mole fraction:

$$T_{(N-I)} = \sum_{i=A}^{N} X_1 T_{(N-I)1}$$

These calculations have been used to predict the nematic ranges and compositions of eutectic mixtures containing up to ten components, although the results have not been tested experimentally beyond five components.

The m.p.s (K–N, S, or I) and nematic–isotropic transition temperatures of the 4′-substituted 4-cyanobiphenyls were determined by optical microscopy using a Reichert polarizing microscope in conjunction with a heated stage, the results being shown in Table 1. Also shown are the latent heats of melting which were determined by differential calorimetry using a Du Pont 900 thermal analyser with a DSC cell. Where polymorphism of the solid occurs, the figures in Table 1 refer to the most stable (highest melting) solid form. Four of the 4′-substituted 4-cyanobiphenyls (R = n-$C_5H_{11}O$, n-$C_6H_{13}O$, n-$C_7H_{15}O$, and n-$C_9H_{19}O$) are known to exhibit less stable solid forms persisting for several hours at 20 °C, whilst the compound with R = n-C_7H_{15} shows a less stable solid form which persists for a few seconds only.

TABLE 1. Mesomorphic transition temperatures and latent heats of melting for the compounds

p-R·C_6H_4·C_6H_4·CN-*p*

R	K–N, S, or I Temp. (*t*/°C)	S–N Temp. (*t*/°C)	N–I Temp. (*t*/°C)	Latent heat (kcal/mol)
n-C_4H_9	46·5	—	(16·5)	5·5
n-C_5H_{11}	22·5	—	35	4·1
n-C_6H_{13}	13·5	—	27	5·8
n-C_7H_{15}	28·5	—	42	6·2
n-C_8H_{17}	21	32·5	40	5·3
n-C_9H_{19}	40·5	44·5	47·5	8·0
n-C_3H_7O	71·5	—	(64)	4·6
n-C_4H_9O	78	—	(75·5)	5·6
n-$C_5H_{11}O$	48	—	67·5	6·9
n-$C_6H_{13}O$	58	—	76·5	7·1
n-$C_7H_{15}O$	53·5	—	75	6·9
n-$C_8H_{17}O$	54·5	67	80	5·9

K = crystal; N = nematic; S = smectic; I = isotropic liquid. Temperatures in parentheses are for monotropic transitions.

Mixtures of these compounds can also exhibit polymorphism, producing a lower melting mixture which slowly reverts to the stable form when kept just below the m.p. This transition can be particularly slow for mixtures melting below 20 °C.

TABLE 2. Some predicted eutectic mixtures of the 4′-substituted 4-cyanobiphenyls and the actual temperature ranges

Mixture	Composition R, molar %	Predicted K–N, Temp. (*t*/°C)	Predicted N–I (*t*/°C)	Actual K–N, Temp. (*t*/°C)	Actual N–I (*t*/°C)
1	n-C_5H_{11}, 59 n-C_7H_{15}, 41	3	37·5	−2	37·5
2	n-$C_5H_{11}O$, 55 n-$C_7H_{15}O$, 45	31	71	20 [30	70·5 70·5][a]
3	n-C_7H_{15}, 52 n-$C_5H_{11}O$, 23 n-$C_8H_{17}O$, 25	10	58	6	56·5
4	n-C_7H_{15}, 44 n-$C_5H_{11}O$, 19 n-$C_7H_{15}O$, 16 n-$C_8H_{17}O$, 21	6	60	4	61
5	n-C_5H_{11}, 55 n-$C_5H_{11}O$, 15 n-$C_7H_{15}O$, 13 n-$C_8H_{17}O$, 17	0	52·5	−2	54·5
6	n-C_7H_{15}, 36 n-$C_8H_{17}O$, 18 n-$C_5H_{11}O$, 15 n-$C_7H_{15}O$, 12 n-$C_8H_{17}O$, 19	0	61	0	60·5

[a] After storage of the solid for several days at 18 °C.

A selection of the eutectic temperatures and compositions of the more useful mixtures is shown in Table 2. Binary mixtures have a typical nematic range of *ca.* 40 °C, ternary of 50 °C, quaternary of 55 °C, and quinary of 60 °C. The midpoint of these nematic ranges is altered by the choice of components.

Although polymorphism is evident in mixture 2, there is no evidence for it in other mixtures. Most of the experimental results in Table 2 are simply for mixtures prepared according to the predicted eutectic compositions, but for mixtures 1 and 2 the eutectic compositions were checked experimentally by examining a range of compositions and found to agree with the predicted values. The tendency is for the experimentally determined eutectic temperature to be slightly lower than the predicted value.

In conclusion, the calculation described is a valuable method of considerably reducing the experimental work involved in the production of eutectic mixtures of nematic liquid crystals. It should also be suitable for mixtures involving smetic and cholesteric liquid crystals.

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