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FORMULATION AND PREDICTED PROPERTIES OF NEMATIC
EUTECTIC MIXTURES OF ESTERS(U) HUGHES RESEARCH LABS
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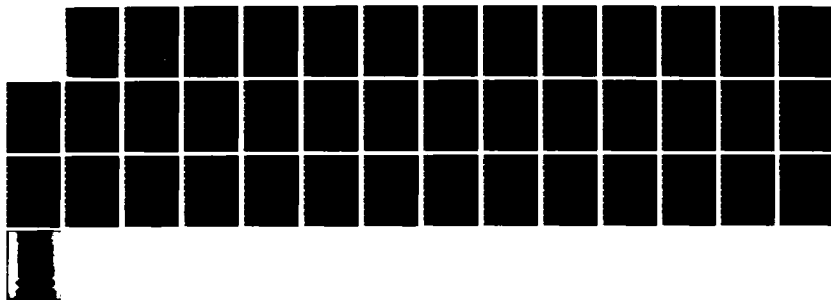
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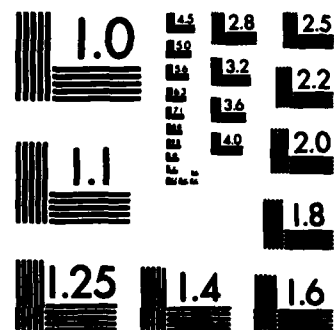
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TECHNICAL REPORT NO. 2

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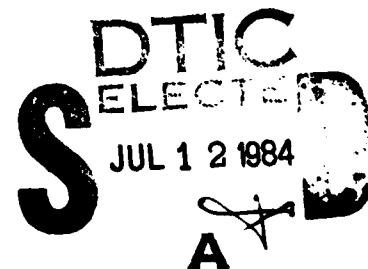
by

J.D. Margerum, A.M. Lackner, J.E. Jensen, L.J. Miller
W.H. Smith, Jr., S.-M. Wong, and C.I. van Ast

Presented at the Fifth International Symposium on Liquid
Crystals and Ordered Fluids, American Chemical Society Meeting,
St. Louis, MO, April 8-13, 1984.

Hughes Research Laboratories
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both from homologous series and from different classes of esters. Approximate class values of birefringence, dielectric anisotropy, and viscosity are assigned to each type of ester structure, based on experimental results in selected mixtures of short molecular length. Properties of multi-component eutectic mixtures are calculated, and comparisons are shown between the predicted and the observed values of melting point, clearpoint, viscosity, dielectric anisotropy, and birefringence of new ester mixtures developed for dynamic scattering devices and displays.

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FORMULATION AND PREDICTED PROPERTIES OF
NEMATIC EUTECTIC MIXTURES OF ESTERS*

J. D. MARGERUM, A. M. LACKNER
J. E. JENSEN, L. J. MILLER, W. H. SMITH, JR.
S.-M. WONG, AND C. I. VAN AST
Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, California 90265

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1. INTRODUCTION

Multicomponent liquid crystal (LC) mixtures are generally needed to obtain a nematic phase with a wide temperature range. In the formulation of LCs for dynamic scattering applications, we have shown that it is advantageous to use short molecular length components to obtain low viscosity and other favorable properties.¹⁻⁵ However, special selection techniques are required in choosing components in order to prepare LC eutectic mixtures when combining short length ester components of similar molecular length. Otherwise, such components can act as solid solutions and not give a lowered melting point. It is also highly desirable to be able to predict key anisotropic properties as well as the nematic temperature range of each new multicomponent mixture being considered for use. In this paper both of these issues are addressed. We describe selection rules for obtaining binary eutectic mixtures with ester components of essentially equal molecular length, and we show how to use these LC pairs in the formulation of multicomponent eutectic mixtures with relatively short molecular length. We also show how we assign approximate class values of birefringence (Δn), dielectric anisotropy ($\Delta \epsilon$), and viscosity (η) to the various types of ester structures being considered for use in our mixtures. Finally, we compare actual experimental values versus our predicted calculations of nematic

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melting point (mp) and clearpoint (clpt.), as well as predicted values of Δn , $\Delta \epsilon$, and η at 25°C for several multicomponent LC ester mixtures of interest for dynamic scattering applications.

2. EXPERIMENTAL

This study includes data on and calculations with 32 different classes of ester LC structures, with specific reference to 95 individual components. Both the classes and the individual compounds are referred to here by a code nomenclature similar to ones we have used previously.¹⁻⁵ Class codes for various structures are shown in Figures 1, 2 and 3. The class structures which we reported previously are shown in Figure 1. The class structure and code of other ester compounds synthesized by us more recently⁶ are shown in Figure 2. The structure and code for other esters obtained commercially are given in Figure 3. The R and R' end groups in each class are n-alkyl groups, and the specific compounds are identified by numbers corresponding to the number of carbon atoms in these alkyl groups. For example, in the R-R' class p-n-heptylphenyl p-n-butylbenzoate is represented by 7-4, while in the RO-R' class p-ethoxyphenyl p-n-propylbenzoate is 20-3. Thus in our code the dash, -, is for the central phenyl benzoate structure, with alternate central structures represented by S for phenyl thiobenzoate, -[C] for phenyl cyclohexanecarboxylate, [C]- for cyclohexyl

STRUCTURE CLASS	CLASS CODE	REFERENCE
RO-  -OOC-  -R'	RO-[C]R'	2, 3, 5
R-  -OOC-  -R'	R-R'	5
RO-  -OOC-  -R'	RO-R'	1, 3, 5
R-  -OOC-  -OR'	R-OR'	4, 5
RO-  -OOC-  -OR'	RO-OR'	3, 5
RO-  -SOC-  -R'	ROSR'	3, 5
R-  -SOC-  -OR'	R $\bar{S}$ OR'	5
RO-  -SOC-  -OR'	RO $\bar{S}$ OR'	3, 5
NC-  -OOC-  -R	NC-R	5
R-  -OOC-  -OOC-R'	R-OOCR'	5
RO-  -OOC-  -OOC-R'	RO-OOCR'	3, 5
R-  -OOC-  -OOC-  -R'	R-OOCPR'	5
R-  -OOC-  -OOC-  -R'	R-(Cl)OOCPR'	3, 5
R-  -  -OOC-  -R'	RP-R'	5
R-  -OOC-  -  -R'	R-PR'	5
R-  -OOC-  -  -R'	R(CN)-PR'	3, 5
R-  -OOC-  -  -OR'	R(CN)-POR'	5

FIGURE 1 Structure and class code of esters previously reported.

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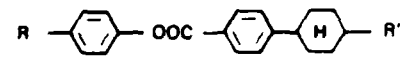
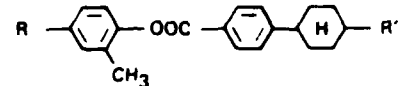
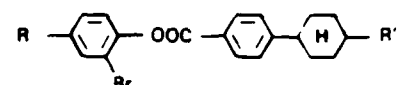
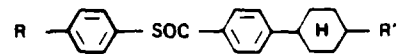
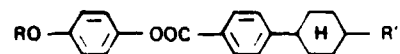
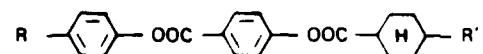
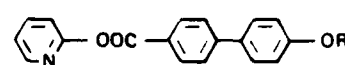
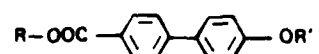
STRUCTURE CLASS	CLASS CODE	COMPOUNDS
	R-YR'	2-Y3, 2-Y5, 4-Y3
	R(CH ₃)-YR'	1(CH ₃)-Y3
	R(Br)-YR'	1(Br)-Y3
	RSYR'	1SY3
	RO-YR'	20-Y3, 20-Y5
	R'-OOCYR'	4-OOCY4
	[Py]-POR	[Py]-PO5
	ROOCPOR'	3OOCPP06

FIGURE 2 Structure and class code of other esters synthesized⁶

benzoate, [C]-[C] for cyclohexyl cyclohexanecarboxylate, and [Py]- for *o*-pyridyl benzoate. Additional rings in the structure are represented by P for phenyl and Y for cyclohexyl, while only *o*-substituents are shown in parenthesis, e.g. 1(Br)-Y3 stands for *o*-bromo-*p*-tolyl *p*-(4-propylcyclohexyl)benzoate.

The molecular length (L) of each compound is

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measured with a molecular model, and thermal analysis data on mp, clpt. and heat of fusion (ΔH_f) are obtained by differential scanning calorimetry. In previous reports,¹⁻⁴ these methods are described and the results were tabulated for many of the compounds used in this study. Table I shows the molecular length and thermal properties of the additional esters used here for eutectic mixture calculations.

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STRUCTURE CLASS	CLASS CODE	COMPOUNDS	SOURCE
R —  — OOC —  — R'	R-[C]R'	5-[C]5	ATOMERGIC
NC —  — OOC —  — R	NC-[C]R	NC-[C]5	ATOMERGIC
RO —  — SOC —  — R'	RO5[C]R'	205[C]5	ATOMERGIC
R —  — OOC —  —  — R'	R-YR'	3-Y3	MERCK
R —  — OOC —  —  — R'	R(CN)-YR'	4(CN)-Y3	MERCK
R —  —  — OOC —  — R'	RY-[C]R'	3Y-[C]4	MERCK
R —  — OOC —  —  — R'	R[C]-YR'	3[C]-Y2, 3[C]-Y4	MERCK
R —  — OOC —  —  — R'	R[C]-[C]YR'	3[C]-[C]Y4	MERCK

FIGURE 3 Structure and class code of commercial esters⁶

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TABLE I Thermal properties of components.^a

Component	L (Å)	m_p (°C)	$C_{\text{opt.}}$ (°C)	ΔH_f (kcal/mole)
10-4	19.70	61.8	24.6	5.99
10-01	17.52	123.8	20.0 ^b	7.39
10-04	21.09	91.5	79.2	9.65
10-06	23.54	93.1	76.4	10.86
20-01	18.72	96.7	93.0	7.78
40-01	21.13	79.1	80.4	8.24
1S04	20.18	81.7	80.0	7.66
10S4	20.00	64.5	57.4	6.66
20S3	19.98	85.4	96.2	6.43
20S5	22.38	81.3	87.5	7.17
40S1	20.12	65.9	78.2	6.66
40S3	22.50	50.9	81.8	5.22
40S6	26.20	40.2	69.6	4.98
2-Y3	23.05	103.8	175.1	5.13
3-Y3	24.28	89.0	186.0	5.00
4-Y3	25.52	91.7	174.2	5.33
1SY3	22.53	120.4	219.0	4.45
3P-4	25.55	93.4	182.3	4.97
4-OOCp4	28.31	88.5	186.0	5.71
4-OOCY4	28.74	64.8	185.0	7.27

^aThese properties for the other components used in this study for eutectic calculations have been reported previously. (References 1-4).

^bEstimated.

The experimental methods of measuring $\Delta\epsilon$ and Δn are the same as reported previously,¹⁻⁴ except that no conductivity dopants are used. In the $\Delta\epsilon$ measurements the field strength is 6.5 kG and the cells are 503 μm thick. The value of the $\Delta\epsilon$ measurement is often independent of the measuring frequency in the 100 to 10,000 Hz range, in which case the value reported is taken at 5,000 Hz. When the $\Delta\epsilon$ values are observed to decrease with

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increasing frequency, then a value at a lower frequency (e.g. 200,500 or 1000 Hz) is used in the range where $\Delta\epsilon$ is not changing with frequency. The flow viscosity measurements and assigned class viscosities are reported in other papers¹⁻⁷ from our laboratory.

The Schroeder-Van Laar relationship, equation 1, is used to estimate the crystal to nematic melting point and the mole fraction of the components in a eutectic mixture.

$$T_i = \frac{\Delta H_f}{\frac{\Delta H_f}{T_M} - R \ln x_i}, \quad (1)$$

Where: T_i = upper end of the melting range of i in the mixture; ΔH_f = molar heat of fusion of pure compound i ; T_M = melting point of pure compounds; x_i = mole fraction of component i in the mixture; and R = gas constant.

When Eq. 1 is satisfied for each component, the mixture will be a eutectic mixture -- assuming that ideal interaction occurs. This calculation, which is made with a computer program for multicomponent mixtures, is assumed to give approximately the correct composition for the actual eutectic mixture. If the mp is considerably higher than the calculated value, then a more accurate eutectic mixture can be determined experimentally by partial freezing

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fractionations of the calculated eutectic mixture.⁸

The nematic to isotropic clearpoint (T_c) of a multicomponent mixture can be estimated from the composition and the clearpoints of the individual components ($T_{c(i)}$):

$$T_c = \sum_{i=1}^n \left(x_i T_{c(i)} \right). \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Selection of Short Length Mixtures

Although ester mixtures with shorter average molecular length (L) show superior dynamic scattering properties over similar mixtures with longer L , special care must be taken to select short L components which will form eutectic mixtures with one another. If the compounds are too similar in structure and length they can form a solid solution mixture rather than a eutectic mixture. This is the case, for example, with a mixture of 60-4 and 60-5 which show a melting point between those of the two pure components rather than one below both of them as is expected from an eutectic mixture. Often this problem had previously been avoided by selecting mixture components which were each different in length by at least two methylene groups. However, multicomponent ester mixtures are needed to obtain broad nematic temperature ranges, and when

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many components are used together it is very difficult to obtain short mixture if each component is two or more methylene groups different in length from all of the others. To circumvent this problem we have devised methods of selecting equal length components which can be used together in eutectic mixtures.⁹

One technique (Method I) is to use a binary eutectic mixture consisting of equal length ester components from a homologous series by selecting components in which the alkyl endgroups are substantially different at the same molecular position. Several sets of such binary mixtures are listed in Table II under Method I. In general if the number of carbon atoms in the n-alkyl end groups are represented by R_a and R_a' in compound A, and by R_b and R_b' in compound B, then a binary eutectic mixture with A and B of equal length (i.e. $R_a + R_a' = R_b + R_b'$) can be made by selecting alkyl groups that differ by 2 carbons or more at each specific end of the structure, i.e. $|R_a - R_b| \geq 2$ and $|R_a' - R_b'| \geq 2$. This is illustrated for three different homologous series in Table II, by combinations of such as 20-3/40-1, 20S5/40S3, and 10-04/40-01.

Another technique (Method II) is to use a binary eutectic mixture consisting of two essentially equal length components from different classes of esters. In the notation above for compounds A and B of different classes, binary eutectics can be made when

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TABLE II Binary LC eutectics with equal length components.

Components	Thermal Data ^a	Mole Fraction ^b	Nematic Calc. (°C)	Temp. Range Obs. (°C)
<u>Method I</u>				
20-3	1,3	0.515	53.0-60.6	52.1-61.9
40-1	1	0.484		
20-5	1,3	0.581	47.3-60.2	43.8-60.8
40-3	1	0.419		
20S3	Table I	0.367	50.5-84.7	45.4-84.4
40S1	Table I	0.633		
20S5	Table I	0.256	39.4-83.3	39.2-75.5
40S3	Table I	0.744		
10S4	Table I	0.505	42.7-67.6	28.8-65.8
40S1	Table I	0.495		
10-04	Table I	0.366	66.0-80.0	64.8-81.2
40-01	Table I	0.634		
<u>Method II</u>				
10-4	Table I	0.583	43.6-38.2 ^c	43.1-39.0 ^c
10S4	Table I	0.417		
10-4	Table I	0.680	48.0-42.3 ^c	49.5-38.2 ^c
1S04	Table I	0.320		
10S5	3	0.358	24.8-70.9	27.9-68.4
10-[C]5	2,3	0.642		
20-3	1,3	0.319	36.4-74.6	37.8-73.9
20-[C]3	2,3	0.681		
40-6	1,3	0.412	20.7-61.1	21.9-61.8
40S6	Table I	0.588		

^aSource of experimental mp, clpt., ΔH_f , and molecular length.

^bCalculated mole fraction from Schroeder-Van Laar equation.

^cMonotropic mixture.

$R_a + R_a' = R_b + R_b'$. In the cases shown in Table II, Method II, the alkyl groups can be the same at each specific end of the structure,

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e.g. $R_a = R_b$ and $R_a' = R_b'$ in binary combinations such as 10-4/1094 and 20-3/20-[C]3, etc.

However, it is also all right if $R_a \neq R_b$ when other equal length components from these classes are combined, e.g. 20-3/10-[C]4. In some cases (not shown in Table II) it is necessary to use a combination of Methods I and II. For example the calculated binary mixture for 60-01/60901 gives a solid state solution, while the mixture 60-01/10906 gives an eutectic type depressed melting point.

Each of the binary sets in Table II is formulated with the mole fractions calculated by the Schroeder-Van Laar relationship (equation 1), and experimentally each set is a eutectic type mixture with a melting point similar to the calculated (ideal) value. The observed clearpoints are also shown for these binaries in Table II, and are all close to the ideal values calculated by equation 2. However, the clearpoints are often near (usually slightly below) the values calculated whether or not the mixture shows eutectic properties.

The binary set of LC components described by our methods I and II, and illustrated by the examples in Table II, can be used in the formulation of multicomponent LC eutectic mixtures with relatively short L by combining one or more sets of these short length binaries together with other short length ester LC components. Combining sets of binary mixtures

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with common components can give tertiary and quaternary eutectics of equal length LCs. Our selection rules for the other components are that in general they should differ from the binaries and from one another either by being from a different ester class or by being about two methylene groups (2.5A) or more different in length. An exception is that some very short length components of the same class can be used together when differing by only one methylene group if this difference is between a methyl and an ethyl end group. As explained in the experimental section, the mole fraction composition is calculated for each new multicomponent eutectic by using the Schroeder-Van Laar equation. This is assumed to give a relatively close approximation to the true eutectic composition (if it exists for the components selected), and this theoretical composition is the one that we use to test the mixture.

A very short E eutectic mixture of RO-R' components is the HRL-2N42 mixture whose composition and properties are shown in Table III. This five component homologous mixture contains two set of Method I binaries (20-3/40-1 and 20-5/40-3) along with 10-1, which is a pseudo-nematic component.¹ The observed nematic range is actually better than the calculated range, and this particular mixture is used extensively in the present work as a host LC for

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TABLE III RO-R' eutectic mixture HRL-2N42.

Composition ¹		Characteristics		
Components	Mole. Fraction	Property	Calc.	Obs.
10-1	0.112	mp(°C)	28.8	5.3
20-3	0.222	Clpt.(°C)	57.0	57.7
20-5	0.283	Length(Å)	20.39	-
40-1	0.191	$\Delta n(23^\circ)$	-	0.158
40-3	0.192	$\Delta \epsilon(25^\circ)$	-	-0.21
		$n(25^\circ, cP)$	-	32.6

experiments in determining the relative class Δn and $\Delta \epsilon$ contributions of other LC components. Several other such RO-R' eutectic mixtures have been described¹ which include equal length binary set components. Another relatively short L eutectic mixture from a different homologous group is the 7-component RO-OR' mixture HRL-2N54 shown in Table IV. It contains the two binary sets 10-04/40-01 and 10-06/60-01. It also contains the short length components 10-01 and 20-01. The observed nematic range of 2N54 is wider than the calculated one. Table V shows an example of the short length thioester eutectic mixture HRL-5N3. This is a 7-component eutectic made with two classes of thioester LCs. It includes three components of the same length (corresponding to three binary sets), namely 10S4/20S3/40S1. The 5N3 mixture has a nematic range very close to the calculated range. Before examining other multi-component eutectics formulated with our selection rules, the following sections describe the assignments of

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TABLE IV RO-OR' eutectic mixture HRL-2N54.

Composition			Characteristics		
Components	Ref.	Mole. Fraction	Property	Calc.	Obs.
10-01	I	0.145	mp(°C)	24.9	-
10-04	I	0.051	Clpt.(°C)	78.3	80.2
10-06	I	0.033	Length(Å)	23.23	-
20-01	I	0.078	$\Delta n(23^\circ\text{C})$	-	0.171
40-01	I	0.118	$\Delta \epsilon(25^\circ)$	-	-0.35
40-05	3	0.291	$n(25^\circ, \text{cP})$	-	106
60-01	3	0.385			

TABLE V Thioester eutectic mixture HRL-5N3.

Composition			Characteristics		
Components	Ref.	Mole Fraction	Property	Calc.	Obs.
10S4	I	0.094	mp(°C)	-0.6	-
10S5	3	0.123	Clpt.(°C)	78.6	76.0
10S06	3	0.110	Length(Å)	23.05	-
20S3	I	0.058			
40S1	I	0.097			
40S3	I	0.217			
40S6	I	0.302			

class values of Δn , $\Delta \epsilon$, and n . These are used in our calculations to predict these anisotropic properties, as well as the nematic temperature range, for new mixtures.

3.2 Assignment of Class Birefringence

The Δn of a nematic ester LC depends mainly on the class of the ester structure, and somewhat upon the length of its alkyl end groups. This has been shown previously for 100% mixtures of RO-R', RO-[C]R', and R-OR' structures.^{1,2,4} Because it

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is not easy to prepare 100% mixtures for each ester class structure of interest, we instead obtain approximate Δn class values by measuring the Δn of mixtures containing specific components of a given class added to a standard host LC. The RO-R' mixture 2N42 is used as the host, and it is generally mixed with 25 mole percent of the components being studied. The Δn contribution of the added component is estimated by the approximation of simply subtracting out the contribution due to the host. Thus with 25% added components to 75% 2N42 at 23°C, the Δn_{calc} for the added components is obtained from equation 3.

$$\Delta n_{\text{obs}} = 0.25(\Delta n_{\text{calc}}) + 0.75(0.158) \quad (3)$$

For example a Δn_{obs} of 0.170 is measured when 25% of 4093 is added to 2N42, giving a Δn_{calc} of 0.206 from which we assign RO9R' a Δn_{class} of 0.21 in the environment of a short length RO-R' host LC. This is the manner in which most of the Δn_{class} values are assigned for the 30 different ester classes shown in Table VI. In several cases these extrapolated Δn_{class} values are found to be in good agreement with Δn_{obs} for 100% mixtures of the same class, as noted in Table VI for RO-OR', R-(Cl)OOCPR', and RO-[C]R' mixtures. The Δn_{class} assignments for RO-R' and R-OR' mixtures are estimated from 100% mixtures at an λ of 22 Å. The Δn_{class} for R-R' is taken from the average value obtained from measuring three

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TABLE VI Assignment of class birefringence values.

Class	$\Delta n_{\text{class}}^a$	Components Measured ^b
RP-R', R-PR'	0.25	3P-4, 5P-4, 5-P5
R(CN)-PR'	0.25	7(CN)-P5
R(CN)-POR'	0.23	4(CN)-PO3
ROSOR'	0.23	1OSO4, 1OSO6
RSYR'	0.23	1SY3 (10%)
ROSR'	0.21	4OS3
RSOR'	0.21	1SO6
R-OOCPR'	0.18	2-OOCP2, 4-OOCP4
RO-OR'	0.17	4O-O5, 6O-O5, 100% 2N54)
RO-YR'	0.17	2O-Y3, 2O-Y5
ROOCPOR'	0.17	3OOCPP06
R-(Cl)OOCPR'	0.16	2-(Cl)OOC2, 5-(Cl)OOC5 (also, 100% 2P37)
R-YR'	0.15	2-Y3, 4-Y3
RO-R'	0.15	2N42; 2N43 etc. ¹ (100%)
R-OR'	0.14	2P13; etc. ⁴ (100%)
R(Br)-YR'	0.14	1(Br)-Y3
NC-R	0.13	NC-4, NC-7
R(CH ₃)-YR'	0.13	1(CH ₃)-Y3
RO-OOCR'	0.13	4O-OOC4, 6O-OOC5
R-OOCR'	0.12	3-OOC5, 7-OOC5
R(CN)-YR'	0.11	4(CN)-Y3
RO[C]R'	0.11	2OS[C]5
R-OOCYR'	0.11	4-OOCY4
RO-[C]R'	0.09	2O-[C]5 (also, 100% 6N7) ²
NC-[C]R	0.08	NC-[C]5
R[C]-YR'	0.08	3[C]-Y2, 3[C]-Y4
RY-[C]R'	0.07	3Y-[C]4, 3Y-[C]5
R-R'	0.07	7-6; 7-4; 5-5
R-[C]R'	0.04	5-[C]5
R[C]-[C]YR'	0.04	3[C]-[C]Y4

^aExtrapolated value of Δn at 23°C for ester classes in environment of short length RO-R mixtures.

^bMeasured in HRL-2N42 with 25% concentration of components (total) unless noted otherwise.

different mixtures of R-R' components in the host. In many cases more than one component of a

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given class is needed to obtain a 25% solution, such as the use of 10S04 and 10S06 together in 2N42. When such component mixtures are used for the additives, the mole percent of each individual component is the same as those reported in our viscosity studies.^{5,6}

Higher birefringence values in LC structures are generally related to higher molecular polarizability along the director axis. This is particularly noticeable in Table VI for the Δn_{class} values of biphenyl ester and thioester structures. Lower Δn_{class} values are found when cyclohexyl rings replace phenyl rings and when alkyl groups replace alkoxy groups. Thus the ester class $R[C]-[C]YR'$ with neither phenyl nor alkoxy groups has the lowest Δn_{class} in Table VI.

3.3 Assignment of Class Dielectric Anisotropy

As in the birefringence studies, we assign class values of $\Delta\epsilon$ based largely on measurements of selected components mixed with the RO-R' host 2N42. We are aware that intermolecular association effects in LCs can substantially alter observed values of $\Delta\epsilon$, as was noted previously particularly for longer length R-OR' mixtures.⁴ Thus, in the strict sense our extrapolated $\Delta\epsilon_{\text{class}}$ values from measurements in 2N42 represent just the contributions of the added components in the environment of the short length RO-R' host. When the final mixture

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consists of 25% added components and 75% 2N42, then the $\Delta\epsilon_{\text{calc}}$ for the additives at 25°C is obtained from equation 4:

$$\Delta\epsilon_{\text{obs}} = 0.25 (\Delta\epsilon_{\text{calc}}) - 0.75 (0.21) \quad (4)$$

For example, a $\Delta\epsilon_{\text{obs}}$ of 0.138 is measured when 25 mole percent of 1(CH₃)-Y3 is added to 2N42, giving a $\Delta\epsilon_{\text{calc}}$ of 1.18 from which we assign R(CH₃)-YR' a $\Delta\epsilon_{\text{class}}$ of 1.2. A list is shown in Table VII for the assigned $\Delta\epsilon_{\text{class}}$ values of 23 different class ester structures. As indicated in Table VII, most of the assignments are made from measurements of 10 to 25% additives in 2N42. The $\Delta\epsilon_{\text{class}}$ values for the RO-R', and R-OR' structures are taken from the 100% mixtures of these previously studied. ^{1,4}

Several generalizations can be noted from the relative $\Delta\epsilon_{\text{class}}$ values in Table VII. The thiobenzoate structures are all considerably more positive in $\Delta\epsilon_{\text{class}}$ values than the corresponding benzoate structures, e.g. RSYR'(1.6) vs. R-YR'(0.6), ROSOR'(0.4) vs. RO-OR'(-0.3), and ROSR'(0.0) vs. RO-R'(-0.2). Use of a cyclohexanecarboxylate group in place of a benzoate group gives a considerably more negative value of $\Delta\epsilon_{\text{class}}$, e.g. R-OOCYR'(0.3) vs. R-OOCPR'(7.3), RO-[C]R'(-2.1) vs. RO-R'(-0.2), and R-[C]R'(-1.2) vs. R-R'(0.1). These results, which are summarized schematically in Figure 4 for Δn and η as well as $\Delta\epsilon$, are

TABLE VII Assignment of class dielectric anisotropy values.

Class	$\Delta\epsilon_{\text{class}}^a$	Components Measured	Concn. ^b
NC-[C]R	19.8	NC-[C]5	25%
R-(Cl)OOCPR'	7.9(4.7) ^c	2-(Cl)OOC2,5-(Cl)OOC5	10%
R-OOCPR'	7.3(4.7) ^c	2-OOC2, 4-OOC4	25%
RSYR'	1.6	1SY3	12.5%
R(CH ₃)-YR'	1.2	1(CH ₃)-Y3	25%
RP-R', R-PR'	0.8	3P-4, 5P-4, 5-P5	25%
R-YR'	0.6	2-Y3, 4-Y3, 2-Y5	25%
ROSR'	0.4	1OS4, 1OS6	25%
R-OOCYR'	0.3	4-OOCY4	12.5%
R-OR'	0.2	2P13, etc. ⁴	100%
RO-YR'	0.1	2O-Y3, 2O-Y5	25%
R-R'	0.1	7-4	25%
ROSR'	0.0	4OS3	25%
ROOCPOR'	0.0	3OOCPO6	25%
RO-R'	-0.2	2N42; 2N43; etc. ¹	100%
RO-OR'	-0.3	6O-O1; 4O-O5, 6O-O5	25%
R(Br)-YR'	-0.8	1(Br)-Y3	25%
RO-OOCR'	-1.0	4O-OOC4, 6O-OOC5	25%
R-[C]R'	-1.2(-0.3) ^c	5-[C]5	25%
RO-[C]R'	-2.1(-1.4) ^c	2O-[C]3	25%
(Py)-POR	-2.5	(Py)-PO5	10%
R(CN)-PR'	-5.4(-3.7) ^c	7(CN)-P5	25%
R(CN)-YR'	-6.5(-3.7) ^c	4(CN)-Y3	10%

^aExtrapolated value of $\Delta\epsilon$ at 25°C for ester classes in environment of short length RO-R mixtures.

^bConcentration of components (total) added to HRL-2N42 for $\Delta\epsilon$ measurement.

^c $\Delta\epsilon_{\text{class}}$ values extrapolated from 25°C measurements of $\Delta\epsilon$ for the components in the RO-[C]R' mixture HRL-6N7.

consistent with the relative polarizability along the long axis of these molecules.

In Table VII we also note several $\Delta\epsilon'_{\text{class}}$ values calculated for components measured in the short length RO-[C]R' mixture HRL-6N7. These $\Delta\epsilon'_{\text{class}}$ values are all smaller in magnitude

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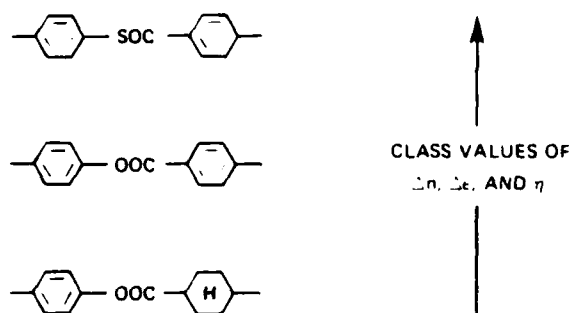


FIGURE 4 Central structure effect on relative class values, showing direction of positive increase

(positive or negative) than the $\Delta \epsilon_{\text{class}}$ values measured in 2N42. We do not yet know what causes the differences between our calculated $\Delta \epsilon_{\text{class}}$ and $\Delta \epsilon'_{\text{class}}$ values. Each molecule in the 2N42 host has two phenyl rings which should provide a strongly positive magnetic anisotropy and correspondingly good magnetic field alignment along the LC direction in the $\Delta \epsilon$ measurements. Each molecule in the 6N7 host has one phenyl ring and one cyclohexyl ring, resulting in a substantially reduced magnetic anisotropy as compared to molecules with two phenyl rings.¹⁰ However, because our measured $\Delta \epsilon$ values are not strongly affected by variations in the magnetic field strength between 3.8 to 6.9 kG, we believe that the 6N7 is nearly fully aligned at the 6.5 kG setting used in our experiments. Perhaps the molecular axis of a guest additive is aligned at a different angle with respect to the director

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of the 6N7 host than that of the 2N42 host. Or, maybe the magnetic field alignment direction is off-axis from the LC director in 6N7. These are only speculations, and additional studies will be necessary to determine the source of the $\Delta\epsilon_{\text{class}}$ and $\Delta\epsilon'_{\text{class}}$ differences.

3.4 Assignment of Class Viscosity

The assignment of relative values of class viscosity for 18 different ester classes (in an RO-R' host LC) has been reported previously.⁵ The class viscosities of many additional classes of esters are assigned similarly in a new paper.⁶ In nearly every case these η_{class} values are assigned by extrapolating the effect of 10 to 25% of the component on the flow viscosity of 2N42 at 25°C. Thus, these η_{class} values are just relative values comparing the effect of each structural class on the η of a standard short length RO-R' mixture. In an environment different from this type of RO-R' mixture, the additives would be expected to show a different η_{class} . Nevertheless, because most of the multi-component mixtures which we are studying contain several short length RO-R' components, the η_{class} values derived from 2N42 are in fact quite useful in predicting the viscosity of new eutectic mixtures, as noted below.

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3.5 Formulation and Predicted Properties of Mixtures

Our Method I of using equal length binary sets of short length LC components in multicomponent homologous mixtures is illustrated by previously reported RO-R' mixtures¹ HRL-2N42, -2N43, -2N44, and -2N48, as well as the R-OR mixture⁴ HRL-2P21. In the RO-R' mixtures the binary sets 20-3/40-1 and 20-5/40-3 are used in 2N42 and 2N43, while 20-5/40-3 is used in 2N44, and 60-5/80-3 is used in 2N48. In the R-OR' mixture the binary set 3-05/7-01 is used.

Our Method II of using equal length binary sets of different class LCs in multicomponent mixtures is illustrated by several mixtures previously described.³ In particular: HRL-2N52 contains the binary sets 20-3/10-00C3 and 40-05/40-00C4, HRL-25N4 contains 60-01/10S06, HRL-26N3 contains the tertiary set 60-5/60-[C]5/80-3, HRL-26N4 contains the tertiary set 20-3/20-[C]3/10-00C3, and HRL-256N5 contains this same 20-3/20-[C]3/10-00C3 set along with 60-01/10S06. In Table VII we show the overall class component compositions for these mixtures (along with HRL-246N1) and we compare our calculated values of mp, clpt., Δn , $\Delta \epsilon$, and n with our observed values. The melting point and clearpoint are calculated using equations 1 and 2, respectively, while the other properties are estimated simply by summing the total mole fraction of each class (x_j) times its assigned

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class value (equations 5-7).

$$\Delta n_{\text{mix}} = \sum (\Delta n_{\text{class}})_j \cdot x_j \quad (5)$$

$$\Delta \epsilon_{\text{mix}} = \sum (\Delta \epsilon_{\text{class}})_j \cdot x_j \quad (6)$$

$$\eta_{\text{mix}} = \sum (\eta_{\text{class}})_j \cdot x_j \quad (7)$$

The assigned class values of Δn and $\Delta \epsilon$ are taken from Tables VI and VII, respectively, while the η_{class} values are taken from other publications.^{5,6} For each eutectic mixture composition calculated by the Schroeder-Van Laar equation (e.g. all in Table VIII except HRL-256N5) our computer is programmed to calculate the other properties as well. The computer contains a file on the mp, clpt, ΔH_f , L, and class values of Δn , $\Delta \epsilon$, and η for each component. The program calculates the mole fraction of each component for the idealized eutectic mixture, and these mole fractions are used to calculate the predicted values of Δn , $\Delta \epsilon$, and η for this mixture.

Most of the properties calculated for the mixture in Table VIII are fairly close to their observed values, indicating the general utility of using this technique to predict properties of new mixtures. The observed mps for 2N52, 25N4, and 26N3 are within 5° of those calculated, but both 26N4 and 246N1 have considerably higher observed than calculated mps due to small amounts of crystals that remelt near room temperature after the samples are stored for long periods at -40°C. This indicates that the calculated

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TABLE VIII Calculated and observed properties of prior mixtures.³

Component		Mole Fractions in HRL Mixtures					
Classes		2N52	25N4	26N3	26N4	246N1	256N5
RO-R'		0.384	0.420	0.266	0.228	0.181	0.149
RO-OR'		0.315	0.270	0.065	0.194	0.157	0.263
RO-[C]R'				0.500	0.222	0.390	0.142
ROSR'			0.155				0.142
ROSOR'			0.155				0.094
RO-OOCR'		0.302			0.354		0.210
R-(Cl)OOCPR'				0.169			
R(CN)-PR'						0.272	
Properties		2N52	25N4	26N3	26N4	246N1	256N5
Length (Å)		24.9	23.9	26.4	23.3	26.3	23.3
mp	Calc.	3.0	-0.9	-15.0	6.7	1.3	-
	Obs.	7.0	5.0	-20.0	21.0	19.0	-9.0
Clpt.	Calc.	73.0	74.7	77.5	78.0	83.4	-
	Obs.	71.9	71.6	75.8	77.0	81.0	77.4
Δn	Calc.	0.15	0.18	0.12	0.13	0.16	0.16
	Obs.	0.150	0.169	0.118	0.141	0.143	0.158
$\Delta \epsilon$	Calc.	-0.5	-0.1	0.2	-0.9	-2.4	-0.6
	Obs.	-0.45	-0.13	0.06	-0.96	-1.55	-0.49
n	Calc.	63	58	49	54	80	59
	Obs.	64.2	59.2	47.8	49.3	66.6	58.2

eutectic composition of 26N4 and 246N1 is probably slightly different than the true eutectic obtainable with these components. The observed clearpoints in Table VIII are all only about 1 to 3° lower than those calculated. Such differences are generally the case, and are probably indicative of some non-ideality of the mixtures. The observed and calculated Δn are in good agreement, generally within 0.01 of one another. The observed $\Delta \epsilon$ are in good agreement with the calculated values for 2N52, 25N4, 26N4,

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and 256N5, but differ slightly for the 26N3 and considerably for the 246N1 mixture. The strongly positive $\Delta\epsilon$ component 5-(C1)00CP5 is present in 26N3, and as indicated in Table VII its $\Delta\epsilon_{\text{class}}$ of 7.3 (in a RO-R' mixture) is much higher than its $\Delta\epsilon'_{\text{class}}$ of 3.2 measured in a RO-[C]R' mixture--which class makes up 50% of 26N3. The strongly negative $\Delta\epsilon$ component 7(CN)-P5 is present in 246N1, and its $\Delta\epsilon_{\text{class}}$ of -5.4 is lower than its $\Delta\epsilon'_{\text{class}}$ of -3.8. As discussed above, the presence of the RO-[C]R' molecules in the mixtures alters the $\Delta\epsilon$ measurements. The observed values of η are in good agreement with the calculated values for 2N52, 25N4, 26N3, and 256N5, and are lower than those calculated for 26N4 and 246N1. Thus, despite the limitations inherent in using η_{class} values, we find that generally the η_{mix} calculated for many ester mixtures is equal to or slightly higher than the observed values.

Six new eutectic ester mixture compositions are shown in Table IX to illustrate further our techniques of formulating short length ester mixtures with improved properties for dynamic scattering applications.⁷ Their predicted (i.e. calculated) versus their observed properties are shown in Table X. In these formulations we are seeking a wide nematic range (0 to 75°C, or better), a relatively low viscosity ($\eta_{250} < 40$ cP), and a slightly negative $\Delta\epsilon$. Extensive use is made of our formulation methods

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I and II (both separately and combined) in order to obtain short length mixtures, as indicated by the following list of equal length binary, tertiary, and quaternary combinations used:

<u>HRL Mixtures</u>	<u>Equal Length Combinations</u>
2456N1 256N13 256N19	[20-3/40-1/20-[C]3, 20-5/40-3/20-[C]5, 10-[C]5/10S5
26N25	20-3/20-[C]3/10-00C3, 20-5/20-[C]5
26N35	20-3/40-1/20-[C]3/10-00C3, 20-5/40-3/20-[C]5
26N36	20-3/40-1, 20-5/40-3/20-[C]5

The observed mps and clpts. in Table X are all fairly close to our predicted values for these eutectic mixtures. The observed Δn values are in excellent agreement with the calculated values. The observed $\Delta \epsilon$ are generally slightly less negative than the calculated values, apparently due to the presence of substantial percentages of RO-[C]R' components, as discussed above. The observed n values are all close to the calculated values, ranging from 7 to 14% lower than predicted. After adding appropriate dopants with

TABLE IX Compositions of new eutectic mixture.

Component	Ref.	Mole Fraction of Component in HRL Mixture					
		2456N1	256N13	256N19	26N25	26N35	26N36
20-3	1	0.054	0.051	0.050	0.061	0.054	0.057
20-5	1	0.058	0.055	0.053	0.067	0.058	0.062
40-1	1	0.037	0.034	0.033	-	0.037	0.039
40-3	1	0.034	0.032	0.031	-	0.034	0.036
40-6	1	-	-	-	-	-	0.110
60-3	1	0.163	0.156	0.152	-	-	-
60-5	1	-	-	-	0.229	0.204	0.214
10-[C]5	2	0.246	0.236	0.232	0.272	0.245	0.256
20-[C]3	2	0.125	0.118	0.115	0.142	0.124	-
20-[C]5	2	0.066	0.062	0.060	0.077	0.066	0.070
10B5	3	0.133	0.128	0.125	-	-	-
10-OOC3	3	-	-	-	0.037	0.032	-
40-OOC4	3	-	-	-	0.045	-	-
2-Y3	6	-	0.059	-	-	-	-
3-Y3	6	-	-	0.082	-	0.087	0.091
4-Y3	6	-	0.065	-	-	-	-
15Y3	6	-	-	0.066	-	-	-
3P-4	5	0.082	-	-	-	-	-
4-OOC4	5	-	-	-	0.070	-	0.065
4-OOCY4	6	-	-	-	-	0.059	-

high conductivity anisotropy, all of these new mixtures have favorable dynamic scattering properties. The 26N25, 26N35, and 26N36 mixtures with redox dopants ^{3,11} are particularly useful as improved LCs for long life dc-activated dynamic scattering at elevated temperatures.⁷

4. CONCLUSIONS

1. Multicomponent ester eutectic mixtures with short average molecular length can be prepared by including selected binary, tertiary

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TABLE X Calculated and observed properties of
new eutectic mixtures.

Properties		HRL Mixtures					
		2456N1	256N13	256N19	26N25	26N35	26N36
Length($\bar{A}$)		22.1	22.1	22.0	23.2	23.0	23.8
mp	Calc.	-5.1	-6.2	-6.8	-2.3	-5.2	-4.0
	Obs.	0	-5	-15	0	-4	-13
Clpt.	Calc.	78.3	82.4	88.5	79.2	86.3	83.4
	Obs.	73.8	77.7	84.5	73.9	81.9	77.6
Δn	Calc.	0.14	0.13	0.13	0.12	0.12	0.13
	Obs.	0.133	0.127	0.133	0.120	0.12	0.13
$\Delta \epsilon$	Calc.	-0.9	-0.9	-0.8	-0.7	-1.0	-0.3
	Obs.	-0.70	-0.60	-0.52	-0.57	-0.70	-0.28
η	Calc.	30	31	32	36	34	38
	Obs.	27	28.4	28.7	31	32	35.6

and quaternary sets of short length ester LC components of essentially equal molecular length. Two methods are found to be suitable for selecting eutectic LC binary sets (and combinations thereof to give tertiary and quaternary sets) with equal length components. Guidelines are described for combining these binary sets together with other components, and such multicomponent ester eutectics are each found to have a nematic temperature range close to the theoretical one calculated by applying the Schroeder-Van Laar equation.

2. Approximate class values of birefringence and dielectric anisotropy (as well as viscosity, reported elsewhere) can be assigned by measuring the effect of specific class components on these properties in a standard

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short length RO-R' mixture. These class values are found to be useful in several ways. Their relative magnitude provides a basis for qualitative comparisons of structural effects on these anisotropies. The assigned class values are also very useful in predicting, with fairly good accuracy, the room temperature values of Δn , $\Delta \epsilon$, and η for new multicomponent ester mixtures.

3. Several new short length, multicomponent, eutectic mixtures of ester LCs are successfully formulated with the properties desired for dynamic scattering applications. These new mixtures have a wide nematic range, relatively low viscosity, slightly negative dielectric anisotropy, and good compatibility with redox dopants for dc-activation.

5. ACKNOWLEDGMENTS

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