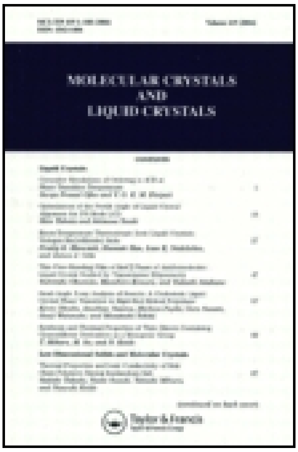

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On the Nature of Molecular Associations, Static Permittivity and Dielectric Relaxation in a Uniaxial Nematic Liquid Crystal

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On the Nature of Molecular Associations, Static Permittivity and Dielectric Relaxation in a Uniaxial Nematic Liquid Crystal

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One fluorinated terphenyl compound was studied by polarizing microscopy, x-ray diffraction and dielectric spectroscopy. It exhibits the nematic phase over a range of 107.8^0. The average intermolecular distance was observed to be more than in systems without any lateral fluorine substitution. Apparent molecular length was found to be more than the molecular model length, suggesting presence of antiparallel molecular associations. Optimized geometry, obtained by molecular modeling, yielded a dipole moment of 6.68 D. The observed principal dielectric constants are consistent with respective components of dipole moments and show quite a high value of dielectric anisotropy. The threshold voltage and the splay elastic constant have also been determined. Flip-flop mode dielectric relaxation frequency is found to increase with temperature, and the activation energy for the process is found to be 35.53 kJ mol^{-1}.

Keywords Activation energy; dielectric and elastic constants; dielectric anisotropy; flip-flop relaxation mode; molecular association; terphenyl fluorinated nematic

Introduction

Performance of a liquid crystal (LC) display device depends on the nature of the LC material and the construction of the device. Fluoro-substituted LC materials are found to be useful in large information content display devices. These are also promising materials for photonic applications because of their high birefringence [1–6]. A number of nematogenic molecules with a biphenyl cyclohexylcore or a phenyl bicyclohexyl core and terminal and/or lateral fluoro-substitution were investigated previously by x-ray diffraction and optical birefringence methods [7,8]. The crystal and molecular structures of a few such compounds were also determined from single crystal x-ray diffraction data and their structure property relationships were explored [9,10]. In continuation, we report here the results of x-ray diffraction and static and frequency dependent dielectric studies on a novel laterally bifluoro-substituted terphenylisothiocyanatouniaxialnematogenic compound (2TP-3′,3-4NCS in short).

X-ray diffraction is an important tool to identify different liquid crystalline phases as well as to find various molecular parameters, like average intermolecular distances (*D*),

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apparent molecular length (*l*) in the nematic phase and layer spacing in the smectic phase. The x-ray study provides information about the nature of molecular associations in the liquid crystalline phase. On the other hand, dielectric studies on nematogenic substances have played an important role in the development of electro-optical devices. The dielectric anisotropy, $\Delta\varepsilon = (\varepsilon_{\|} - \varepsilon_{\perp})$, depends on molecular polarizability and magnitude and direction of the dipole moment with respect to the long molecular axis. Here, $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ are the dielectric constants parallel and perpendicular to the nematic director in static field. Moreover, when subject to an ac field two noncollective molecular mode dielectric relaxations are observed in nonchiral low molecular mass nematic LCs. One is associated with rotation of the molecules around the short axis, the other occurs when the molecule rotates around the long axis. Other than positional ordering, reorientations of entire molecules around their short and long axes are one of the features that distinguish the liquid crystalline state from crystalline phase where these reorientations as well as intramolecular reorientations are usually frozen, vibration of atoms about their equilibrium positions still persist. Therefore, information about the nature of molecular dynamics is possible to obtain from frequency and temperature dependent dielectric spectroscopic study. Although static dielectric data is available in the literature on some fluoro-substituted nematics, the authors are not aware of any report on their dielectric relaxation behavior.

Experimental Details

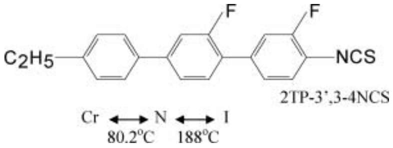
The nematic compound used in this investigation was synthesized by Dabrowski et al. [11]. Phase transitions were studied using Linkam THMS 600 hot stage and an Olympus BX42 polarizing microscope. X-ray diffraction photographs were taken using Ni filtered CuK$_{\alpha}$ radiation from ENRAF NONIUS FR590 X-Ray generator. The sample was filled in thin glass capillary, which was inserted in a brass block with heating arrangement. The temperature was measured with the help of a thermocouple inserted in the block and regulated with accuracy of ±0.1°C by a Eurotherm temperature controller (2216e). Diffraction photographs were recorded on a flat film with an exposure time of about 1 h to 1.30 h using a custom-built camera [12]. In order to determine the various parameters, photographs were scanned digitally and analyzed following procedures detailed before [7].

The dielectric measurements were made using HP 4192A (50 Hz to 13 MHz) and HIOKI 3532-50 (50 Hz to 5 MHz) impedance analyzers equipped with data acquisition system through RS232 interface. Commercial cells, of thickness 3.2 μm, were used in the form of a parallel plate capacitors made of indium tin oxide (ITO) coated glass plates, which were pre-rubbed by polymer for achieving homogeneous (HG) alignment of the molecules. By applying sufficient DC bias field (5 V μm^{-1}), homeotropic (HT) alignment of the molecules was achieved in the same cell. HG cell gives the $\varepsilon_{\perp}$ component when the measuring electric field was perpendicular to the nematic director and HT cell gives the $\varepsilon_{\|}$ component, measuring field being parallel to the director. On the other hand, custom-built gold cells of thickness 19 μm were used for frequency dependent complex dielectric permittivity measurements. In both cases, cell temperature was maintained within ±0.1^{0}C. Measuring field of amplitude 100 mV was used so that no hydrodynamic instabilities are introduced.

Results and Discussion

Optical Polarizing Microscopy Study

Molecular structure and phase transition temperatures obtained from optical polarizing microscopy are given below:



The compound possesses only a nematic phase over a very wide temperature range of 107.8^0.

X-Ray Diffraction Study

The diffraction photographs were taken at different temperatures starting from crystalline phase at room temperature to nematic phase. Heating to the isotropic phase was not possible because the material began to decompose. The photographs have two major diffraction maxima, the inner one having Bragg spacing of about 28Å and the outer one of about 6Å. The inner ring is related to the apparent length of the molecule (l) and the outer ring arises due to interaction of the neighboring molecules in a plane perpendicular to the molecular axis thus giving idea about the average intermolecular distance (D). These values have been calculated using the relations given by de Vries [13]. Variation of D with temperature is shown in Fig. 1. We see that D increases very slowly with temperature indicating a slight decrease in molecular packing. Average value of D is found to be 5.66Å, which is higher than in nonfluorinated alkylcyclohexylisothiocyanatobenzenes wherein it varies from 5.06 Å to 5.12 Å [14]. This may be due to the presence of lateral fluorine atoms associated with two phenyl groups in 2TP-3′,3-4NCS. When one lateral fluorine atom was present in the benzene ring of a nematogenic a molecule, D value was observed as 5.48 Å whereas it showed a value of 5.60Å when two fluorine atoms were connected on opposite sides of a benzene ring [8]. These molecules were having fluorine atom at the terminal position whereas 2TP-3′,3-4NCS molecules are having NCS terminal group. Therefore, present observation on D is consistent with previous reported data.

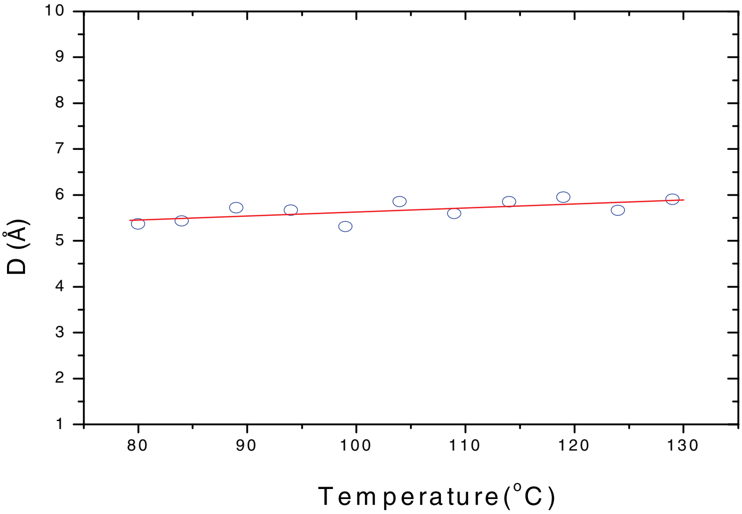


Figure 1. Variation of inter molecular distance (D) with temperature.

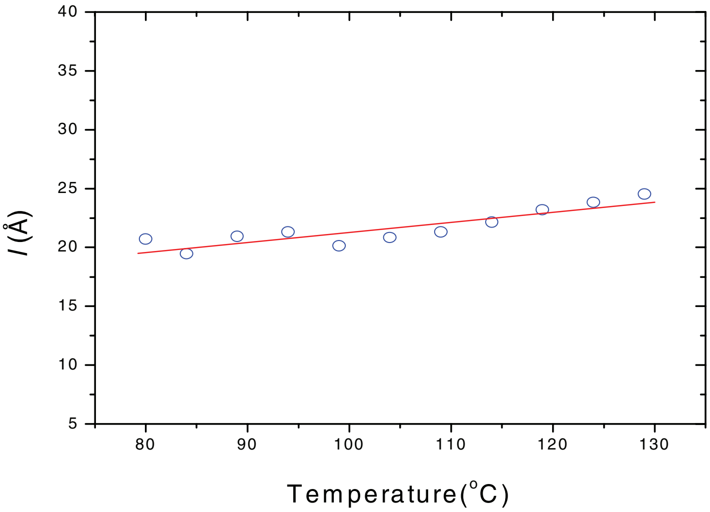


Figure 2. Variation of apparent molecular length (*l*)with temperature.

Effective length of the molecules (*l*) is found to increase from 20.7 Å to 24.5 Å, variation of *l* with temperature is shown in Fig. 2. The maximum molecular length (*L*) measured on molecular model in all *trans* conformation is found to be approximately 18.05 Å. Thus, the effective length of the molecules is considerably higher (1.15 to 1.36 times) than model length. This suggests presence of some sort of molecular association among the neighboring molecules, usually antiparallel molecular associations are suggested in molecules having terminal polar groups [15], no such association is observed in systems having no terminal polar groups from either X-ray study or dielectric study [16,17]. Crystal structure analysis on structurally similar fluorinated compounds also revealed such type of association [9,10]. To find the strength of terminal dipole of the investigated molecule, a preliminary molecular modeling calculation was carried out using semi-empirical PM3 method in Hyperchem [18]. Optimized geometry yielded a dipole moment of 6.68 Debye with a slightly higher molecular length, 18.63 Å. In the homologues of nonfluorinated alkylcyclohexylisothiocyanatobenzenes we observed *l* to vary from 1.04 to 1.16 at $T = 0.98\ T_{NI}$ [14]. Although dipole moment of 2TP-3′,3-4NCS molecules are much larger than that of alkylcyclohexylisothiocyanatobenzenes (∼3.5 D) [14], slightly less molecular overlap in the antiparallel dimeric association is observed in the present case compared to the nonfluorinated isothiocyanatobenzenes, and this may be the result of increased steric interaction due to the presence of lateral fluorine atoms and shorter terminal chain. With increasing temperature thermal energy probably helps to overcome the dipolar interaction partially, thereby increasing the apparent molecular length.

Static Dielectric Study

In order to determine switching voltage required to switch molecular alignment from planar (*HG*) to homeotropic (*HT*) configuration, dielectric constant was measured as a function of DC bias voltage across the cell, shown in Fig. 3. It was observed that 10% increase from minimum value occurred at 3.8 V and 90% of the maximum value was

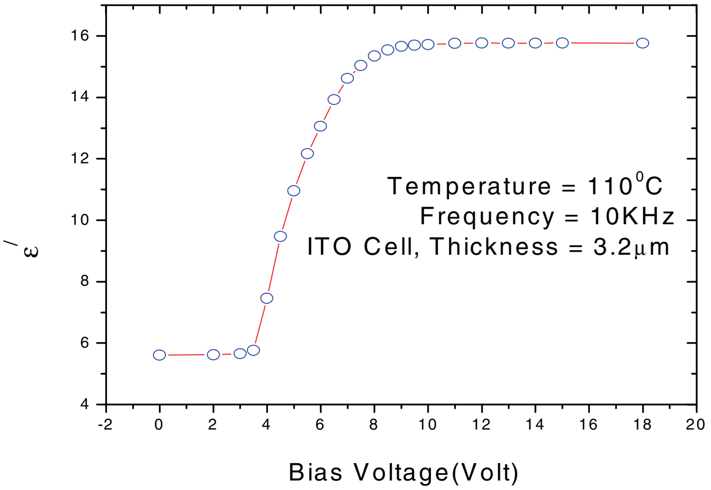


Figure 3. Real part of dielectric constant (ε') as function of bias voltage at 10 kHz in ITO cell.

obtained at 7 V, which may respectively be taken as the threshold (V_{th}) and driving (V_d) voltage for switching. Therefore, 5 V μm^{-1} field was used for switching from HG to HT configuration. Principal dielectric constants ($\varepsilon_\parallel$ and $\varepsilon_\perp$) of the sample were measured at 10 kHz and their temperature variation is shown in Fig. 4. The average values of the dielectric constants $\varepsilon_{\mathrm{av}} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$ are also shown in the same figure. Since the molecules possess quite strong axial dipole moment, value of dielectric constant parallel to the molecular axis is found to be large (about 17 near Cr–N transition) compared to component perpendicular to the molecular axis (about 6). This is expected since, from

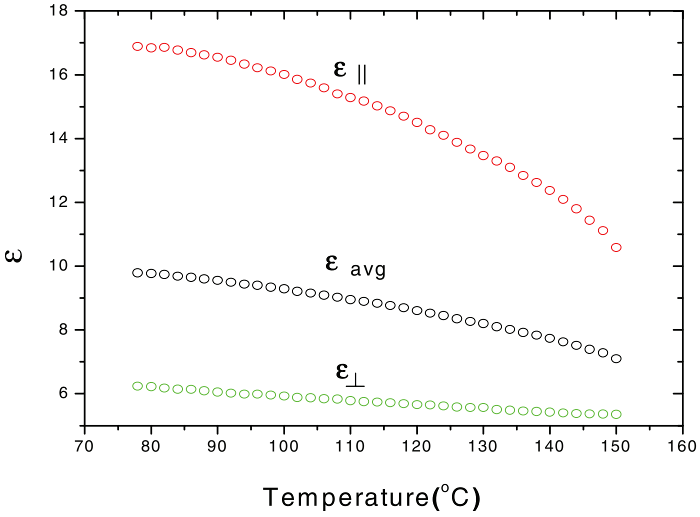


Figure 4. Variation of static dielectric constants as a function temperature at 10 KHz in ITO cell.

molecular mechanics calculation, components of dipole moments along and perpendicular to molecular axes were found to be 6.39 D and 1.95 D respectively. Temperature variation of dielectric anisotropy ($\Delta\varepsilon$) is shown in Fig. 5, it is found to decrease systematically except very near to melting point. Observed $\Delta\varepsilon$ near Cr–N transition is 10.6. In a 4-propylphenylbicyclohexyl-3,4-difluorobenzene compound with two fluorine substituents at terminal position of the benzene ring (abbreviated as $3PBC^{3,4}F_2$), maximum value of $\Delta\varepsilon$ was found to be about 6 [19], whereas in a 4,4′-propylterphenyl compound having the same alkyl chain at both ends but with two fluorine substituents at vicinal position of the central benzene ring it was about −1.2 [20]. Thus, present observation on $\Delta\varepsilon$ is consistent with previous reports on structurally similar compounds. Because of high $\Delta\varepsilon$, it is observed that 2.2 V μm^{-1} was sufficient for switching the orientation configuration of the molecules.

The splay elastic constant (K_{11}), another important parameter for switching in nematic display devices, was determined using the following formula derived for Freédericksz transition [21]:

$$V_{\mathrm{th}} = \pi\sqrt{\frac{K_{11}}{\varepsilon_0 \Delta\varepsilon}}$$

where $\varepsilon_0 = 8.85$ pF m^{-1} is the dielectric permittivity in free space. It is, as expected, found to exhibit similar decreasing trend as observed in dielectric anisotropy (Fig. 6). Value of K_{11} near Cr–N transition is found to be similar to that observed in nonfluorinated hexylcyclohexylisothiocyanatobenzene [22] and in singly fluorinated 4-propylphenylbicyclohexyl-3-fluorocyanobenzene [19] but more than that observed in doubly fluorinated $3PBC^{3,4}F_2$ [19].

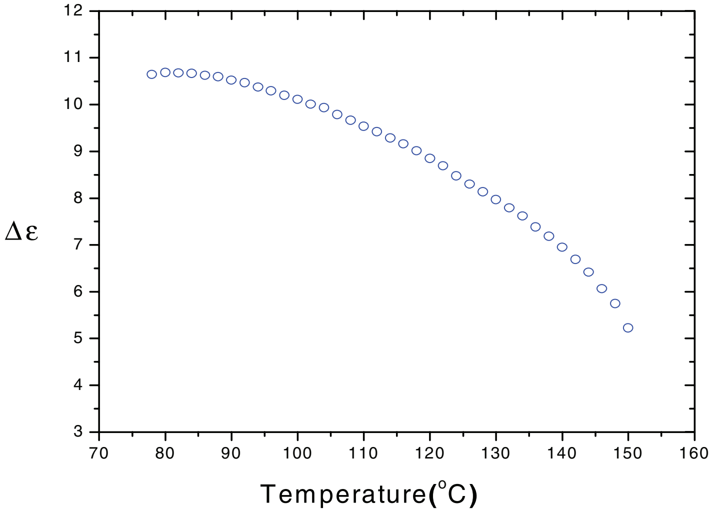


Figure 5. Temperature variation of dielectric anisotropy in 2TP-3′,3-4NCS in ITO cell.

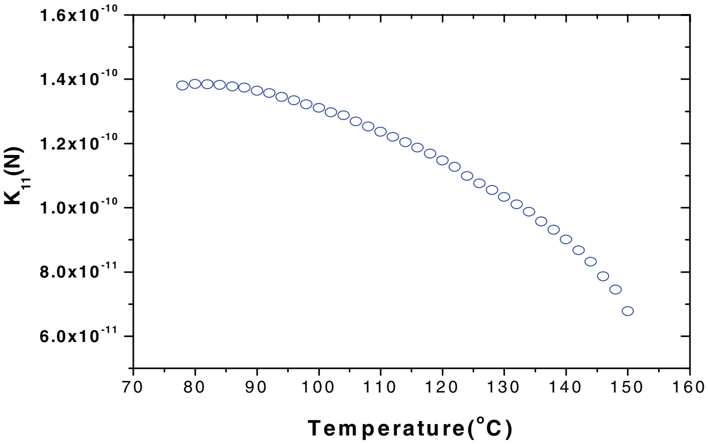


Figure 6. Temperature variation of splay elastic constant (K_{11}) in 2TP-3′,3-4NCS.

Dielectric Relaxation Behavior

In frequency dependent dielectric spectra, made in gold cell, only one strong absorption process is observed as evident from Fig. 7, for clarity spectra only at some selected temperatures are presented. We fitted the spectra to the following modified Cole–Cole complex dielectric permittivity function [23] to get actual values of relaxation frequency (f_c) and symmetric distribution parameter (α). The Cole–Cole function was modified to include contribution related to charge carriers [24]:

$$\varepsilon^* = \varepsilon^{/} - i\varepsilon^{//} = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} - \frac{i\sigma}{\omega\varepsilon_0}$$

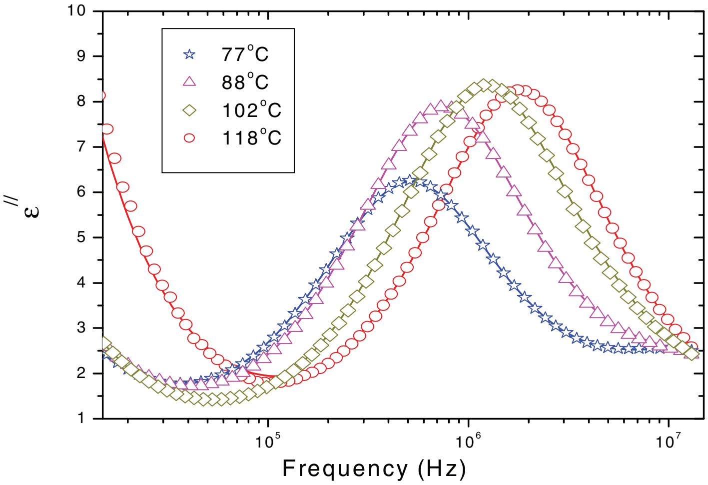


Figure 7. Dielectric absorption spectra of 2TPNCS-ff at some selected temperatures in gold cell.

which can be separated into two components:

$$\varepsilon^{/}(\omega) = \varepsilon_{\infty} + \Delta\varepsilon \frac{1 + (\omega\tau_0)^{1-\alpha} \sin\left(\left(\frac{1}{2}\right)\pi\alpha\right)}{1 + 2(\omega\tau_0)^{1-\alpha} \sin\left(\left(\frac{1}{2}\right)\pi\alpha\right) + (\omega\tau_0)^{2(1-\alpha)}}$$

$$\varepsilon^{//}(\omega) = \Delta\varepsilon \frac{(\omega\tau_0)^{1-\alpha} \cos\left(\left(\frac{1}{2}\right)\pi\alpha\right)}{1 + 2(\omega\tau_0)^{1-\alpha} \sin\left(\left(\frac{1}{2}\right)\pi\alpha\right) + (\omega\tau_0)^{2(1-\alpha)}} + \frac{\sigma}{\omega\varepsilon_0}$$

where ω is the angular frequency ($\omega = 2\pi f$), $\Delta\varepsilon = (\varepsilon_0 - \varepsilon_{\infty})$ is the dielectric strength or increment, τ_0 is the most probable relaxation time related to the critical frequency f_c as $\tau_0 = 1/(2\pi f_c)$ and α is a parameter responsible for symmetric distribution of relaxation times and σ is the conductivity related to motion of charge carriers. Fitting was made for two absorption processes (flip-flop mode and gold mode) considering first term of $\varepsilon//$ twice, as an example fitted parameters, at 77^0C,the value of dielectric increment ($\Delta\varepsilon$), relaxation frequency (f_c), symmetric distribution parameter (α) for flip-flop mode are 12.22, 509.4 kHz, and 0.012 respectively and the corresponding values for gold relaxation mode are 4.62, 16.1 MHz, and 0.07. The conductivity (σ) of the cell is found to be 1.718×10^{-6} mho m^{-1}. Fitted curves are also shown in Fig. 7. Nature of absorption process is almost Debye type since fitted α is in no case more than 0.012. The relaxation frequencies (f_c) of the absorption process are found to increase systematically from 510 kHz to 1.77 MHz with temperature. It is presumed that the relaxation process is connected with reorientations of the LC molecules around the short axis, since the reorientation around long axis is usually observed in GHz region. Observed relaxation frequency (f_c) is less than in cyanobiphenyls, e.g., in 5CB, it is 15.6 MHz [25]. This is expected since for rigid molecules f_c varies inversely with square root of moment of inertia [26], 2TP-3′,3-4NCS molecules have larger moments of inertia mainly because of large increase in their molecular mass compared to 5CB. Indeed, molecular mechanics calculation revealed that principal moments of inertia of 2TP-3′,3-4NCS and 5CB were respectively 76.7×10^{-46}, 1550.0×10^{-46}, 1626.6×10^{-46} g cm^2, and 42.9×10^{-46}, 844.1×10^{-46}, 884.3×10^{-46} kg m^2 where the first inertial axis is along the molecular long axis and the second one is along short molecular axis. In a structurally more closely related compound–propyl-terphenylisothiocyanatobenzene with fluorine atoms at 3,5 positions of isothiocyanatobenzene group (which may be abbreviated as 3TP-3,5-4NCS)–relaxation frequency was found to vary from 900 kHz to 4 MHz [27], closer to present observation. It was reported that in heptyl-bicyclohexylisothiocyanatobenzene maximum absorption occurred at 4 kHz compared to heptyl-cyclohexylisothiocyanatobenzene wherein observed relaxation frequency was about 6 MHz [28], this observation cannot be explained only because of larger moment of inertia in former compounds. In various smectic phases, however, critical frequencies were found to increase as the homologous series is ascended and was explained by introducing the idea of their dependence on anisotropic free volume [24,29].

Reorientations of entire molecule around their short axis are influenced by nematic potential barrier, which increases with increasing molecular length and decreasing temperature. Relaxation frequency thus increases with temperature and is found to obey Arrhenius law [24,30]. From a plot of ln(τ) versus inverse temperature (Fig. 8), the activation energy of the thermally activated relaxation process is found to be 35.53 kJ mol^{-1}. In 5CB, it is reported to be about 66 kJ mol^{-1} [31], very large compared to the present case, but in this case critical frequency, estimated from the graph, was found to vary between 4 MHz to

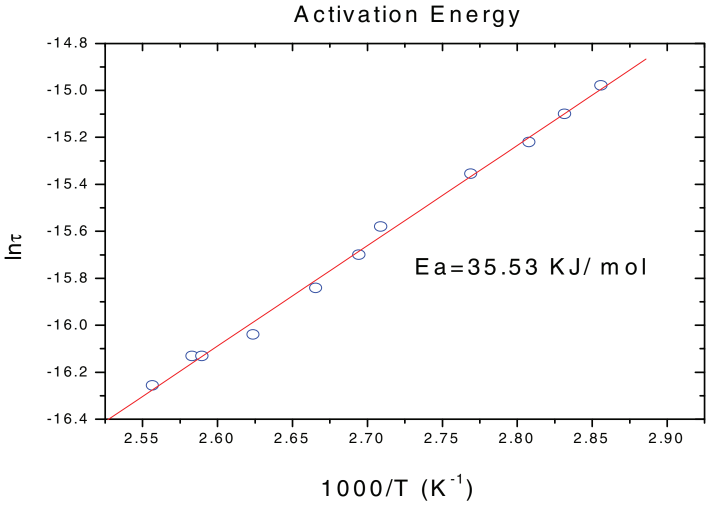


Figure 8. Variation of ln τ against 1000/T showing Arrhenius behavior.

8 MHz, almost half the value quoted in reference [25]. Thus, relaxation of 2TP-3′,3-4NCS molecules is substantially slower than of 5 CB.

Conclusions

Newly synthesized laterally fluorinated terphenyl compound 2TP-3′,3-4NCS exhibit nematic phase over a very wide temperature range –107.8^0. Molecular mechanics calculation revealed that the molecule possesses a strong axial dipole moment of 6.39D and a perpendicular component of 1.95D. From X-ray diffraction study average intermolecular distance is found to be higher than in nematic systems composed of molecules without any lateral fluorine substitution. Apparent molecular length is observed to be from 1.15 to 1.36 times the molecular model length in all *trans* conformation suggesting presence of antiparallel molecular association as reported in many systems with strong axial dipole moments. Threshold and driving voltages for the cell were found to be 3.8 V and 7 V respectively. Static dielectric constant parallel to molecular axis is large compared to perpendicular component, consistent with respective components of dipole moments. Dielectric anisotropy, positive throughout the phase, is found to decrease monotonically with temperature quite fast. Splay elastic constant was also determined using threshold voltage and $\Delta\varepsilon$ and found to follow similar decreasing trend with temperature as in $\Delta\varepsilon$. Only one relaxation process with strong absorption is observed from frequency dependent dielectric study, critical frequency of which, when fitted to modified Cole–Cole function, is found to increase with temperature from 510 kHz to 1.77 MHz exhibiting Arrhenius behavior. Relaxation process is connected with reorientations of the LC molecules around the short axis and the activation energy of the thermally activated relaxation process is found to be 35.53 kJ mol^{-1}.

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References

[1] Gauza, S., Wang, H., Wen, C. H., Wu, S. T., Seed, A., & Dabrowski, R. (2003). *Jpn. J. Appl. Phys.*, *42*, 3463.

[2] Gasowska, J. S., Cowling, S. J., Cockett, M. C. R., Hird, M., Lewis, R. A., Raynes, E. P., & Goodby, J. W. (2010). *J. Mater. Chem.*, *20*, 299.

[3] Moria, A., Hashimoto, M., & Ujiiec, S. (2011). *Liq. Cryst.*, *38*, 263.

[4] Demus, D., Goto, Y., Swada, S., Nakagawa, E., Saito, H., & Tarao, R. (1995). *Mol. Cryst. Liq. Cryst.*, *260*, 1.

[5] Nishi, T., Matsubara, A., Okada, H., Onnagawa, H., Sugimori, S., & Miyashita, K. (1995). *Jpn. J. Appl. Phys.*, *34*, 236.

[6] Petrov, V. F. (1995). *Liq. Cryst.*, *19*, 729.

[7] Biswas, S., Haldar, S., Mandal, P. K., & Haase, W. (2007). *Liq. Cryst.*, *34*, 365.

[8] Haldar, S., Barman, S., Mandal, P. K., Haase, W., & Dabrowski R. (2010). *Mol. Cryst. Liq. Cryst.*, *528*, 81.

[9] Haldar, S., Biswas, S., Mandal, P. K., Goubitz, K., Schenk, H., & Haase, W. *(*2008). *Mol. Cryst. Liq. Cryst.*, *490*, 80.

[10] Haldar, S., Mandal, P. K., Prathap, S. J., Guru Row, T. N., & Haase, W. (2008). *Liq. Cryst.*, *35*, 1307.

[11] Dabrowski, R., & Szczucinski, Ł. (In preparation).

[12] Jha, B., Paul, S., Paul, R., & Mandal, P. (1989). *Phase Transit.*, *15*, 39.

[13] Vries, A. De. (1970). *Mol. Cryst. Liq. Cryst.*, *10*, 219.

[14] Sarkar, P., Mandal, P., Paul, S., Paul, R., Dabrowsski, R., & Czuprynski, K. (2003). *Liq. Cryst.*, *30*, 507.

[15] Leadbetter, A. J., Richardson, R. M., & Cooling, C. N. (1975). *J. Phys. (Paris).*, *36-C1*, 37.

[16] Sarkar, P. K., Paul, S., & Mandal, P. (1995). *Mol. Cryst. Liq. Cryst.*, *265*, 249.

[17] Madhusudana, N.V., & Chandrasekhar, S. (1975). *Pramana Suppl.*, *1*, 57.

[18] Hyperchem 6.03, Hypercube Inc., Gainesville, FL, USA.

[19] Ishikawa, H., Toda, A., okada, H., Onnagawa, H., & Sugimori, S. (1997). *Liq. Cryst.*, *22*, 743.

[20] Urban, S., Kula, P., Spadlo, A., Geppi, M., & Marini, A. (2010). *Liq. Cryst.*, *37*, 1321.

[21] Kundu, B., Pal, S. K., Kumar, S., Pratibha, R., & Madhusudana, N. V. (2010). *Physical Review E.*, *82*, 061703.

[22] Dhar, R., Pandey, A. S., Pandey, M. B., Kumar, S., & Dabrowski, R. (2008). *Appl. Phys. Express*, *1*, 121501.

[23] Cole, K. S., & Cole, R. S. (1941). *J. Chem. Phys.*, *9*, 341.

[24] Schacht, J., Zugenmaier, P., Buivydas, M., Komitov, L., Stebler, B., Lagerwall, S. T., Gouda, F., & Horii, F. (2000). *Phys. Rev. E.*, *61*, 3926.

[25] Gu, M., Yin, Y., Shiyanovskii, S. V., & Lavrentovich, O. D. (2007). *Phys. Rev. E.*, *76*, 061702.

[26] Baessler, H., Beard, R. B., & Labes, M. M.(1970). *J. Chem. Phys.*, *52*, 2292.

[27] Czub, J., Dabrowski, R., Dziaduszek, J., & Urban, S. (2009). *Phase Transit.*, *82*, 485.

[28] Urban, S., Dabrowski, R., Dziaduszek, J., Janik J., & Moscicki, J. K. (1999). *Liq. Cryst.*, *26*, 1817.

[29] Benguigui, L. (1983). *Phys. Rev. A*, *28*, 1852.

[30] Diogo, A. C., & Martins, A. F. (1982). *J. Phys. (Paris).*, *43*, 779.

[31] Czub, J., Gubernat, U., Gestblom, B., Dabrowski, R., & Urban, S. (2004). *Z. Naturforsch.*, *59a*, 316.