Asian Journal of Chemistry; Vol. 23, No. 7 (2011), 3247-3451

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Conductance and Dielectric Anisotropy Properties of 4'-Hexyl-4-biphenylcarbonitrile and 4'-Octyloxy-4-biphenylcarbonitrile Liquid Crystals and Their Composite

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(*Received*: 16 December 2010; *Accepted*: 24 March 2011) AJC-9773

The absorbance, conduction and dielectric properties of 4'-hexyl-4-biphenylcarbonitrile, 4'-octyloxy-4-biphenylcarbonitrile and their composite liquid crystals have been investigated. The absorbancies of samples have been studied using the ultraviolet visible spectrometry. The conduction and dielectric measurements of liquid crystals and their composite have been prepared in the frequency range of 0 kHz to 1 MHz at the room temperature. The difference of birefringence index is negative after a certain frequency when increased frequency. This frequency is 780 kHz for 4'-hexyl-4-biphenylcarbonitrile liquid crystal. The splay elastic constant K_{11} values decreases with increasing frequency. The dielectric and birefringence index difference of the 4'-hexyl-4-biphenylcarbonitrile/4'-octyloxy-4-biphenylcarbonitrile composite decreases with mixing of 4'-octyloxy-4-biphenylcarbonitrile to 4'-hexyl-4-biphenylcarbonitrile. The capacitance is large for low voltage, small for high voltage and it decreases with increasing frequency. The conductance is large for high voltage, small for low voltage and it increases with increasing frequency.

Key Words: Liquid crystals, Dielectric properties, 4'-Hexyl-4-biphenylcarbonitrile, 4'-Octyloxy-4-biphenylcarbonitrile.

INTRODUCTION

The states of matter whose physical properties are intermediate between those of a crystalline solid and an isotropic liquid are called liquid crystal. Liquid crystal is obtained with two different ways, thermal and solvent. According to the used processes, these liquid crystal are called thermotropic and liyotropic liquid crystals respectively. Liquid crystals are used for display systems of television, laptop, personal computer and other optical devices increasing in size. There is no known single mesogen that has all of the desired properties needed for displays. Such a material can be achieved only by preparing a mixture of mesogen which collectively have the desired properties[1-8]. The two eutectic nematic mixture liquid crystals E7 and E8 of cyanobiphenyls and terphenyl were developed with positive and high dielectric anisotropy[9].

The absorbance and molar absorptivity of liquid crystals and their mixtures have been studied by UV spectroscopy[10-12]. Liquid crystals and their composites have attracted much attention over a number of years because of their unique electro-optic and magneto-optic properties and novel display application[13]. 4'-Hexyl-4-biphenylcarbonitrile is one of the best known liquid crystalline substances and it has a strong dipole moment, good stability for application of nematic phase[14]. The relationship between static dielectric permittivity and molecular properties of liquid crystals has long been an objective of dielectric studies[15,16]. The static dielectric measurement has been shown to be successful technique in characterizing molecular anisotropy and intermolecular ordering in nematic liquid crystals. Liquid crystal mixture with a positive dielectric anisotropy is currently used in most active matrix display. The physical and optical properties of liquid crystals can be developed by mixing of different organic materials and thus new crystalline materials with high clearing temperature, large dielectric anisotropy and low viscosity may be prepared[17].

In this study, firstly, the absorbance, conduction and dielectric properties of 4'-hexyl-4-biphenylcarbonitrile, 4'-octyloxy-4-biphenylcarbonitrile and their composite liquid crystals have been investigated. The absorbance of 4'-hexyl-4-biphenylcarbonitrile and 4'-octyloxy-4-biphenylcarbonitrile composite has been determined by UV/Vis spectroscopy. Secondly, at room temperature, the capacitance and conductivity have been studied as a function of voltage at different frequencies at room temperature. The dielectric, birefringence index difference and splay elastic constant have been obtained as a function of frequency.

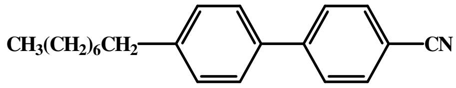
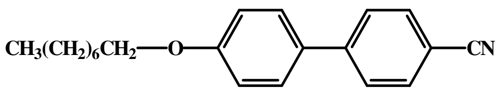
Liquid crystal	Linear formula	Chemical structure	m.w. (g)
4'-Hexyl-4-biphenylcarbonitrile (6CB)	$CH_3(CH_2)_5C_6H_4C_6H_4CN$		263.39
4-Octyloxy-4'-cyanobiphenyl (8OCB)	$CH_3(CH_2)_7OC_6H_4C_6H_4CN$		307.43

Fig. 1. Chemical structures of the liquid crystals: 4'-hexyl-4-biphenylcarbonitrile and 4-octyloxy-4'-cyanobiphenyl

EXPERIMENTAL

The 4'-hexyl-4-biphenylcarbonitrile and 4-octyloxy-4'-cyanobiphenyl liquid crystal materials were purchased from Sigma-Aldrich Corporation. The structure formula of 4'-hexyl-4-biphenylcarbonitrile and 4'-octyloxy-4-biphenylcarbonitrile nematic liquid crystals used in this study is shown in Fig. 1. While 4'-hexyl-4-biphenylcarbonitrile liquid crystal is a little viscous liquid, 4'-octyloxy-4-biphenylcarbonitrile is solid powder at room temperature. Solutions of mixtures within the concentration range 1.7×10^{-5} and 4.1×10^{-5} M were prepared by weighting and dissolved in chloroform. Uniform samples of 4'-hexyl-4-biphenylcarbonitrile and 4'-octyloxy-4-biphenyl-carbonitrile are prepared by magnetic mixing. Absorption measurements were carried out in real time, in the wavelength interval of between 200 and 400 nm using a Perkin-Elmer Lambda 45 UV/vis spectrophotometer. The spectra were recorded at room temperature using 1 cm quartz cuvette. The samples were separately placed in the spectrometer and another quartz cuvette was used as reference for transmission measurements. Before starting in transmission measurements, auto zero count was taken using two cuvettes. The capacitance-voltage and conductance-voltage measurements of 4'-hexyl-4-biphenylcarbonitrile and 95 % of 4'-hexyl-4-biphenyl-carbonitrile and 5 % of 4'-octyloxy-4-biphenyl-carbonitrile mixture were carried out at room temperature with using a KEITHLEY 4200-SCS (semiconductor characterization system). Before the construction of the cells, glass substrates coated with indium tin oxide were spin coated with a polyimide layer about 100 nm thick. Measurement cell was made up of two glass slides separate by Mylar sheets having 14.1 µm thicknesses. The mixture of 4'-hexyl-4-biphenylcarbonitrile and 4'-octyloxy-4-biphenylcarbonitrile liquid crystals was mixed in bandeling sonorex and heiddolp type reaxtop for 10 min, respectively. The liquid crystals cells were filled by insulin hypo with the prepared samples on hot plate with 50 ºC.

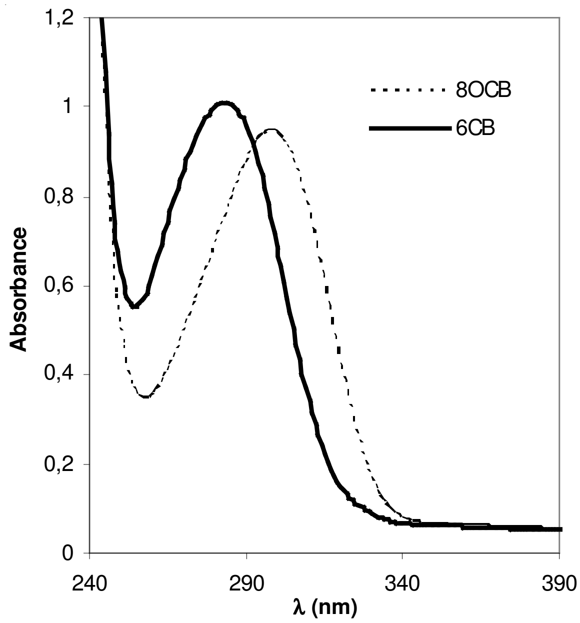


Fig. 2. UV absorbance spectrum of 4'-hexyl-4-biphenylcarbonitrile (6CB) and 4-octyloxy-4'-cyanobiphenyl (8OCB) liquid crystals

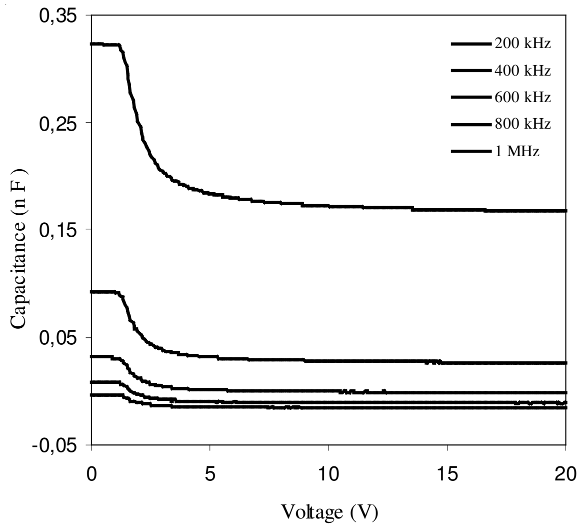


Fig. 3. Plots of capacitance-frequency of the 4'-hexyl-4-biphenylcarbonitrile liquid crystal for V = 0 and V = 20 Volt

RESULTS AND DISCUSSION

The UV absorption spectra of 4'-hexyl-4-biphenyl-carbonitrile and 4'-octyloxy-4-biphenylcarbonitrile in chloroform solutions were measured between 200 and 400 nm at room temperature (Fig. 2). The 4'-hexyl-4-biphenyl-carbonitrile and 4'-octyloxy-4-biphenylcarbonitrile spectrum gave a maximum absorption wavelength located at 283 and 298 nm, respectively, in agreement with λ_{max} reported in literature[18]. Fig. 3 shows the plot of capacitance-voltage of 4'-hexyl-4-biphenylcarbonitrile liquid crystals at different frequencies. The capacitance indicates a threshold voltage, capacitance value drops suddenly and molecular reorientation occurs above a threshold voltage. The capacitance is big at low voltage values from the threshold voltage and it is small at higher voltages than the threshold voltage. The threshold voltage is about 1.7 V. This voltage is called as Frederiks threshold voltage. Frederiks threshold electric field is a key parameter for any electro-optic application of liquid crystal materials[19]. The applied electric field to liquid crystal induces a torque on the molecules due to the dielectric anisotropy. The capacitance values decrease with frequency increasing. The capacitance values decrease from the initial value $C_{\parallel}$ to the final value $C_{\perp}$. The dielectric constant components, the parallel $\varepsilon_{\parallel}$ and the perpendicular $\varepsilon_{\perp}$ to the plane and the dielectric anisotropy are expressed as:

$$\varepsilon_{\parallel} = C_{\parallel}/C_o, \quad \varepsilon_{\perp} = C_{\perp}/C_o, \quad \lambda_{\varepsilon} = \varepsilon_{\parallel} - \varepsilon_{\perp} \qquad (1)$$

where C_o is the capacitance that when the cell is empty.

The variations of dielectric constant components and dielectric anisotropy with frequency are shown for 4'-hexyl-4-biphenylcarbonitrile liquid crystal in the Fig. 4. The dielectric constants and dielectric anisotropy are big at low frequency but they decrease with increasing frequency. The capacitance values are obtained as a function of frequency for 0 and 20 V voltages in Fig. 5. The capacitance is changes with frequency inversely proportional. The capacitance is big at low voltages and that is right for *vice-versa* due to liquid crystal molecules having reorientation at applied voltage.

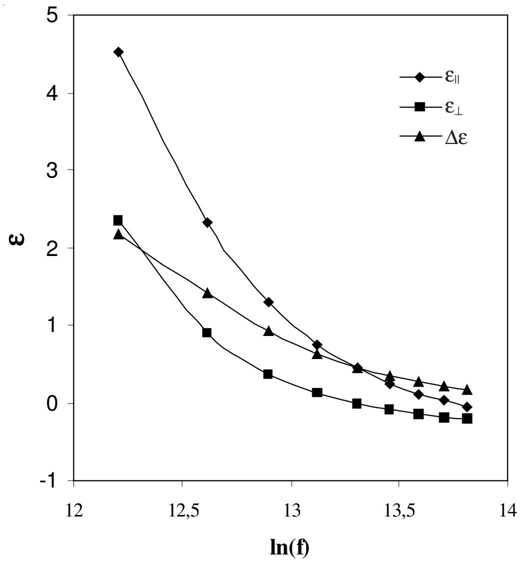


Fig. 4. Dielectric anisotropy dependence on frequency for 4'-hexyl-4-biphenylcarbonitrile

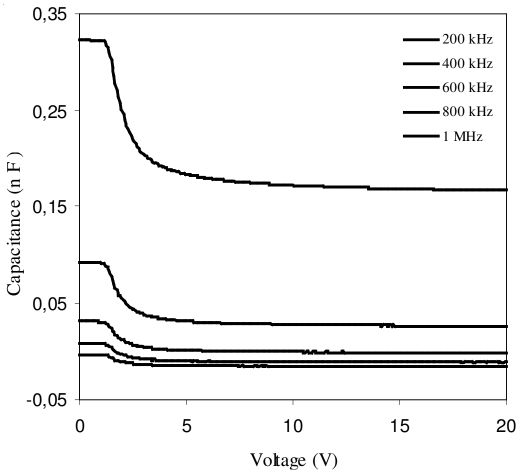


Fig. 5. Plots of capacitance-frequency of the 4'-hexyl-4-biphenylcarbonitrile liquid crystal for V = 0 and V = 20 Volt

The electrical conductivity of 4'-hexyl-4-biphenylcarbonitrile liquid crystal is obtained as a function of voltage at different frequencies in Fig. 6. The conductance is small at low voltages from the threshold voltage; it rises at the threshold voltage suddenly and it is big at higher voltages. The difference between the conductance at big and low voltages than the threshold voltage is larger at low frequencies. The variation of conductance-frequency is given for 0 and 20 V in Fig. 7. The conductance increases with frequency increasing. The conductance at 20 V is bigger than at 0 V and the conductance difference is bigger at low frequencies than high frequencies.

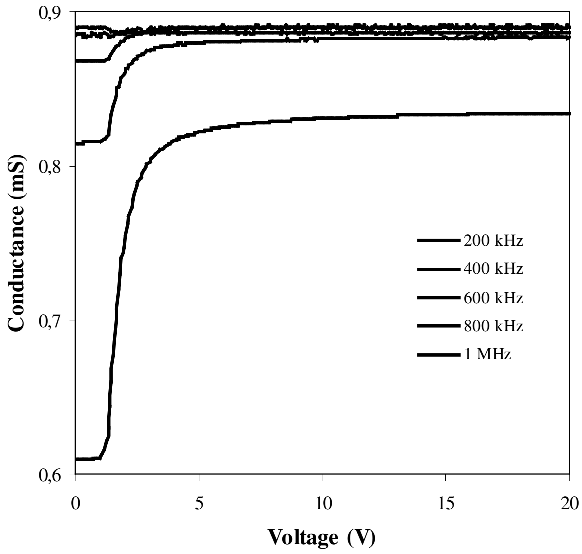


Fig. 6. Plots of conductance-voltage of the 4'-hexyl-4-biphenylcarbonitrile liquid crystal at the different frequencies

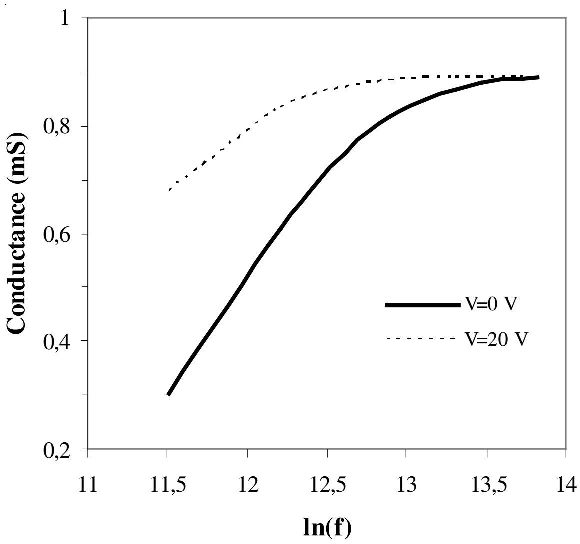


Fig. 7. Plots of conductance-frequency of the 4'-hexyl-4-biphenylcarbonitrile liquid crystal for V = 0 and V = 20 Volt

The difference of birefringence index and its parallel and perpendicular components are written as a function of dielectric constant as[6]:

$$n_{\parallel}^2 = \varepsilon_{\parallel}, \quad n_{\perp}^2 = \varepsilon_{\perp}, \quad \Delta n = n_{\parallel} - n_{\perp} \qquad (2)$$

The variation of birefringence index difference and parallel and perpendicular components with frequency is given for 4'-hexyl-4-biphenylcarbonitrile liquid crystal in Fig. 8. The birefringence index difference is almost constant toward a certain frequency then it decreases with frequency increasing. The difference of birefringence index is negative after a certain frequency when increased frequency. This frequency is 780 kHz.Threshold voltage for liquid crystals samples is described as[20]:

$$V_{th} = \pi(K_{11}/\varepsilon_o \Delta\varepsilon)^{1/2} \quad (3)$$

where ε_o is the dielectric constant of the vacuum, K_{11} the splay constant and $\Delta\varepsilon$ the dielectric anisotropy. The splay K_{11} values were calculated by using eqn. 3. The K_{11} values for 4'-hexyl-4-biphenylcarbonitrile liquid crystal as a function of frequency is shown in Fig. 9. The splay constant K_{11} decreases with increasing frequency.

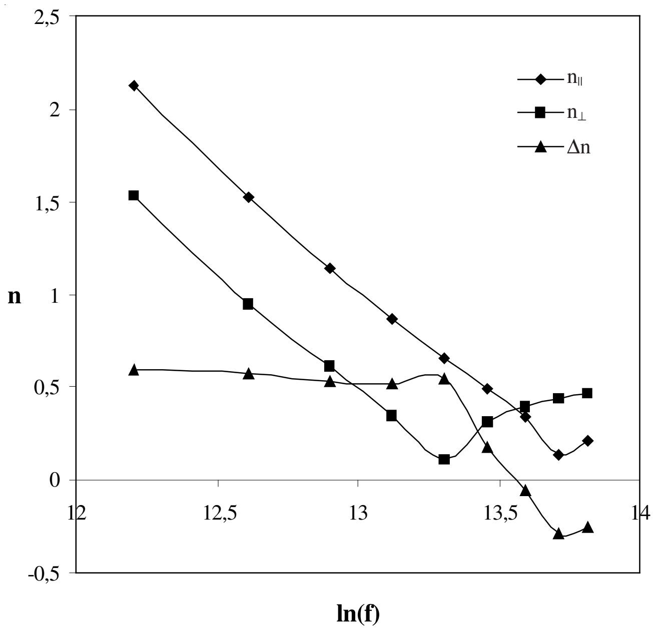


Fig. 8. Birefringence index dependence on frequency for 4'-hexyl-4-biphenylcarbonitrile

The values of dielectric anisotropy, birefringence index difference and their parallel and perpendicular components and the splay constant at different frequencies are given for 4'-hexyl-4-biphenylcarbonitrile liquid crystal in Table-1. All these values decrease at increasing frequencies. The perpendicular component of dielectric constant and the birefringence index difference take negative values after a certain frequency value.

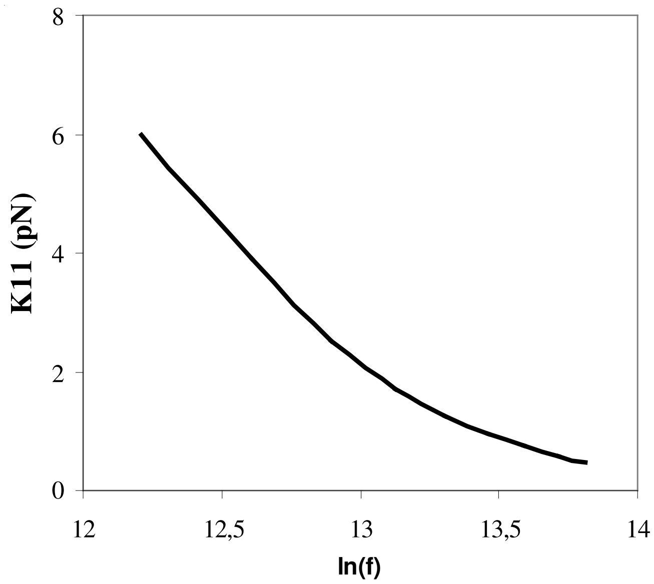


Fig. 9. Splay constant dependence on frequency for 4'-hexyl-4-biphenylcarbonitrile

Conclusion

The absorbancies of 4'-hexyl-4-biphenylcarbonitrile and 4'-octyloxy-4-biphenylcarbonitrile liquid crystals were obtained together by UV spectrometer. The capacitance-voltage and conductance-voltage plots for 4'-hexyl-4-biphenylcarbonitrile liquid crystal have been given at the different frequencies. The dielectric anisotropy, birefringence index difference, parallel and perpendicular components of dielectric and birefringence index and splay constant have been investigated as a function of frequency. The composite of 4'-hexyl-4-biphenylcarbonitrile (95 %) and 4'-octyloxy-4-biphenylcarbonitrile (5 %) has been made. The effect of 4'-octyloxy-4-biphenylcarbonitrile to the obtained results for 4'-hexyl-4-biphenylcarbonitrile has been investigated. The dielectric anisotropy of 4'-hexyl-4-biphenylcarbonitrile and the 4'-hexyl-4-biphenylcarbonitrile/4'-octyloxy-4-biphenyl-carbonitrile composite was given in the Fig. 10. The dielectric anisotropy decreases with increasing frequency and the difference in low frequencies is bigger than in high frequencies. The birefringence index difference of both 4'-hexyl-4-biphenylcarbonitrile and the 4'-hexyl-4-biphenylcarbonitrile /4'-octyloxy-4-biphenylcarbonitrile composite is shown in Fig. 11.

The values of dielectric anisotropy, birefringence index difference and their parallel and perpendicular components and the splay constant at different frequencies are given for

TABLE-1
DIELECTRIC, BIREFRINGENCE INDEX, SPLAY CONSTANT AT THE DIFFERENT FREQUENCIES FOR 4'-HEXYL-4-BIPHENYLCARBONITRILE

f (kHz)	ln (f)	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	$n_{\parallel}$	$n_{\perp}$	Δn	K_{11}
200	12.20607	4.518042	2.342378	2.175664	2.125569	1.530483	0.595086	5.969805
300	12.61154	2.322937	0.906294	1.416643	1.524118	0.951995	0.572124	3.887128
400	12.89922	1.293147	0.372448	0.920699	1.137166	0.610285	0.526881	2.526307
500	13.12236	0.751888	0.122098	0.629790	0.867115	0.349425	0.517690	1.728081
600	13.30468	0.437762	-0.012870	0.450629	0.661636	0.113433	0.548203	1.236482
700	13.45884	0.241678	-0.097900	0.339580	0.491608	0.312893	0.178715	0.931775
800	13.59237	0.113427	-0.153290	0.266713	0.336789	0.391518	-0.054730	0.731835
900	13.71015	0.020140	-0.189230	0.209371	0.141915	0.435007	-0.293090	0.574492
1000	13.81551	-0.044900	-0.216920	0.172028	0.211885	0.465750	-0.253870	0.472028

TABLE-2
DIELECTRIC, BIREFRINGENCE INDEX ANISOTROPY AND SPLAY CONSTANT FOR 4'-HEXYL-4-BIPHENYLCARBONITRILE AND 4'-HEXYL-4-BIPHENYLCARBONITRILE/4'-OCTYLOXY-4-BIPHENYLCARBONITRILE

f (kHz)	ln (f)	$\Delta\varepsilon$	$\Delta\varepsilon_c$	Δn	Δn_c	K_{11}	K_{11c}
200	12.20607	2.175664	1.928319	0.595086	0.536805	5.969805	5.291114
300	12.61154	1.416643	1.327303	0.572124	0.550942	3.887128	3.641988
400	12.89922	0.920699	0.903576	0.526881	0.519335	2.526307	2.402570
500	13.12236	0.629790	0.601362	0.517690	0.519597	1.728081	1.650078
600	13.30468	0.450629	0.433687	0.548203	0.467595	1.236482	1.189993
700	13.45884	0.339580	0.323439	0.178715	0.139703	0.931775	0.887485
800	13.59237	0.266713	0.249975	-0.054730	-0.095426	0.731835	0.685906
900	13.71015	0.209371	0.198195	-0.293090	-0.360738	0.574492	0.543826
1000	13.81551	0.172028	0.161503	-0.253870	-0.229535	0.472028	0.443149

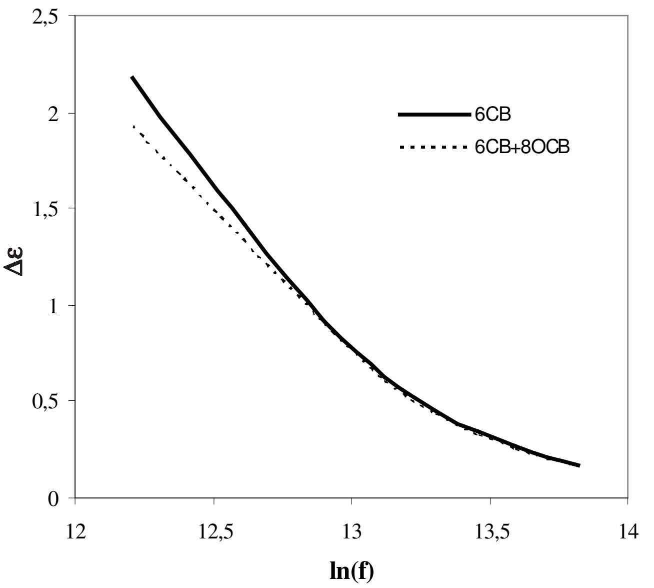


Fig. 10. Dielectric anisotropy dependence on frequency for 4'-hexyl-4-biphenylcarbonitrile and its composite

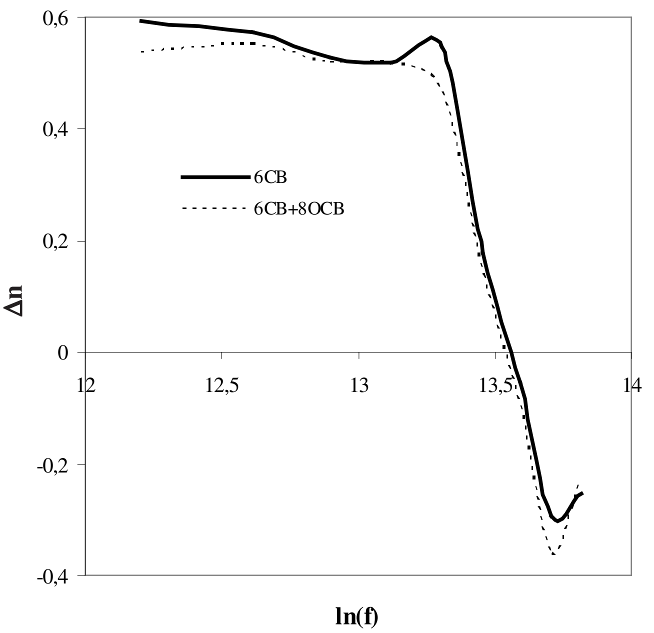


Fig. 11. Splay constant dependence on frequency for 4'-hexyl-4-biphenylcarbonitrile and its composite

4'-hexyl-4-biphenylcarbonitrile and the 4'-hexyl-4-biphenylcarbonitrile /4'-octyloxy-4-biphenylcarbonitrile composite in Table-2. The c subscript indicates the values of 4'-hexyl-4-biphenylcarbonitrile/4'-octyloxy-4-biphenylcarbonitrile composite. All these values decrease with mixing 4'-octyloxy-4-biphenylcarbonitrile to the 4'-hexyl-4-biphenylcarbonitrile liquid crystal.

ACKNOWLEDGEMENTS

The work has been supported by Kahramanmaras Sütcü Imam University Scientific Research Projects Coordination Department under Project Number: 2009/2-9YLS.

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