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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713644168>

Influence of Molecular Core Structure and Chain Length on the Physical Properties of Nematogenic Fluorobenzene Derivatives

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First published on: 20 October 2010

To cite this Article Haldar, S. , Barman, S. , Mandal, P. K. , Haase, W. and Dabrowski, R.(2010) 'Influence of Molecular Core Structure and Chain Length on the Physical Properties of Nematogenic Fluorobenzene Derivatives', *Molecular Crystals and Liquid Crystals*, 528: 1, 81 – 95

To link to this Article: DOI: 10.1080/15421406.2010.504617

URL: <http://dx.doi.org/10.1080/15421406.2010.504617>

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Influence of Molecular Core Structure and Chain Length on the Physical Properties of Nematogenic Fluorobenzene Derivatives

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The influence of molecular core structure and chain length on various physical properties of nine nematogenic fluorobenzene derivatives obtained by optical polarizing microscopy, differential scanning calorimetry, X-ray diffraction, and optical birefringence techniques have been studied. It is observed that the temperature range of the nematic phase decreases when a cyclohexyl ring is replaced by a phenyl ring and when the number of fluorine atoms in the benzene group is increased. A change of some properties was noticed in difluoro (ff) derivatives compared to monofluoro (f) and trifluoro (fff) derivatives. The average intermolecular distance is found to increase systematically from mono to trifluoro derivatives. Effective molecular length (l) is found to be higher than the most extended length of the molecules, suggesting the presence of anti-parallel-type dimers. l is also found to be less in ff derivatives than in f and fff derivatives, indicating that the overlap between dimerized molecules in ff derivatives is more than in f and fff derivatives. The optical anisotropy (Δn) is found to be highest in an ff system compared to f and fff systems in 5ccp and 5cpp series, but the opposite behavior is observed in 3ccp series. 5ccp-f, having the lowest Δn and nematic phase over a large temperature, is expected to be useful for high-information-content display devices. The density of fff derivatives is found to be more than in ff derivatives in all systems, which is also true in the crystalline state of a 3ccp system. The orientational order parameters $\langle P_2 \rangle$ obtained from polarizability data are found to be slightly more, whereas the X-ray order parameters are found to be close to the mean field values in all the systems. A decreasing trend of $\langle P_2 \rangle$ is observed as one moves from $f \Rightarrow fff \Rightarrow ff$ system.

Keywords Density and polarizability; nematogenic fluorobenzene derivatives; optical birefringence; orientational order parameters; X-ray diffraction study

Introduction

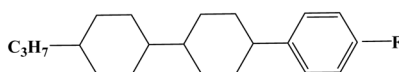
Nine fluorobenzene derivatives (the structures are shown in Fig. 1) have been studied by optical polarizing microscopy (OPM), differential scanning calorimetry (DSC), X-ray diffraction, and optical birefringence techniques. These materials have a wide range of nematic phase, high chemical stability, moderate dielectric anisotropy ($\Delta\epsilon = 4\text{--}12$), low optical anisotropy, high bulk resistivity, and very good voltage holding ratio. All these features are important for liquid-crystal displays (LCDs) with large information contents as in color TVs and computer terminals. These materials are very important as base materials for use in active matrix displays (AMDs) such as in thin-film-transistor (TFT) and metal-insulator-metal (MIM) systems [1–4]. Their physical properties such as anisotropy ($\Delta\epsilon$), birefringence (Δn), are known at room temperature (usually at 20°C) as the extrapolated values from measurement of their solution in a host nematic mixture, but the results of direct measurement have not yet been reported.

The physical properties of difluorobenzene derivatives were investigated by using OPM, DSC, X-ray diffraction, and optical birefringence techniques [5]. In this article we report the influence of molecular core structure and chain length on their physical properties like optical indices, density, apparent length, intermolecular distance, and order parameters obtained or calculated employing different techniques. Crystal and molecular structures of two such compounds were also determined from single crystal X-ray diffraction data and their structure-property relationships were explored [6,7].

Experimental

The phase behavior of the compounds has been reinvestigated by optical polarizing microscopy and DSC methods (Mettler FP82 and 84 Thermosystems). X-ray diffraction photographs of magnetically oriented samples are taken using a home-built high-temperature camera [8]. The diffraction photographs have been scanned by a HP2400C scanner (Hewlett Packard) in 24 bit RGB color format. Optical densities of the pixels are calculated from the color values and subsequently converted to X-ray intensities with the help of a calibration strip prepared by exposing the film (Kodak) for several known time intervals. Intensity distribution, obtained from the linear scan of X-ray photographs along the equatorial and meridional diffraction peaks, is used to determine average intermolecular distance (D) and apparent molecular length (l) with an accuracy of ± 0.02 and ± 0.1 Å, respectively. Similarly, circular intensity distribution data along the outer diffraction feature of the X-ray photographs are used to calculate the orientational distribution function following Leadbetter and Norris [9] and orientational order parameters ($\langle P_2 \rangle$ and $\langle P_4 \rangle$) were calculated from the distribution functions with an accuracy of ± 0.02 . Order parameters have also been calculated following Maier-Saupe theory [10]. Detailed procedures have been described previously [11–13].

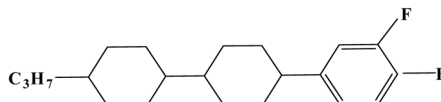
Densities of the compounds were measured as a function of temperature using a dilatometer. Ordinary and extraordinary refractive indices (n_e and n_o) are measured for three different wavelengths 5461 Å (green), 5780 Å (yellow), and 6907 Å (red) using the thin prism technique [14]. Accuracy of measurement is 0.1%. From the measured refractive indices and density values, the principal polarizabilities are calculated following the methods of Neugebauer [15] and Vuks [16], which were developed respectively on the assumption of isotropic and anisotropic internal fields.

1. *trans*-4-propyl-*trans*-4'-(4-fluorophenyl) bicyclohexane (3ccp-f)

Cr 90.0 (71.0) N 158.0 I

Cr 88.6 N 158.5 I [18]

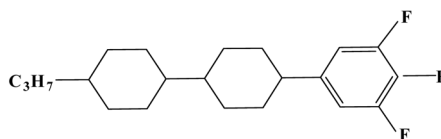
2. 4-propyl-4'-(3,4-difluorophenyl) bicyclohexane (3ccp-ff)



Cr 46.0 (38.5) N 123.8 I

Cr 46.0 N 124.1 I [19]

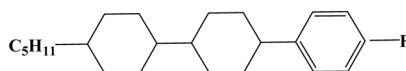
3. 4-propyl-4'-(3,4,5-trifluorophenyl) bicyclohexane (3ccp-fff)



Cr 66.0 (49.0) N 94.1 I

Cr 64.9 N 93.8 I [20]

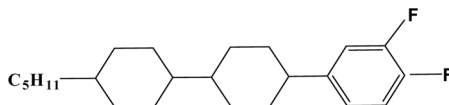
4. 4-pentyl-4'-(4-fluorophenyl) bicyclohexane (5ccp-f)



Cr 68.0 (44.0) SmB 75.5 N 157.0 I

Cr 68.0 SmB 75 N 157.0 I [21]

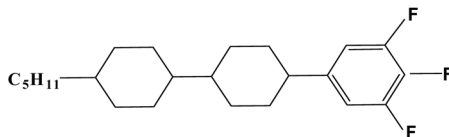
5. 4-pentyl-4'-(3,4-difluorophenyl) bicyclohexane (5ccp-ff)



Cr 47.0 (26.8) N 125.2 I

Cr 45.2 N 125 I [1]

6. 4-pentyl-4'-(3,4,5-trifluorophenyl) bicyclohexane (5ccp-fff)

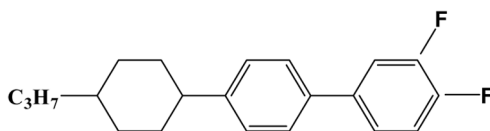


Cr 88.0 (57.0) N 102.4 I

Cr 87.3 N 101.2 I [2]

Figure 1. Molecular formulae, structures, and observed transition temperatures (°C). Literature values [1,2,18–21] are also shown.

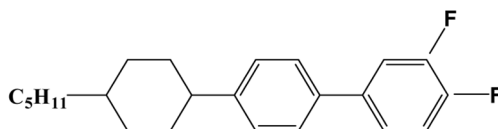
7. 3, 4-difluoro-4'-(4-propylcyclohexyl)-biphenyl (3cpp-ff)



Cr 68.5 (46.4) N 97.9 I

Cr 67.9 N 98.6 I [1]

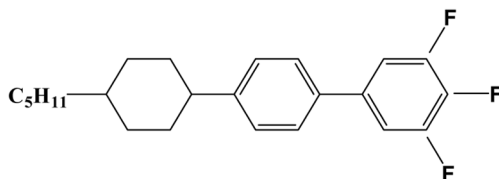
8. 3, 4-difluoro-4'-(4-pentylcyclohexyl)-biphenyl (5cpp-ff)



Cr 56.0 (38.7) N 105.8 I

Cr 55.1 N 108.2 I [1]

9. 3, 4, 5-trifluoro-4'-(4-pentylcyclohexyl)-biphenyl (5cpp-fff)



Cr 33.0 (27.0) N 54.8 I

Cr 30.4 N 58.1 I [2]

Figure 1. Continued.

Orientational order parameters are calculated using the relation $\langle P_2 \rangle = (\alpha_e - \alpha_o) / (\alpha_{\parallel} - \alpha_{\perp})$. The value of $(\alpha_{\parallel} - \alpha_{\perp})$, polarizability anisotropy of the medium in the perfectly ordered state, is calculated by Haller *et al.*'s extrapolation procedure [17].

Results and Discussions

Molecular formulae and structures of the investigated compounds along with their transition temperatures (in °C), as obtained from OPM, are given in Fig. 1; crystallization temperatures are shown in parentheses. All the investigated compounds exhibit the nematic phase; only compound 4(5ccp-f) shows smectic B (SmB) phase in addition. Observed transitions agree well with reported data, except for compounds 8 and 9, wherein clearing points are about 3 degrees lower. In some cases small differences in transition temperatures are observed from microscopy and DSC studies. Also, transition temperatures obtained from X-ray and refractive indices studies are found to vary slightly, indicating that sample geometry and thermal history are influential. Moreover, in all cases crystallization temperatures are found to be considerably less than melting points. Such small variation has also been reported previously [22]. Temperature range of the nematic phase (ΔT) and changes in enthalpy (ΔH) and entropy (ΔS) values at transitions are shown in Table 1. It is

Table 1. Table of important data. Values in columns 6–15 are at 80°C

Compounds	N range (°C)	$\Delta H_{\text{G-N}},$ $\Delta H_{\text{N-I}}$ (kJ mol ⁻¹)	$\Delta S_{\text{G-N}},$ $\Delta S_{\text{N-I}}$ (J mol ⁻¹ K ⁻¹)	L_{calc} (Å)	l (Å)	l/L	D (Å)	n_e	n_o	$\langle P_2 \rangle$ (RI)	$\langle P_2 \rangle$ (XRD)	ρ (g cm ⁻³)	$\Delta\alpha$ $\times 10^{24}$	μ (D)
1 (3cp-f)	87.0	14.32 0.31	39.47 0.71	17.00	25.11	1.48	5.50	1.573	1.457	0.77	0.70	1.07	11.02	1.93
2 (3cp-ff)	85.3	12.85 0.38	40.35 0.96	17.64	22.61	1.28	5.48	1.578	1.512	0.70	0.73	1.00	4.93	3.21
3 (3cp-fff)	45.1	15.98 0.20	46.92 0.56	17.00	24.44	1.44	5.60	1.554	1.460	0.60	0.61	1.05	7.85	3.72
4 (5cp-f)	81.5	9.72 0.27	28.51 0.64	19.10	25.89	1.36	5.45	1.587	1.520	0.78	0.71	1.06	6.75	1.93
5 (5cp-ff)	98.4	16.76 0.37	52.39 0.93	19.38	23.80	1.23	5.55	1.581	1.484	0.72	0.77	0.98	8.01	3.12
6 (5cp-fff)	45.4	16.53 0.17	45.83 0.44	19.10	27.41	1.44	5.60	1.534	1.480	0.74	0.61	0.99	4.08	3.73
7 (3cp-ff)	51.5	14.05 0.21	41.34 0.57	17.25	21.90	1.27	5.41	1.598	1.465	0.63	0.62	1.05	9.08	3.66
8 (5cp-ff)	67.1	12.19 0.45	37.20 1.19	19.29	23.04	1.19	5.39	1.629	1.488	0.71	0.67	1.01	10.57	3.48
9 (5cp-fff)	27.8	10.45 0.04	34.12 0.11	19.10	24.80	1.30	5.60	—	—	—	—	1.09	—	4.25

observed that the temperature range of the nematic phase decreases when a cyclohexyl ring is replaced by a phenyl ring [3ccp-ff(**2**) \Rightarrow 3cpp-ff(**7**) 33.8°C; 5ccp-ff(**5**) \Rightarrow 5cpp-ff(**8**) 31.3°C; 5ccp-fff(**6**) \Rightarrow 5cpp-fff(**9**) 17.6°C] and when the number of fluorine atoms in the benzene group is increased [3ccp-f(**1**) \Rightarrow 3ccp-ff(**2**) 1.7°C; 3ccp-ff(**2**) \Rightarrow 3ccp-fff(**3**) 40.2°C; 5ccp-ff(**5**) \Rightarrow 5ccp-fff(**6**) 53.0°C; and 5ccp-ff(**8**) \Rightarrow 5cpp-fff(**9**) 39.3°C]. However, only a slight variation of nematic range with chain length is observed.

X-ray diffraction photographs show that the phases are ordinary nematic in all cases, and a representative photograph of compound **3** is shown in Fig. 2. The average intermolecular distances (D), calculated from the outer diffraction peaks, are found to increase with temperature from 5.52 to 5.74 Å, 5.36 to 5.67 Å, 5.53 to 5.71 Å, 5.45 to 5.64 Å, 5.48 to 5.69 Å, 5.62 to 5.66 Å, 5.37 to 5.51 Å, 5.28 to 5.47 Å, and 5.23 to 5.41 Å in compounds **1** to **9**, respectively. The variations of average intermolecular distance (D) with temperature (T) are shown in Fig. 3. D values are found to increase systematically from mono to trifluoro derivatives (f \Rightarrow fff) for all of the compounds. It is observed that the D value decreases when a cyclohexyl ring is replaced by a phenyl ring (**2** \Rightarrow **7**), (**5** \Rightarrow **8**), and (**6** \Rightarrow **9**) but no systematic variation of D with chain length is observed.

Effective lengths of the molecules (l) in the liquid-crystal (LC) phase are found to be considerably higher than the calculated lengths of the molecules (L) in the most extended conformation. By optimizing the geometry of the molecules using the software Hyperchem V6.03 [23], L values were calculated for all and were found to be in good agreement with the model lengths of the molecules in all *trans* conformations. l values are found to increase with the chain length in the systems (**1** \Rightarrow **4**, **2** \Rightarrow **5**, **3** \Rightarrow **6** and **7** \Rightarrow **8**), as well as when the phenyl group is replaced by the cyclohexyl group in the systems (**7** \Rightarrow **2**, **8** \Rightarrow **5** and **9** \Rightarrow **6**). The ratio (l/L) is found to vary between 1.19 and 1.48 in all the compounds, suggesting the presence of some short-range antiferroelectric-type associations between the neighboring molecules. Such associated dimers are found to exist also in the crystalline state of samples **2**(3ccp-ff) and **3**(3ccp-fff) respectively [6,7]. As a consequence of increased steric hindrance, overlap of the dimerized molecules slightly decreases (l/L ratio increases) when a phenyl group is replaced by a cyclohexyl group. Formation of dimers is characteristic for cyano compounds, for example, for cyanobiphenyls; however, the observed ratio is usually high (~ 1.4) in all members of the series [24]. However, in one terminal fluorinated ester compound this ratio in the smectic phase was reported to be about 1.0 [25].

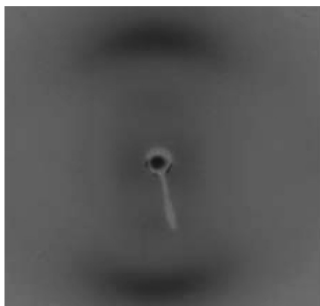


Figure 2. X-ray diffraction photograph of ordinary nematic phase of compound **3**(3ccp-fff).

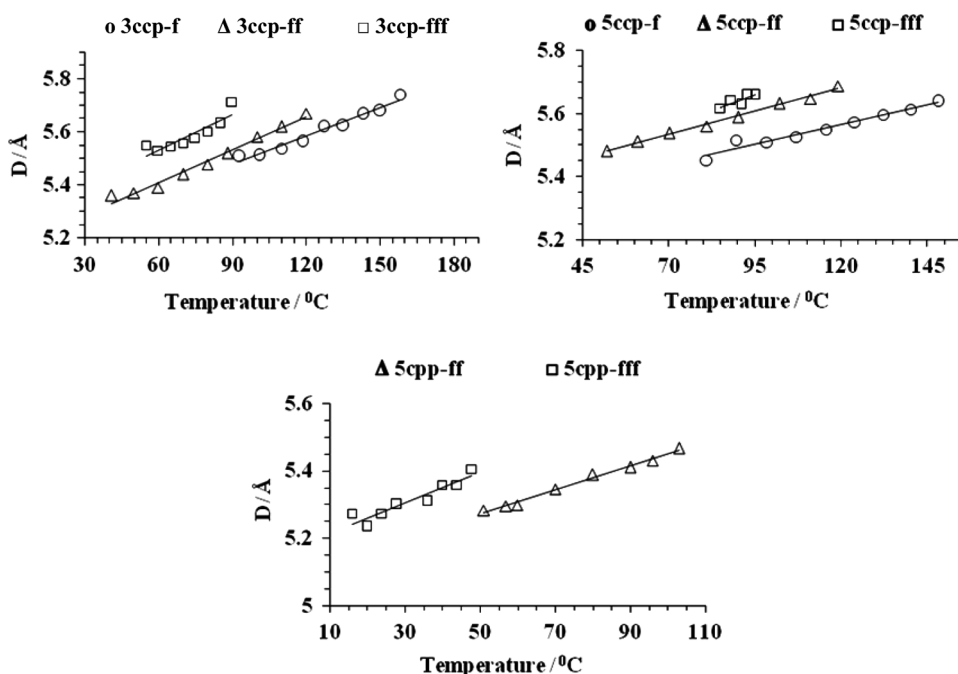


Figure 3. Variation of D with temperature for different compounds.

Apparent molecular length (l) of the molecules is found to be less in ff derivatives than in f and fff derivatives (shown in Table 1). This indicates that the overlap between neighboring molecules in ff derivatives is more than in f and fff derivatives or dimer concentration is smaller or both. For all the compounds, l is found to decrease slightly with temperature as shown in Fig. 4, indicating that the molecular overlap increases with temperature or concentration of dimer falls.

The values of molecular dipole moment (μ) were calculated using the semi-empirical PM3 force field in software Hyperchem and are shown in the Table 1. Difluoro derivatives differ from mono and trifluoro derivatives in the direction of the dipole moment along the molecular axis. It is strongly tilted for ff compounds, whereas in others it is concordant with the molecular axis. It is observed that the dipole moment (μ) increases systematically as one moves from f \Rightarrow fff derivatives in all systems. However, the increment is more for f \Rightarrow ff derivatives than for ff \Rightarrow fff derivatives and there is no change in the dipole moment with chain length, as expected [26].

Variation of density with reduced temperature ($T^* = T/T_{NI}$) for all the compounds is shown in Fig. 5. It is evident that as the chain length increases (1 \Rightarrow 4 or 2 \Rightarrow 5 or 3 \Rightarrow 6 or 7 \Rightarrow 8) density decreases. Also when more flexibility is introduced in the core structure of the molecules, replacing a phenyl ring by a cyclohexyl ring, (7 \Rightarrow 2 or 8 \Rightarrow 5 or 9 \Rightarrow 6) reduction in density is observed. Thus molecular packing is less efficient, as expected, with increasing flexibility either in the chain or in the core structure. Density in fff derivatives is found to be more than in ff derivatives in all systems—3ccp, 5ccp, and 5cpp. This is also found to be true in the crystalline states of the 3ccp system and the measured values are 1.191(3ccp-fff) [7] and 1.145 (3ccp-ff) [6], respectively. Density is found to decrease linearly with temperature in

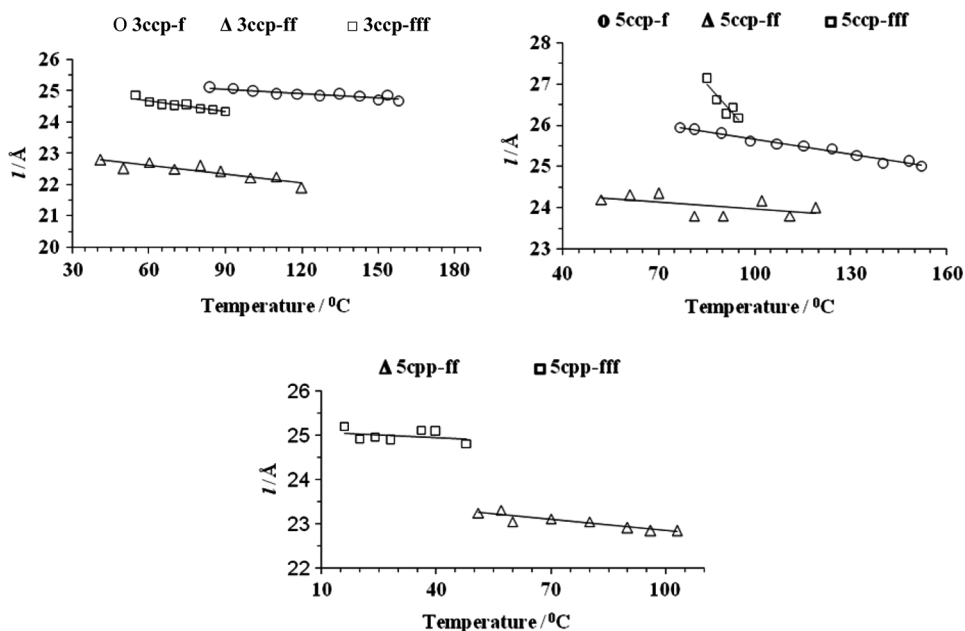


Figure 4. Temperature variation of l for different compounds.

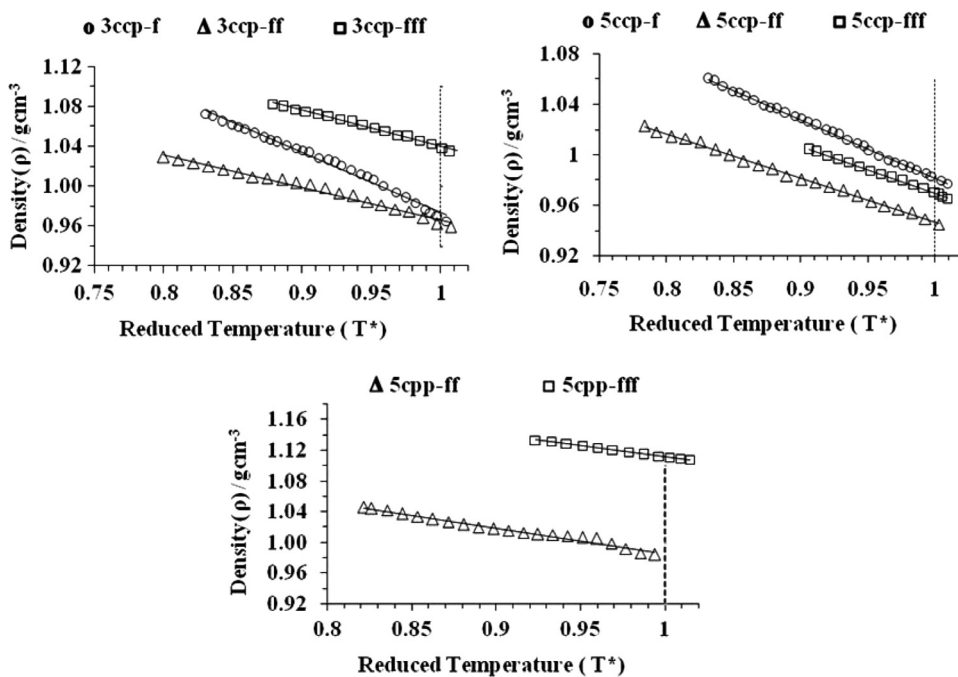


Figure 5. Variation of density (ρ) with reduced temperature $T^* = T/T_{NI}$ for different compounds.

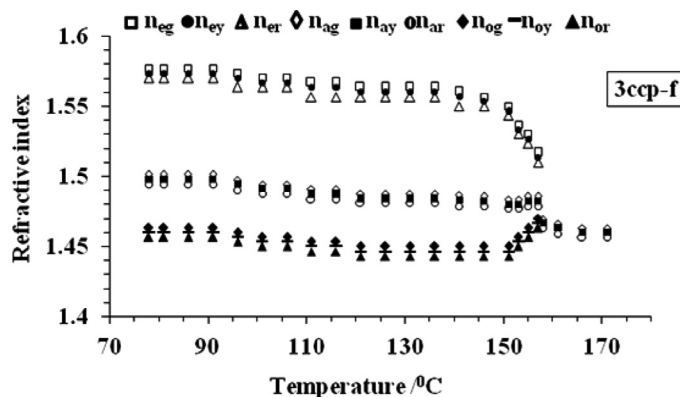


Figure 6. Temperature variation of n_e , n_o , and n_{av} of compound 1(3ccp-f) for three wavelengths ($\lambda_g = 5461$, $\lambda_y = 5780$, $\lambda_r = 6907$ Å).

all the systems. The f compounds show stronger temperature dependence of density than ff and fff compounds.

Temperature variations of the refractive indices, measured at wavelengths 5461, 5780, and 6907 Å, are shown in Fig. 6 for the compound 1(3ccp-f) as an example, and for other compounds this is shown Fig. 7 only for yellow color, because variations with wavelength are similar. All the refractive indices exhibit normal dispersive behavior; that is, the parameters decrease with increasing wavelength. This type of behavior was reported earlier in many systems like nCBs [27], Schiff's bases

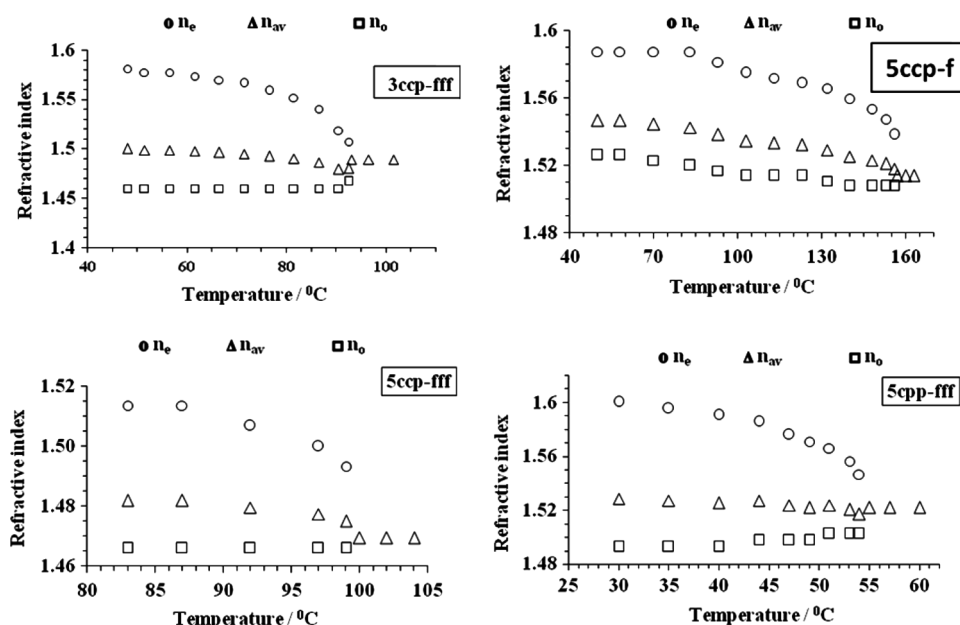


Figure 7. Temperature variation of n_e , n_o , and n_{av} of different compounds for yellow color (5780 Å).

[28–30], benzoyloxybenzoates [31], and isothiocyanatobenzenes [32]. It is found that refractive indices of the extraordinary ray decrease quite fast with temperature, whereas for the average refractive indices (n_{av}) calculated for uniaxial nematic phase as $(2n_o + n_e)/3$ the rate of decrease is less. Ordinary refractive indices do not vary appreciably with temperature. The pretransition effect is observed very near to T_{NI} . Refractive indices in the isotropic phase (n_{iso}) are found to be less than n_{av} within the phase for compounds **1**, **4**, and **6** but in compounds **3** and **9** it is greater- (shown in Fig. 7). Moreover, compounds **3** and **9** (fff derivatives) have a different temperature dependence of the n_o index. It decreases with decreasing temperature, whereas for the f and ff substitution, n_o changes in the opposite manner. The first behavior is characteristic for strongly polar compounds, for example, 5CB, and second for weakly polar compounds like NCS compounds [33].

A positive optical anisotropy (Δn) is observed in all the compounds, which decreases with temperature as shown in Fig. 8. The Δn values are found to be largest in ff systems compared to f and fff systems in 5ccp and 5cpp series; however, in 3ccp series ff systems possess the lowest value. This may be due to lower chain length. The decreasing rate with temperature for compounds **1**, **4**, **6** is quite low when far from the T_c but near T_c it is highest. The rate of decrease is low throughout for compound **2** and moderate for compounds **3**, **5**, **8**, and **9**. Low optical anisotropy is required for developing fast and high-information-content LCDs [34]. Compounds **4** and **6**, having Δn in the range 0.067 to 0.034, will therefore be more suitable in this respect. As mentioned earlier, compound **4** also exhibits a nematic phase over a wide temperature (81.5°C).

Molecular polarizabilities (α_e , α_o , and α_{av}) are calculated for all compounds for three wavelengths and their temperature variation for yellow light is shown in Fig. 9

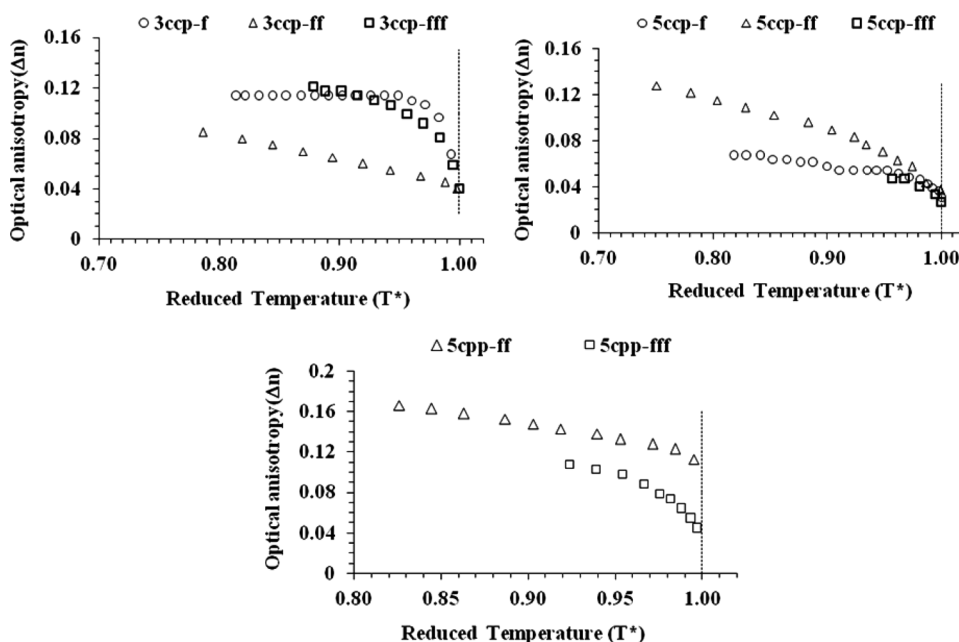


Figure 8. Variation of Δn with reduced temperature (T^*) for different compounds.

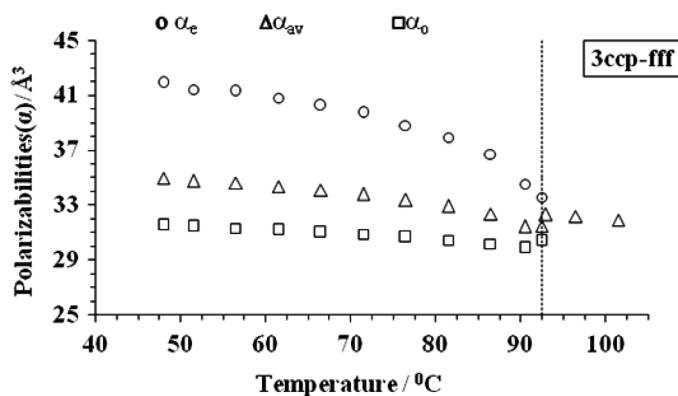


Figure 9. Variation of α_e , α_o , and α_{av} with temperature for compound 3(3ccp-fff) for yellow light.

for compound 3 as a representative example. Similar variations are observed for other wavelengths and remaining compounds. It is observed that like Δn , polarizability anisotropy ($\Delta\alpha$) is at a maximum in 5ccp-ff and 5cpp-ff systems and a minimum in 3ccp-ff. $\Delta\alpha$ is found to decrease with temperature as shown in Fig. 10; the nature of variation is similar to that observed in Δn .

Molecules in the nematic phase have no positional correlation but they do have long-range orientational ordering. The extent of ordering is usually qualified by orientational order parameters (OOPs), which are uniaxial and are expressed by a traceless symmetric tensor of rank 2. Many physical properties like optical

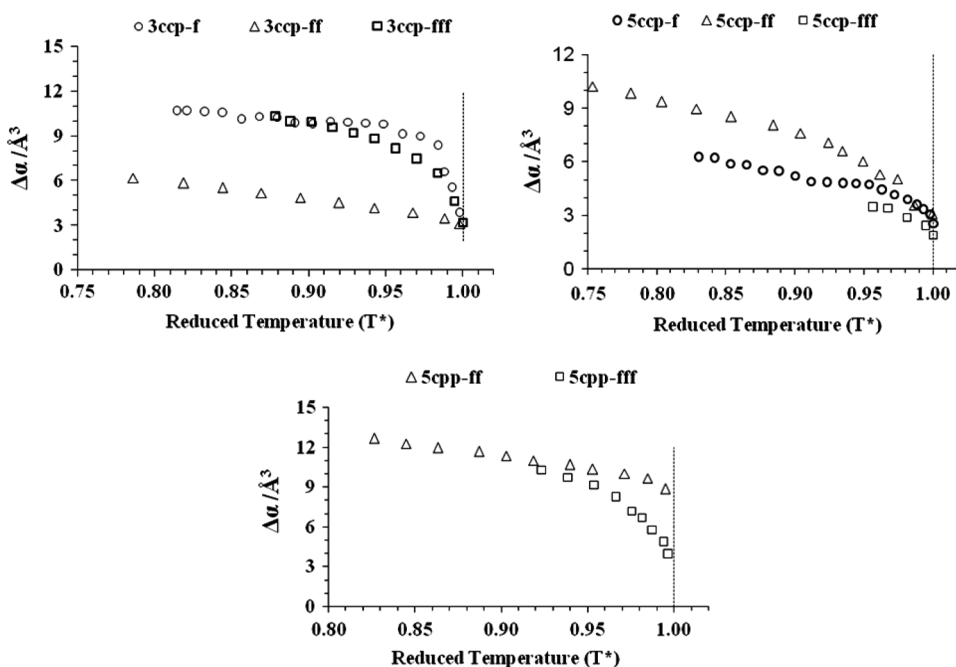


Figure 10. Variation of $\Delta\alpha$ with reduced temperature (T^*) for different compounds.

birefringence, dielectric anisotropy, threshold voltage for switching, etc., which are important device parameters, depend upon the OOPs. Although by determining the orientational distribution functions from the azimuthal intensity distribution of the X-ray diffraction photographs one can, in principle, determine different order OOPs, we have determined only the second- and fourth-order OOPs, viz. $\langle P_2 \rangle$ and $\langle P_4 \rangle$. Temperature variation of OOPs determined from the polarizability and X-ray data are shown in Fig. 11. $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values, calculated following Maier-Saupe mean field theory [10], are also shown in Fig. 11. $\langle P_2 \rangle$ values obtained from polarizability data are found to be slightly more than the mean field values, but X-ray order parameters are found to be close to the mean field values in all the systems. $\langle P_2 \rangle$ values obtained from different techniques agree fairly well in most of the compounds, though in some compounds the agreement is not good. Difference in $\langle P_2 \rangle$ values obtained from two such different techniques were reported earlier [35–37]. This may be due to different averaging procedures involved in the two methods. Moreover, there may be error in the estimation of polarizability values of the crystalline state obtained by extrapolation method of Haller *et al.* [17].

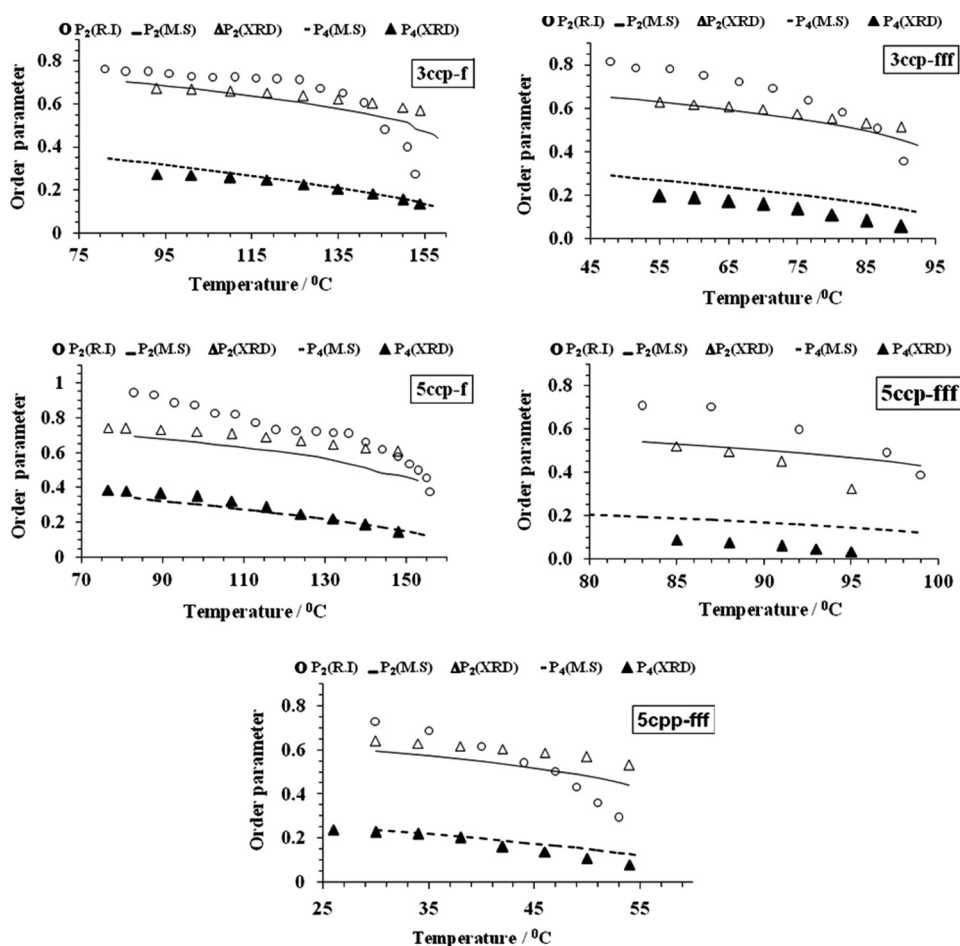


Figure 11. Temperature variation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for different compounds.

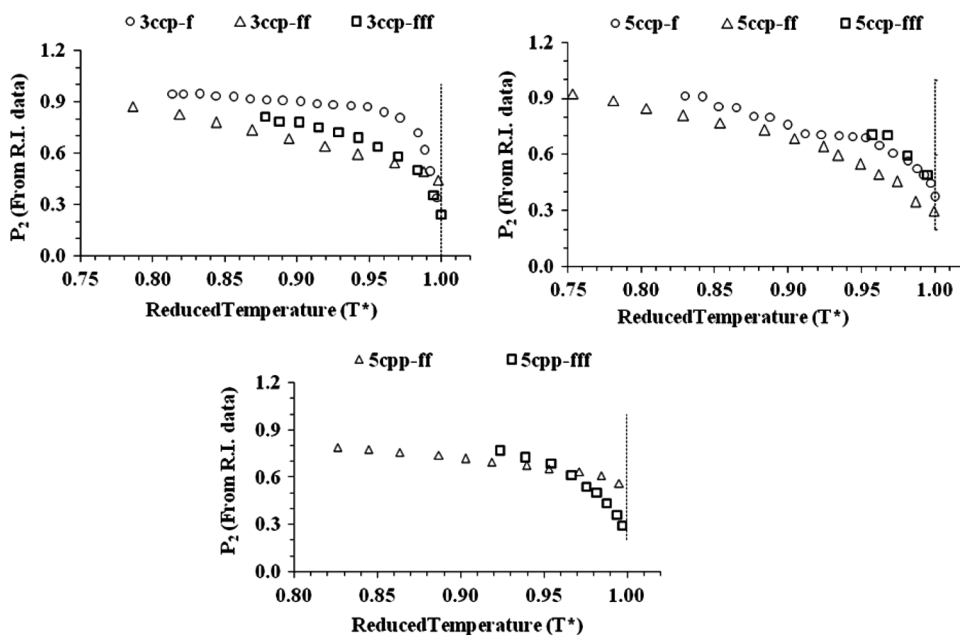


Figure 12. Variation of $\langle P_2 \rangle$, obtained from refractive index data, with T^* for different compounds.

In Fig. 12, the order parameter $\langle P_2 \rangle$, obtained from refractive indices data, has been plotted as a function of reduced temperature for all the compounds of a series to see the effect of molecular structure on $\langle P_2 \rangle$. X-ray data show a similar trend. There is a decreasing trend of $\langle P_2 \rangle$ as one moves from (f \Rightarrow fff \Rightarrow ff) system.

Conclusions

Fluorobenzene derivatives are important materials because they possess several optimal physical properties required for liquid-crystal displays (LCDs) with large information contents. The influence of molecular core structure and the extent of fluorination of the core structure and chain length on the physical properties, like optical indices, density, apparent molecular length, intermolecular distance and order parameters, of nine nematogenic fluorobenzene derivatives obtained by optical polarizing microscopy, differential scanning calorimetry, X-ray diffraction, and optical birefringence techniques, have been discussed.

It is observed that the temperature range of the nematic phase decreases when a cyclohexyl ring is replaced by a phenyl ring and when the number of fluorine atoms in the benzene group is increased. Change of some properties was noticed in the difluoro (ff) derivatives compared to mono- (f) and trifluoro (fff) derivatives. Average intermolecular distance between the molecules is found to increase systematically from mono to trifluoro derivatives. Effective molecular length (l) is found to be higher than the most extended length of the molecules, suggesting the presence of anti-parallel-type dimers. l is also found to be less in ff derivatives than in f and fff derivatives, indicating that the overlap between dimerized molecules in ff derivatives is more than in f and fff derivatives. For all the compounds l is found to decrease

with temperature. It is observed that the dipole moment (μ), calculated using the semi-empirical force field in software Hyperchem, increases systematically as one moves from $f \Rightarrow fff$ derivatives in all systems. However, the increase is greater from $f \Rightarrow ff$ derivatives than from $ff \Rightarrow fff$ and there is no change in the dipole moment with chain length, as expected.

It is found that the refractive indices of the extraordinary ray decrease quite fast with temperature whereas for the average refractive indices (n_{av}), the rate of decrease is less. All the refractive indices exhibit normal dispersive behavior. Moreover, compounds 3ccp-fff and 5cpp-fff have different temperature dependence of the n_o index. It decreases with decreasing temperature, whereas for the f and ff substitution n_o changes in the opposite manner. The first behavior is characteristic for strongly polar compounds, for example, 5CB, and second for weakly polar compounds like NCS compounds. Optical anisotropy (Δn) is found to be highest in an ff system compared to f and fff systems in 5ccp and 5cpp series, but the opposite behavior is observed in 3ccp series. Low optical anisotropy is required for developing fast and high-information-content LCDs, so compounds 5ccp- f and 5ccp-fff will therefore be more suitable in this respect. Incidentally, 5ccp- f also possesses a nematic phase over a wide temperature.

The density of fff derivatives is found to be more than in ff derivatives in all systems, which is also true in the crystalline state of the 3ccp system. The orientational order parameters $\langle P_2 \rangle$ obtained from polarizability data are found to be slightly higher, whereas X-ray order parameters are found to be close to the mean field values in all the systems. A decreasing trend of $\langle P_2 \rangle$ is observed as one moves from ($f \Rightarrow fff \Rightarrow ff$) system.

Acknowledgment

The work was supported by Indo-German Joint Research Project No. IND 00/007. Financial assistance under Indo-Polish collaboration is also gratefully acknowledged.

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