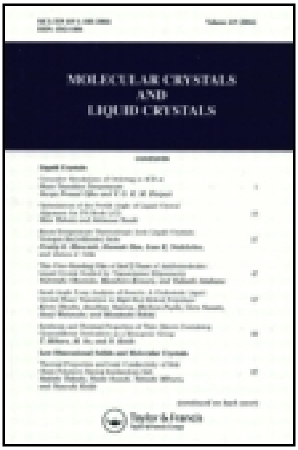

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Effects of Molecular Length on Nematic Mixtures. III. Anisotropic Properties of 4-Alkylphenyl 4-Alkoxybenzoate Mixtures

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Effects of Molecular Length on Nematic Mixtures. III. Anisotropic Properties of 4-Alkylphenyl 4-Alkoxybenzoate Mixtures.

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Properties of multicomponent nematic mixtures of 4-alkylphenyl 4-alkoxybenzoates are studied as a function of temperature and their average molecular length ($\bar{L}$). The $\bar{L}$'s vary between 21.47 and 27.67 Å for mixtures with clearpoints in the 43 to 60°C range. The refractive indices, density, and the $\epsilon_\perp$ component of dielectric permitivity all decrease approximately linearly as $\bar{L}$ increases. There are much larger changes in flow viscosity (η), conductivity anisotropy ($\sigma_\parallel/\sigma_\perp$), and dielectric anisotropy ($\Delta\epsilon$). At 25°C as $\bar{L}$ increases: The η is relatively high and increases sharply (from 47 to 78 cP), the $\sigma_\parallel/\sigma_\perp$ decreases and drops below unity (from 1.35 to 0.58), and the $\Delta\epsilon$ changes from positive to negative (from +0.27 to −0.26). The temperature dependence of $\sigma_\parallel/\sigma_\perp$, with tetrabutylammonium tetraphenylboride as a dopant, indicates cybotactic nematic characteristics are present for the longer $\bar{L}$ mixtures in which there are an average of about nine or more alkyl carbons from both end groups. The large decrease in $\Delta\epsilon$ at higher $\bar{L}$ is attributed to increased molecular association effects in the cybotactic nematic mixtures.

I INTRODUCTION

We have found that the anisotropic properties of nematic liquid crystals (LCs) in two series of ester mixtures depend strongly on their average molecular length ($\bar{L}$), which was varied by using mixtures of components with different length alkyl end groups.[1,2] The present study is designed to determine if similar correlations also pertain to mixtures of 4-alkylphenyl 4-alkoxybenzoates (R–OR′ mixtures), and particularly to find out how $\bar{L}$ affects their cybotactic nematic characteristics and the related anisotropic properties of flow viscosity (η), conductivity anisotropy ($\sigma_\parallel/\sigma_\perp$), and dielectric anisotropy ($\Delta\epsilon$). Comparisons are made with the other two series of esters already studied, namely 4-

alkoxyphenyl 4-alkylbenzoate (RO–R') mixtures[1] and 4-alkoxyphenyl 4-alkylcyclohexanecarboxylate (RO–[C]R') mixtures.[2]

II EXPERIMENTAL

The components in the LC mixtures are phenylbenzoate esters made by reacting the appropriate *p*-alkylphenols and *p*-alkoxybenzoyl chlorides. Most of the reactants are obtained commercially from either Aldrich Chemical, Frinton, or Eastman Organic. The hexyloxy-, pentyloxy-, and octyloxybenzoyl chlorides are prepared from the corresponding benzoic acids. The esters are purified by several recrystallizations and are checked for impurities by thin-layer chromatography and by high-performance liquid chromatography (Waters Assoc. Model ALC-202/401 with a microporasil column). The esters all show less than 0.5% impurities, and their undoped LC mixtures all have resistivities greater than 10^{11} Ω-cm at 25°C. The equipment used for studies on thermal analysis, flow viscosity, density, refractive index, dielectric anisotropy, and conductivity anisotropy were described previously.[1,2]

III RESULTS AND DISCUSSION

III.A LC Components and Mixtures

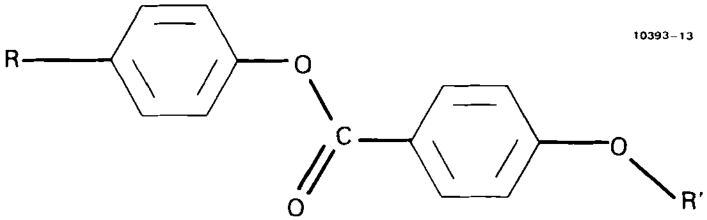
The thermal properties of the phenyl benzoate compounds used in our mixtures are shown in Table I, where R and R' are *n*-alkyl groups indicated by the general structure in Figure 1a. The melting points and heats of fusion from

TABLE I

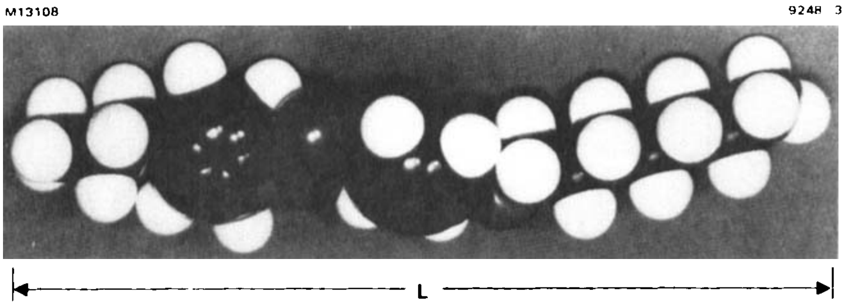
Thermal Properties of Components

Compound R	Compound OR'	Code	mp, °C Obs.	mp, °C Lit.	Clpt, °C Obs.	Clpt, °C Lit.	ΔH_f K_{cal}/Mole
CH_3	OC_4H_9	1-04	77.4	—	[a]	—	6.96
CH_3	OC_6H_{13}	1-06	62.5	—	50.7	—	5.86
C_3H_7	OC_5H_{11}	3-05	42.5	41[b]	51.7	47[b]	6.76
C_3H_7	OC_7H_{15}	3-07	65.0	65[b]	56.5	58[b]	6.63
C_5H_{11}	OCH_3	5-01	28.6	29.5[b]	42.1	43.5[b]	3.56
C_5H_{11}	OC_6H_{13}	5-06	49.8	48[b]	62.2	62[b]	5.23
C_7H_{15}	OCH_3	7-01	32.6	34[c]	42.8	42.5[c]	5.56
C_7H_{15}	OC_6H_{13}	7-06	46.0	45.5[c]	63.5	63[c]	5.77
C_7H_{15}	OC_8H_{17}	7-08	47.7	—	67.3	—	6.92

[a] No clpt observed, but 30°C is used as an approximate virtual nematic clpt.
[b] J. P. Van Meter and B. H. Klanderman, *Mol. Cryst. Liq. Cryst.*, **22**, 271 (1973).
[c] R. Steinstrasser, 4th International Liq. Cryst. Conf., Kent, Ohio (1972).



(a)



(b)

FIGURE 1 (a) General structure of R–OR' LC mixture components; (b) Model of 4-*n*-propylphenyl 4-*n*-heptyloxybenzoate (3–07) showing the molecular length used (L = 25.87Å).

Table I are used to calculate the eutectic mixtures shown in Table II. The molecular length (L) of each compound is measured from the end-to-end distance in CPK models as indicated in Figure 1, using a fully extended conformation. Table III shows the average molecular length of each mixture and the observed nematic range compared to the calculated nematic range. In several mixtures, components with only small differences in L are used together. This can be done when the R and R' end groups of one component differ substantially from those of another component (e.g., 3–05 with 7–01, and 1–06 with 5–01). All of the mixtures are nematic in the temperature ranges of this study, but mixture M (HRL–2P36) has a smectic to nematic transition just below room temperature, at 20°C.

III.B Refractive Index, Birefringence, Density, and Dielectric Constant

The effect of $\bar{L}$ on the refractive indices ($n_{\parallel}$ and $n_{\perp}$) and birefringence (Δn) are shown in Figure 2. Changes in the density (d), and dielectric constant ($\epsilon_{\perp}$) as a function of $\bar{L}$ are shown in Figure 3. Both $n_{\parallel}$ and $n_{\perp}$ decrease as $\bar{L}$ increases, as

TABLE II

Composition of Liquid Crystal Mixtures

Compound Code[a]	L, Å	A	B	C	D	E	F	G	H	I	J	K	M
		Mole Fraction in Mixtures											
1-04	19.81	—	0.067	—	—	—	—	—	—	—	—	—	—
1-06	22.25	0.238	0.149	0.172	0.133	—	—	—	—	—	—	—	—
3-05	23.51	—	0.211	0.229	—	—	0.249	—	—	0.264	—	—	0.216
3-07	25.87	—	—	—	—	0.200	0.126	—	—	—	0.173	—	0.110
5-01	21.23	0.762	0.573	0.599	0.535	0.800	0.625	0.680	0.682	—	—	—	—
5-06	27.15	—	—	—	—	—	—	0.320	—	—	—	0.308	0.254
7-01	23.57	—	—	—	0.332	—	—	—	—	0.446	0.551	0.466	—
7-06	29.61	—	—	—	—	—	—	—	0.318	0.290	—	—	0.245
7-08	32.00	—	—	—	—	—	—	—	—	—	0.276	0.226	0.174
HRL Mixture No.		2P13	2P14	2P15	2P17	2P16	2P18	2P19	2P20	2P21	2P31	2P32	2P36

[a] See Table I.

TABLE III

Average Length and Nematic Range of R-OR' Mixtures[a]

Mixture	Average Length, $\bar{L}$, Å	Average Carbons, in R + R'	mp, °C Calc.	mp, °C Obs.[b]	Clpt., °C Calc.	Clpt., °C Obs.[c]
A	21.47	6.24	15.3	—	44.2	43.2
B	21.77	6.50	2.7	—	44.6	44.8
C	21.93	6.63	4.6	—	45.8	44.5
D	22.15	6.80	−0.2	—	43.5	43.0
E	22.16	6.80	17.6	—	45.0	44.6
F	22.38	7.00	6.4	—	46.3	45.6
G	23.13	7.60	10.1	—	48.6	49.1
H	23.89	7.59	10.3	—	48.9	49.5
I	25.31	9.45	7.8	—	51.1	51.5
J	26.29	10.28	13.8	—	52.0	53.0
K	26.58	10.51	9.0	—	54.3	55.3
M	27.67	11.42	3.3	(19.9)[d]	60.5	60.6

[a] Calculated as eutectic compositions, with $\bar{L}$ calc. from Table II.
[b] All mixtures are nematic at room temperature.
[c] Clpt. observed in viscometer bath.
[d] Smectic to nematic transition obs. by DSC.

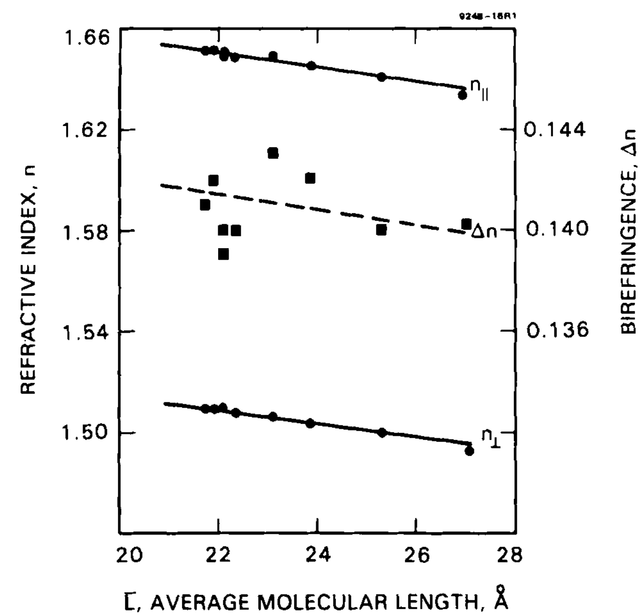


FIGURE 2 Refractive index and birefringence of R-OR' LC mixtures as a function of $\bar{L}$. (589 nm, 21°C).

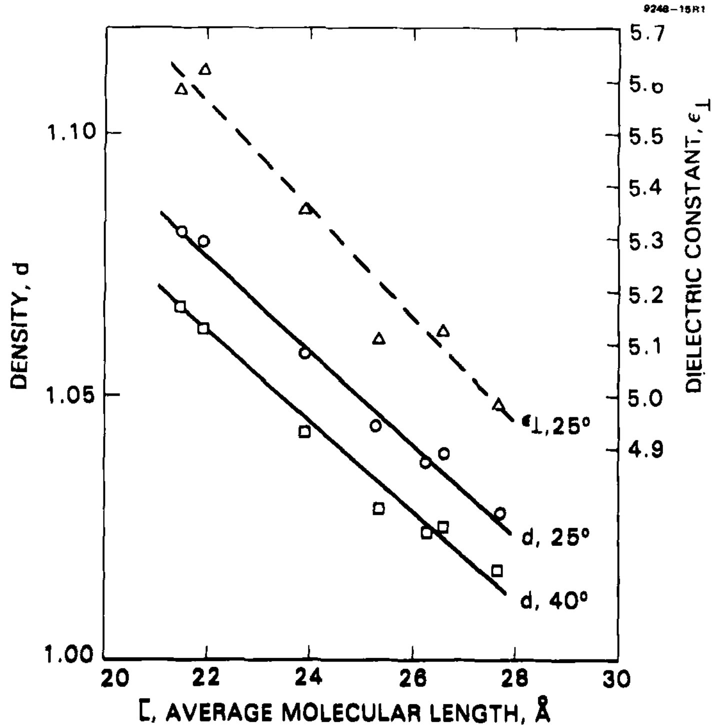


FIGURE 3 Effect of $\bar{L}$ on density and dielectric constant of R–OR′ LC mixtures.

expected since longer $\bar{L}$ increases just the aliphatic end group length of the molecules, while the more polarizable central part of the structure is the same. There is an overall trend in which Δn decreases with $\bar{L}$, although the results are somewhat variable from mixture to mixture. The d and $\epsilon_\perp$ values decrease linearily as $\bar{L}$ increases, due to the increasing contribution of alkyl groups to the molecular volume of these aromatic esters. The value of $\epsilon_\perp$ at 25°C decreases by about 0.12 units per added methylene group, which is similar to the changes observed in the RO–R′ series.

IV VISCOSITY

The effect of temperature on the flow viscosity is shown for four of the mixtures in Figure 4. The plots of log η versus T^{-1} are not quite linear; similar curves are found for all of the other mixtures, whose plots are all within the range of those shown in Figure 4. The sharp rise in each viscosity curve at higher temperatures corresponds to the clearpoint transition to the isotropic

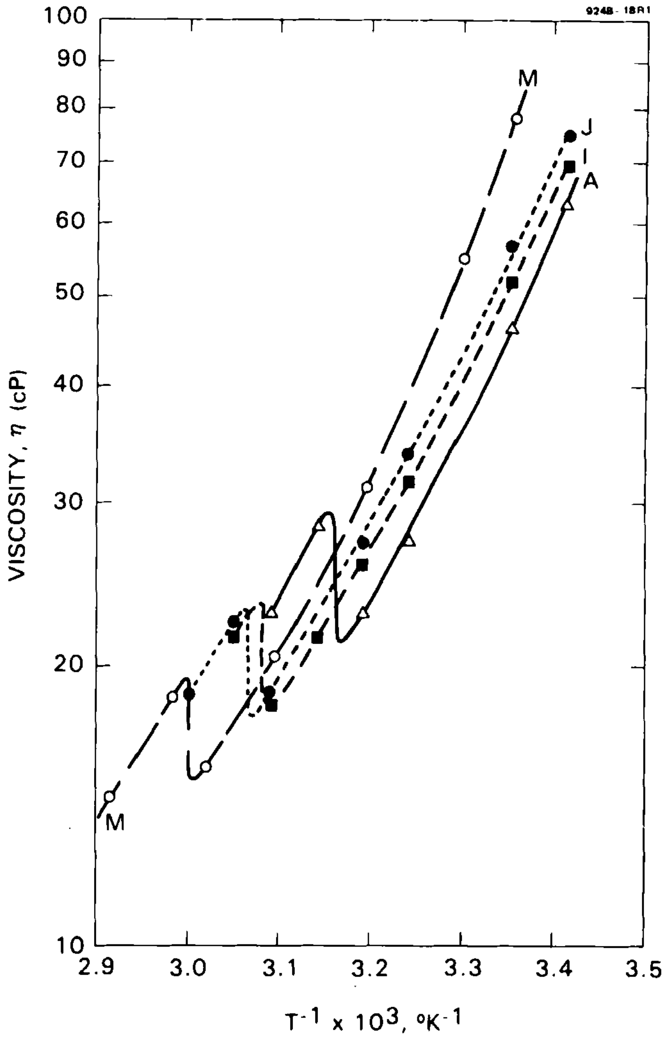


FIGURE 4 Temperature dependence of viscosity of R–OR′ mixtures.

liquid, which has a higher η than that of the nematic mixture. This rise of η at the clearpoint is expected because LC flow viscosities are often approximately equal to the Helfrich viscosity η_2, which has been shown to increase near the clearpoint.[3,4a] The effect of $\bar{L}$ on viscosity is shown in Figure 5. Although there is considerable scatter in the η values at 25°C, both the 25 and 40°C curves indicate that, in general, η increases rapidly with increasing $\bar{L}$. These values of η at 25°C range from about 47 to 78 cP, which are considerably higher than the

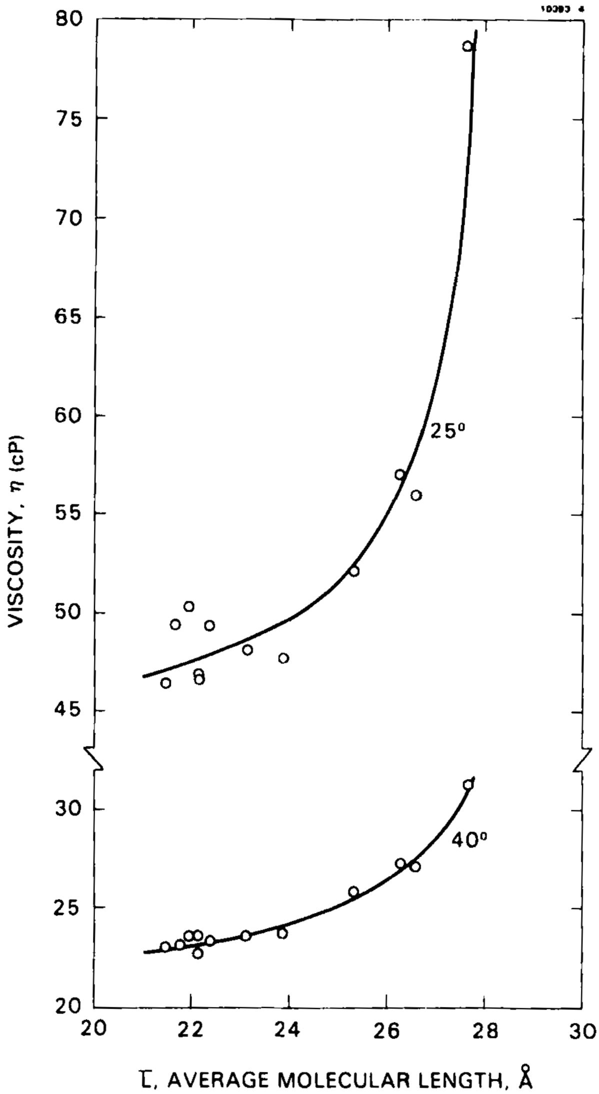


FIGURE 5 Effect of $\bar{L}$ on flow viscosity of R–OR′ LC mixtures.

33 to 44 cP values observed for RO–R′ mixtures over the same $\bar{L}$ variation. Presumably, the higher η of the R–OR′ mixtures is partly due to the increased polarity of its molecules, in which the electron-donating alkoxy group is in a *para*-position to the electron-accepting carbonyl group of the aromatic ester. The exponential increase of η_{25° as $\bar{L}$ increases from 25 to 28 Å is attributed to

the presence of cybotactic nematic characteristics (short range smectic ordering) as described below.

V CONDUCTIVITY ANISOTROPY

The conductivity anisotropy ($\sigma_{\parallel}/\sigma_{\perp}$) of tetrabutylammonium tetraphenylboride (TBATPB) in six different R-OR' LC mixtures is shown as a function of temperature in Figure 6. Included are mixtures with the shortest as well as the longest average molecular length in this series. The temperature dependence of $\sigma_{\parallel}/\sigma_{\perp}$ in mixtures K and M, in which $\sigma_{\parallel}/\sigma_{\perp}$ increases substantially as the temperature increases, is indicative of cybotactic nematic characteristics.[5,6,7,8] Mixture M shows smectic-like $\sigma_{\parallel}/\sigma_{\perp}$ values (less than 1.0) below 41°C, with a value of only 0.58 at 25°C, although we observe its smectic nematic transition to be at 20°C. Cybotactic nematic effects are just discernible in mixtures H and I, where the total average number of carbon atoms in the R + R' end groups are 7.8 and 9.5 respectively. Thus, in the R-OR' mixtures, short range smectic ordering appears when the sum of the end group *n*-alkyl carbons is about nine or more. Similar cybotactic nematic effects were observed in the RO-R' series when the sum of the alkyl end group carbons reached an average

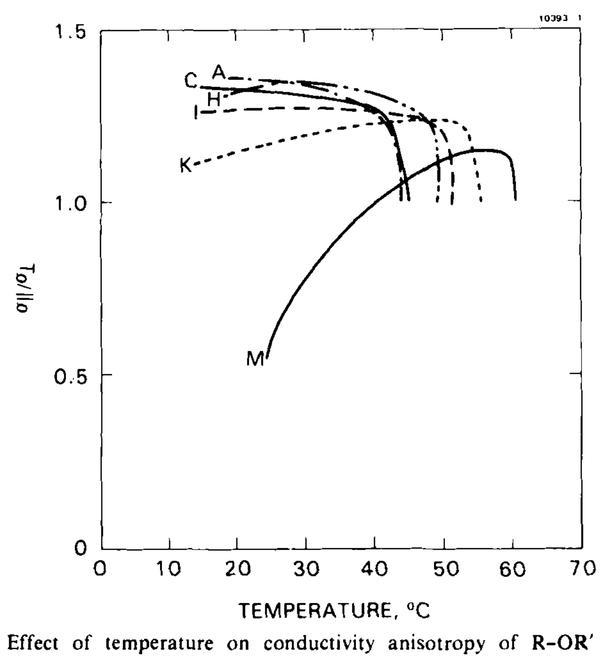


FIGURE 6 Effect of temperature on conductivity anisotropy of R-OR' mixtures with TBATPB dopant.

of ten or more. The cybotactic nematic effects are stronger and occur at shorter $\bar{L}$s in these R–OR′ mixtures than in the RO–R′ mixtures.[1] The effect of $\bar{L}$ is shown more clearly in Figure 7, where the $\sigma_{\parallel}/\sigma_{\perp}$ values are all compared at the same reduced temperature of $T = 0.93T_c$. At the shorter $\bar{L}$s the $\sigma_{\parallel}/\sigma_{\perp}$ values of TBATPB in these R–OR′ mixtures are just a little lower than those in the RO–R′ mixtures at the same reduced temperature. However, the steep decrease of $\sigma_{\parallel}/\sigma_{\perp}$ above 26Å which is shown in Figure 7 for these R–OR′ mixtures was not observed in the RO–R′ series. Because the viscosity of these R–OR′ mixtures also increases sharply above 26Å (Figure 5), we attribute the $\eta_{25°}$ changes to the corresponding increase in cybotactic nematic character.

VI DIELECTRIC ANISOTROPY

The temperature effects on $\Delta\epsilon$ are shown for six of the mixtures in Figure 8. In the shorter length mixtures (A and C) the $\Delta\epsilon$ decreases steadily with temperature and drops to zero, as expected for positive nematic mixtures. The medium length mixtures (H and I) and the longer length mixtures (K and M) all show an increase of $\Delta\epsilon$ with increasing temperature, with maximum values not far below their clearpoints. At 25°C mixture K is nearly zero and M has a negative

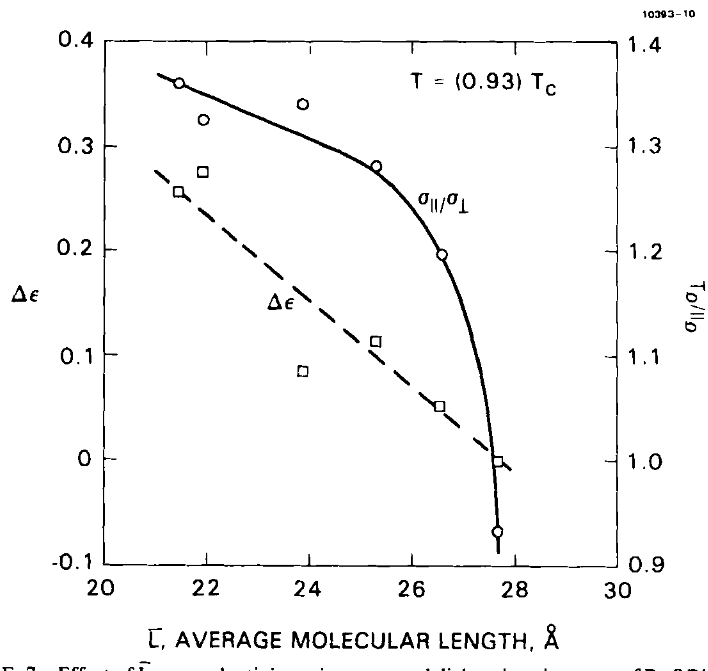


FIGURE 7 Effect of $\bar{L}$ on conductivity anisotropy and dielectric anisotropy of R–OR′ mixtures (T = temperature, °K and T_c = clearpoint, °K).

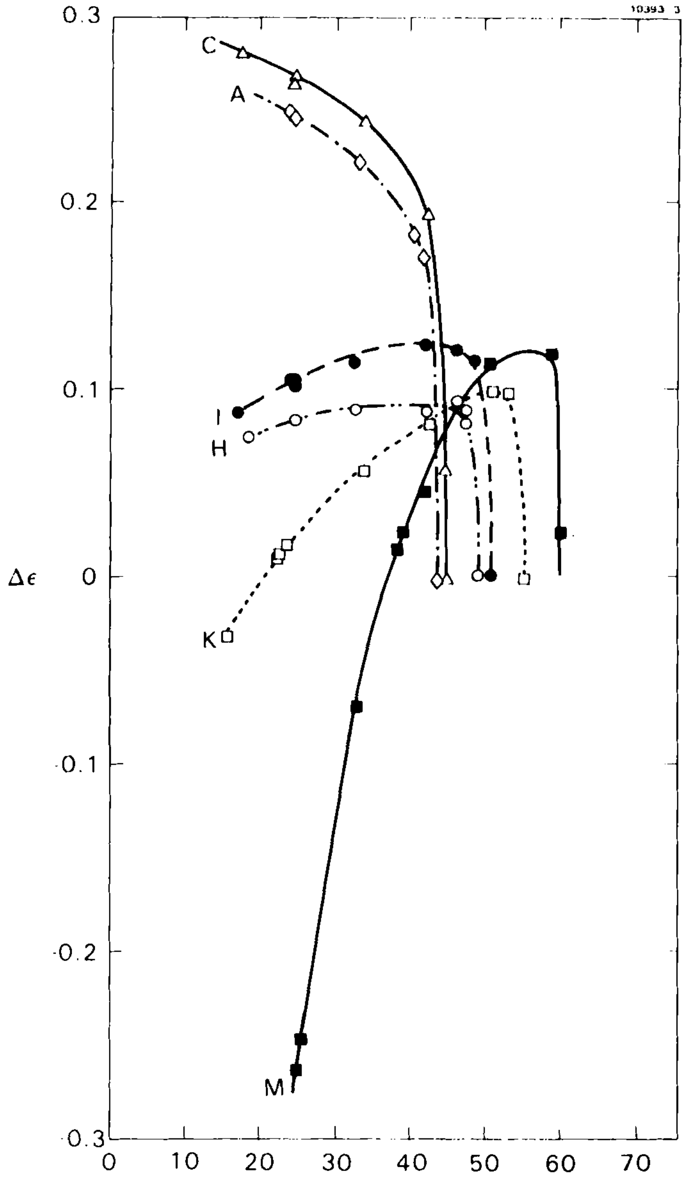


FIGURE 8 Effect of temperature on dielectric anisotropy in R–OR' mixtures.

$\Delta\epsilon$ value rather than the positive $\Delta\epsilon$ usually associated with R–OR′ LCs; the $\Delta\epsilon$ mixture of M is as negative as that of mixture A is positive. The effect of $\bar{L}$ on $\Delta\epsilon$ is shown in Figure 7 at the reduced temperature of $T = 0.93T_c$, where there is a linear decrease of $\Delta\epsilon$ with increasing $\bar{L}$. The effects of temperature on the $\epsilon_\perp$ is similar in all of these mixtures, as shown in Figure 9. Thus, the maxima seen for the $\Delta\epsilon$ of H, I, K and M in Figure 8 are caused mainly by the changes in the $\epsilon_\parallel$ of these mixtures. This is probably due to increased polar associations of the central part of the molecules in the cybotactic nematic phase. Such an increase in the anti-parallel correlation of the dipoles along the director has

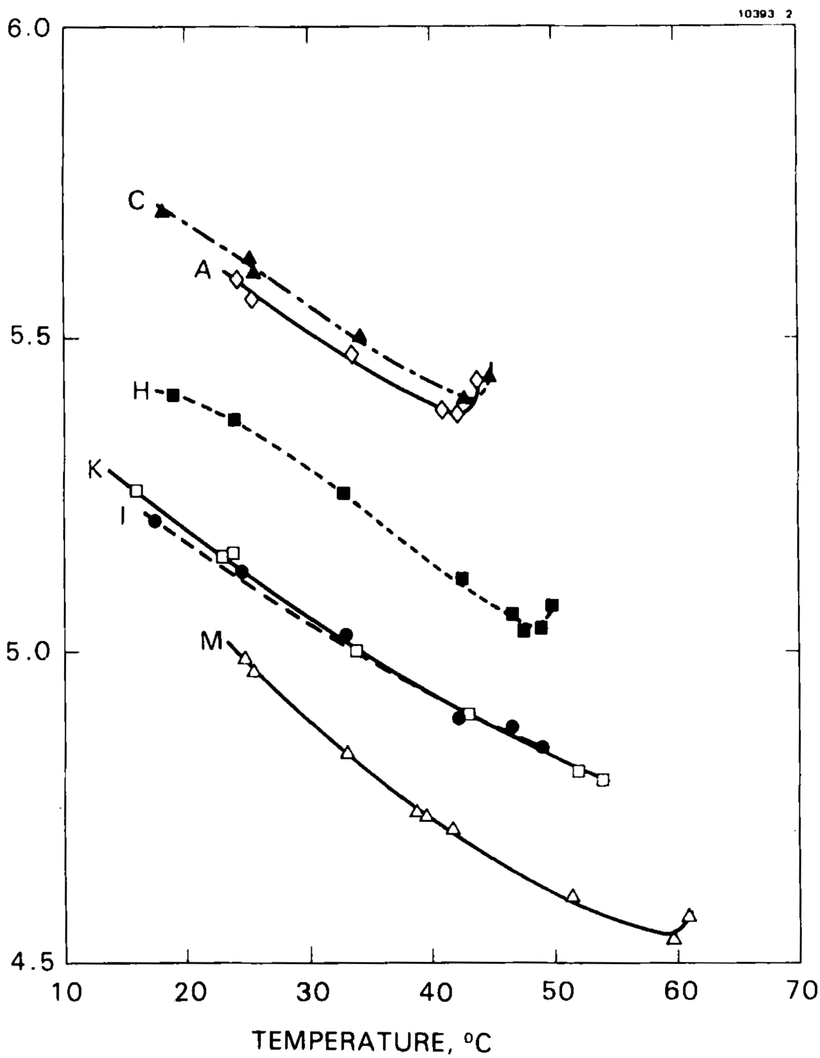


FIGURE 9 Effect of temperature on the $\epsilon_\perp$ dielectric constant of R–OR′ mixtures.

been described in general by deJeu[4b] for pre-transitional smectic order in the nematic phase. He cited 4,4′-diheptylazoxybenzene as an example in which $\Delta\epsilon$ decreased as the nematic phase approached the smectic transition. We observe here a much larger $\Delta\epsilon$ effect in mixture M in the 25 to 50°C range. However, we note from prior studies[2,3] that cybotactic nematic ordering alone is not sufficient to cause decreases in $\epsilon_{\parallel}$ and $\Delta\epsilon$. This can be seen in Figure 10, where the

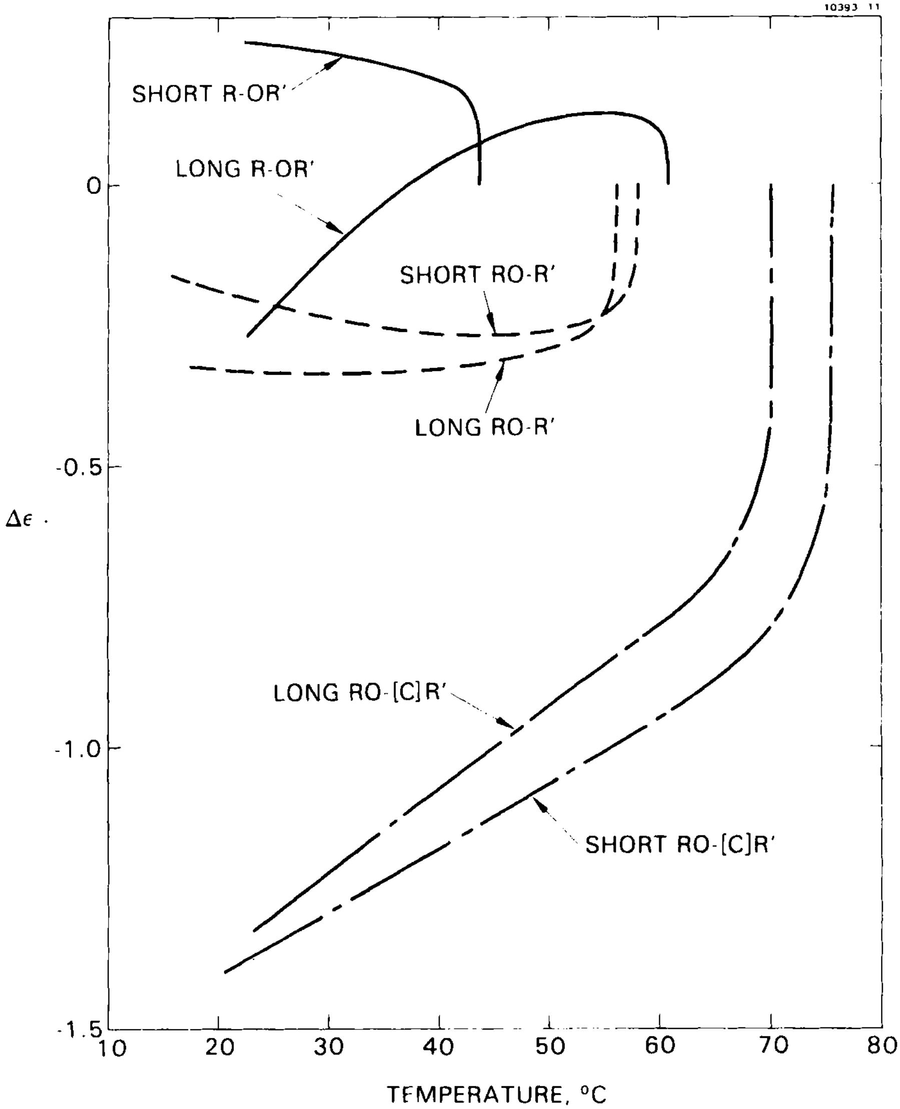


FIGURE 10 Comparison of $\bar{L}$ and temperature effects on $\Delta\epsilon$ in three series of mixtures. The $\bar{L}$s for R-OR′ are 21.47 and 27.67Å, for RO-R′ are 20.39 and 27.14Å, and for RO-[C]R′ are 21.20 and 26.15Å.

temperature effects on $\Delta\epsilon$ are shown for both short and long $\bar{L}$ mixtures in the three series R–OR′, RO–R′, and RO–[C]R′. The $\Delta\epsilon$ of each of these structural classes is affected differently by $\bar{L}$, although cybotactic nematic effects are observed in each class at long $\bar{L}$. There are strong cybotactic nematic characteristics in the long RO–[C]R′ mixtures but the $\Delta\epsilon$ is less negative in the long $\bar{L}$ mixtures than in the short $\bar{L}$ mixtures where no cybotactic effects are observed. The intermolecular association effects appear to be much larger in the R–OR′ mixture, probably due to the dipolar character of the *p*-alkoxybenzoate structure.

VII CONCLUSIONS

The flow viscosity of R–OR′ mixtures increases strongly with increasing $\bar{L}$, and the η values are substantially higher than in RO–R′ LC mixtures of comparable length. Cybotactic nematic effects are observed when the total average number of R + R′ alkyl end group carbons is 9 or more. The $\sigma_{\parallel}/\sigma_{\perp}$ and $\Delta\epsilon$ values decrease with increasing $\bar{L}$. The R–OR′ nematic mixtures with long $\bar{L}$ have smectic-like characteristics of $\sigma_{\parallel}/\sigma_{\perp} < 1$, $\Delta\epsilon < 0$, and high η instead of the usual (nearly opposite) characteristics found at short $\bar{L}$. The behavior in long $\bar{L}$ mixtures appears to be related to increased anti-parallel association of central molecular dipoles along the director as the cybotactic nematic character is increased by the longer alkyl end groups.

Acknowledgments

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