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Dielectric Properties of 2,3-Dicyano-4-pentyloxyphenyl 4'-pentyloxybenzoate (DPP) Mixtures with Non-polar Liquid Crystals (LC)

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The static dielectric properties of four binary mixtures of DPP and non-polar LC were investigated. For each system the effective dielectric anisotropy of DPP was calculated by means of linear extrapolation. The essential influence of the polarizability of non-polar LC molecule on the effective value of DPP dielectric anisotropy was shown. The influence of non-polar LC matrix on the effective value of the dielectric permittivity of DPP is discussed.

INTRODUCTION

Liquid crystalline compounds, derived from 2,3-dicyanohydroquinone, are characterized by large values of negative dielectric anisotropy.¹⁻³ Mostly these are non-mesomorphic materials or monotropic LC. However, they are widely used as components in LC mixtures for various electro-optic applications. Dielectric properties of these compounds are commonly estimated by means of linear extrapolation from dielectric permittivities of their mixtures with non-polar LC.

RESULTS AND DISCUSSION

The investigation was carried out using 2,3-dicyano-4-pentyloxyphenyl 4'-pentyloxybenzoate (DPP)

This compound is non-mesomorphic; it exhibits inter-solid phase transition at 76 °C, melts into the isotropic state at 91 °C (the enthalpies of these transitions are 3.0 kcal/mole and 5.8 kcal/mole, correspondingly) and exhibits a virtual phase transition into the nematic state at 48 °C. DPP is characterized by maximum value of negative dielectric anisotropy ($\Delta \epsilon = -25$)³ among the derivatives of 2,3-dicyanohydroquinone. The temperature dependencies of static dielectric permittivities were measured for the following non-polar LC solvents:

The results are presented in Table I. The dielectric properties of binary mixtures (10% DPP with 90% non-polar LC solvent, by weight)

TABLE I

Dielectric properties of non-polar LC (I), (II), (III) and (IV)

LC	T/T_{N-I}	0.94	0.95	0.96	0.97	0.98	0.99	1.01	1.02
(I)	€	4.38	4.36	4.35	4.34	4.33	4.32		
C 30.6 N 49.1 I	$\epsilon_{\perp}^{"}$	4.73	4.70	4.67	4.64	4.61	4.58		
	ϵ_{is}							4.43	4.39
	$\Delta \widetilde{\epsilon}$	-0.35	-0.34	-0.32	-0.30	-0.28	-0.26		
(II)	$\epsilon_{_{ }}$	3.35	3.34	3.32	3.31	3.29	3.28		
C 46 N 81.5 I	$\epsilon_{\perp}^{"}$	3.24	3.23	3.21	3.20	3.18	3.17		
	ϵ_{is}							3.19	3.18
	$\Delta \widetilde{\epsilon}$	0.11	0.11	0.11	0.11	0.11	0.11		
(III)	$\epsilon_{\rm ii}$	3.30	3.28	3.26	3.24	3.21	3.18		
C 61 N 70.5 I	€ "	2.96	2.95	2.94	2.94	2.94	2.94		
	ϵ_{is}							2.96	2.94
	$\Delta \overline{\epsilon}$	0.34	0.33	0.32	0.30	0.27	0.24		
(IV)	$\epsilon_{\shortparallel}$	2.99	2.99	2.99	3.00	3.01	3.05		
C 43 N 102 I	ϵ_{\perp}	3.70	3.68	3.65	3.62	3.58	3.53		
	ϵ_{is}							3.31	3.30
	$\Delta \epsilon$	-0.71	-0.69	-0.66	-0.62	-0.57	-0.48		

TABLE II

Dielectric properties of binary mixtures (10% DPP + 90% non-polar LC, by weight)

System	T/T_{N-I}	0.94	0.95	0.96	0.97	0.98	0.99	1.01	1.02
DPP + (I)	€ _{II}	5.76	5.75	5.77	5.78	5.80	5.90		
C 27 N 43.5 I	ϵ_{\perp}	7.90	7.84	7.72	7.61	7.49	7.35		
	$rac{\epsilon_{ ext{is}}}{\Delta \epsilon}$	-2.14	- 2.09	-1.95	-1.83	-1.69	-1.45	6.73	6.68
DPP + (II)	$\epsilon_{\rm B}$	4.23	4.23	4.24	4.25	4.29	4.35		
C 46 N 72 Î	$\epsilon_{\perp}^{''}$	5.55	5.50	5.44	5.38	5.31	5.21		
	$rac{\epsilon_{ m is}}{\Delta \epsilon}$	-1.32	-1.27	-1.20	-1.13	-1.02	-0.86	4.82	4.78
DPP + (III)	$\epsilon_{\scriptscriptstyle \parallel}$	4.12	4.14	4.15	4.16	4.18	4.25		
C 52 N 67 I	ϵ_{\perp}	5.21	5.17	5.12	5.08	5.03	4.96	4.50	4.60
	$rac{\epsilon_{ m is}}{\Delta \epsilon}$	-1.09	-1.03	-0.97	-0.92	-0.85	-0.71	4.72	4.69
DPP + (IV)	$\epsilon_{_{\mathrm{H}}}$	4.23	4.23	4.24	4.25	4.32	4.42		
C 40 N 92 Î	€⊥	6.08	5.99	5.93	5.86	5.78	5.59		
	$rac{\epsilon_{ m is}}{\Delta\epsilon}$	-1.85	-1.76	-1.69	-1.61	-1.46	-1.17	5.15	5.10

are presented in Table II. The dielectric anisotropy ($\Delta\epsilon$) of DPP was calculated by means of linear extrapolation at reduced temperature $T_{\rm R}=0.94\cdot T_{\rm N-I}$:

$$\Delta \epsilon_{\mathrm{DPP}} = \left[\Delta \epsilon_{\mathrm{LC-DPP}} - 0.9 \cdot \Delta \epsilon_{\mathrm{LC}} \right] / 0.1.$$

The results (Table III) clearly show that the dielectric anisotropy of DPP calculated by means of linear extrapolation depends upon the LC solvent used and grows together with LC solvent's molecular polarizability value.

TABLE~III Extrapolated values of DPP dielectric anisotropy $\Delta \epsilon_{extr}$ at T_{R} = 0.94 \cdot T_{N-1}

System	$\epsilon_{\scriptscriptstyle }$	ϵ_{\perp}	$\Delta\epsilon$	$\Delta\epsilon_{ m extr}$
(I) 10% DPP + 90% (I)	4.38 5.76	4.73 7.90	-0.35 -2.14	-18.3
(II) 10% DPP + 90% (II)	3.35 4.23	3.24 5.55	$0.11 \\ -1.32$	-14.2
(III) 10% DPP + 90% (III)	3.30 4.12	2.96 5.21	$0.34 \\ -1.09$	-14.0
(IV) 10% DPP + 90% (IV)	2.99 4.23	3.70 6.08	-0.71 -1.85	-12.1

EXPERIMENTAL

All the compounds were carefully purified by recrystallisation until reaching a constant melting point. Measurements were made on R571 capacity bridge at 10 kHz in 0.62T aligning magnetic field.

CONCLUSION

The extrapolated dielectric anisotropy values of LC with large dipole moment perpendicular to long molecular axis are correct only for the systems they were measured in and cannot be applied universally.

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