Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

X-ray studies of the crystalline and nematic phases of 4'-(3,4,5-trifluorophenyl)-4-propylbicyclohexyl

S. Haldar[a]; P. K. Mandal[a]; S. J. Prathap[b]; T. N. Guru Row[b]; W. Haase[c]
[a] Physics Department, North Bengal University, Siligur -734 013, India [b] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalor -560012, India [c] Institute of Physical Chemistry, Darmstadt University of Technology, Darmstadt, D-64287, Germany

To cite this Article Haldar, S. , Mandal, P. K. , Prathap, S. J. , Row, T. N. Guru and Haase, W.(2008) 'X-ray studies of the crystalline and nematic phases of 4'-(3,4,5-trifluorophenyl)-4-propylbicyclohexyl', Liquid Crystals, 35: 11, 1307 — 1312

To link to this Article: DOI: 10.1080/02678290802560353

URL: http://dx.doi.org/10.1080/02678290802560353

Liquid Crystals,
Vol. 35, No. 11, November 2008, 1307–1312

X-ray studies of the crystalline and nematic phases of 4′-(3,4,5-trifluorophenyl)-4-propylbicyclohexyl

S. Haldar[a], P. K. Mandal[a]*, S. J. Prathap[b], T. N. Guru Row[b] and W. Haase[c]

[a]*Physics Department, North Bengal University, Siligur –734 013, India;* [b]*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalor –560012, India;* [c]*Institute of Physical Chemistry, Darmstadt University of Technology, Darmstadt, D-64287, Germany*

(Received 10 June 2008; final form 16 October 2008)

The crystal and molecular structures of the nematogenic compound 4′-(3,4,5- trifluorophenyl)-4-propylbicyclohexyl (3ccp-fff) were determined by direct methods using single crystal X-ray diffraction data at 293 K. The compound ($C_{21}H_{29}F_3$) crystallises in the triclinic system with space group $P\bar{1}$ and $Z=2$. The unit cell dimensions are $a=5.3715(14)$ Å, $b=10.559(3)$ Å, $c=16.891(4)$ Å, $\alpha=86.331(5)^\circ$, $\beta=85.196(6)^\circ$ and $\gamma=81.938(5)^\circ$. The structure was refined by the least squares method to an R-value of 0.058 for 1398 observed reflections. The fluorine atoms are in the plane of phenyl ring. Both the cyclohexyl groups are found to be in chair conformation and they are coplanar (dihedral angle 0.8°). The molecules were found to be in the most extended conformation. Results of the crystal structure analysis were compared with that obtained from molecular modelling and also with that of the related bifluorinated compound (3ccp-ff). An antiparallel imbricated mode of packing of the molecules is found in the crystalline state. Several van der Waals interactions are observed between the neighbouring molecules, suggesting evidence for existence of molecular packings in head-to tail configuration. The average fluctuation length of the molecules within the nematic phase, determined from a small-angle X-ray diffraction study, is found to be about 1.4 times more than molecular length, providing further evidence for the existence of antiparallel associations between neighbouring molecules.

Keywords: nematogen; trifluorophenyl derivative; X-ray study; molecular association; crystal structure; molecular modelling

1. Introduction

Partially fluorinated phenylbicyclohexyl and biphenylcyclohexyl compounds are wide-range nematic materials characterised by low viscosity and high chemical stability, large dielectric anisotropy, low optical anisotropy and very good voltage holding ratio. These compounds exhibit mesomorphism at ambient temperatures and have high bulk resistivity and low current consumption. All these features are important for liquid crystal displays (LCDs) with large information contents as in portable colour TVs and computer terminals. These materials are, therefore, expected to be useful in active matrix displays (AMDs) such as in TFT (thin-film transistor) and MIM (metal–insulator–metal) systems (*1–4*). As a result, various physical properties of these compounds have been investigated by many authors employing different experimental techniques (*1–8*). It is observed from the literature (*9*) that unsubstituted 4′-phenyl-4-propylbicyclohexyl (3ccp) and para-substituted 3ccp, i.e. 3ccp-Cl, 3ccp-I and 3ccp-CN, exhibit both smectic and nematic phases, whereas mono-, di- and tri-substituted 3ccp exhibit only a nematic phase (Table 1). Results of X-ray diffraction and optical birefringence studies in the nematic phases of some of these compounds have been published by us recently (*10*). However, the authors are not aware of any report about the crystal and molecular structures of these compounds. Recently, we reported a crystal and molecular structure analysis of one such compound, i.e. 4′-(3,4-difluorophenyl)-4-propylbicyclohexyl (3ccp-ff) (*11*). Introduction of another fluorine atom in the phenyl ring of the above compound causes an increase of the melting point and substantial decrease of the nematogenic range (3ccp-ff: Cr 46.0 (38.5) N 123.8 I; 3ccp-fff: Cr 66.0 (49) N 94.1 I). In order to investigate how the molecular structures of the two compounds differ in the crystalline state and their effect on observed phase behaviour, we have determined the crystal structure of 4′-(3,4,5-trifluorophenyl)-4-propylbicyclohexyl (3ccp-fff). The existence of some sort of antiparallel molecular associations was first reported in nematogenic 5CB and 7CB by Leadbetter *et al.* (*12*) and later found in 5OCB (*13*) and in many isothiocyanato systems (*14*), compounds with a strong dipole moment in the para-position of the terminal phenyl ring. No such information, to the best of our knowledge, is available in the literature for *p*-fluoro-substituted phenyl compounds. Therefore, we

---

*Corresponding author. Email: mandal_pradip@yahoo.com

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290802560353
http://www.informaworld.com

Table 1. Phase transition temperatures (°C) of 3ccp-fff and related compounds.

Compound	Phase sequence
3ccp	Cr 76 B 97 N 103 I
3ccp-F	Cr 88.6 N 158.5 I
3ccp-Cl	Cr 75.1 S 79 N 192 I
3ccp-I	Cr 119 S 139.2 N 189.2 I
3ccp-CN	Cr 73.1 S 81.1 N 238.9 I
3ccp-ff	Cr 45.6 N 123.8 I
3ccp-fff	Cr 64.7 N 93.7 I

also wanted to probe whether fluorophenyl compounds, having strong dipole moments, exhibit such antiparallel association.

2. Experimental, structure determination and refinement

The phase behaviour of the samples was studied by polarising optical microscopy and differential scanning calorimetry. A small-angle X-ray diffraction study on magnetically aligned samples was made using a custom-built camera. Experimental details and data analysis procedures have been described previously (*10*).

Transparent plate-shaped crystals were obtained from a solution of dichloromethane and methyl alcohol by a slow evaporation technique. A crystal with approximate dimensions $0.4 \times 0.35 \times 0.25\,\mathrm{mm}^3$ was used to collect three-dimensional X-ray data using graphite-monochromated Mo K_α radiation and a Bruker SMART CCD single crystal diffractometer. A total of 3331 unique reflections were measured within the range $-6 \leqslant h \leqslant 6$, $-12 \leqslant k \leqslant 12$, $-20 \leqslant l \leqslant 20$. Of these, 1398 reflections were above the significance level of 2σ (*I*) and were treated as observed. The range of $\sin\theta/\lambda$ was 0.048–$0.595\,\text{Å}^{-1}$ ($1.95 \leqslant \theta \leqslant 25.00°$). The structure was solved by direct methods and difference Fourier synthesis. All the hydrogen positions were initially located in the difference Fourier maps and for the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full–matrix least–squares structure refinement against $|F^2|$ was carried out. Data collection and refinement have been done using the following packages: data collection and cell refinement, Bruker SMART (*15*); data reduction, SAINT (*15*); absorption correction, SADABS (*15*); structure solution, SHELXS-86 (*16*); refinement, SHELXL97 (*16*); molecular graphics, CAMERON (*17*). Important crystallographic data and refinement parameters are listed in Table 2. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 679992.

3. Results and discussions

A perspective view of the molecule is shown in Figure 1, where an atom numbering scheme is also depicted. Final positional coordinates with equivalent temperature factors of the non-hydrogen atoms are listed in Table 3. The average aromatic bond length and the bond angle of 3ccp-fff in the phenyl ring are found to be 1.368(6) Å and 120.0(4)°; corresponding values in 3ccp-ff are 1.377(6) Å and 120.0(4)°. These values are in agreement with the geometry of the other phenyl moieties reported in the literature for mesogenic compounds (*18–20*). The cyclohexyl groups are in chair conformation, as was observed in 3ccp-ff and other mesogenic molecules (*21–24*). The alkyl chain is in an all-trans conformation with mean bond distance 1.520(6) Å and bond angle 111.6(4)°, as found in other mesogenic compounds (*25–27*); corresponding values in 3ccp-ff are 1.519(8) Å and 113.7(5)°, respectively. C1–F1, C2–F2 and C6–F3 bond lengths are found to be 1.344(5) Å, 1.354(4) Å and 1.354(5) Å, close to the values observed in 3ccp-ff [1.351(4) Å, 1.353(5) Å] and in other fluorophenyl compounds, i.e. 1.347(3) Å (*28*) and 1.363(4) Å (*29*).

Table 2. Important crystallographic data for 3ccp-fff.

Formula	$C_{21}H_{29}F_3$
Formula weight	338.44 g mol^{-1}
T (K)	293(2)
Radiation, λ (Mo K_α)	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
a	5.3715(14) Å
b	10.559(3) Å
c	16.891(4) Å
α	86.331(5)°
β	85.196(6)°
γ	81.938(5)°
V	943.9(4) Å^3
Z	2
D_{cal}	1.19 g cm^{-3}
F(000)	364
Crystal size	$0.4 \times 0.35 \times 0.25\,\mathrm{mm}^3$
Independent reflections	3331
No. of observed reflections	1398 [$I > 2\sigma(I)$]
Refinement method	full-matrix least-squares on F^2
R (observed reflection)	0.058
R_W (observed reflection)	0.086

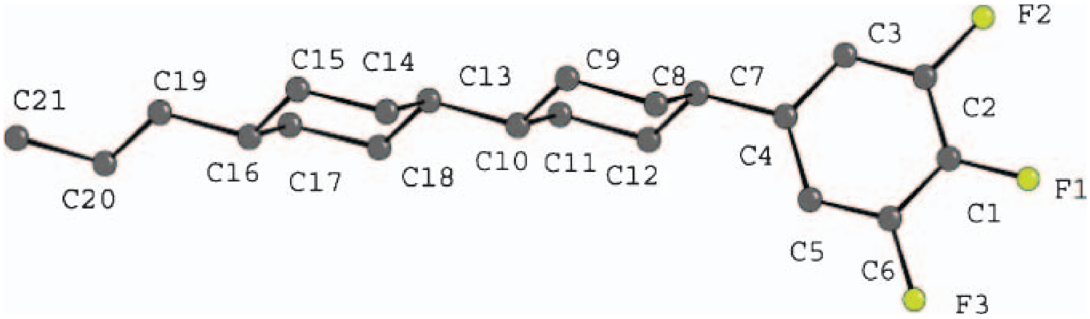

Figure 1. A perspective view of the 3ccp-fff molecule with atom numbering scheme.

The geometry of the 3ccp-fff molecule may be described in terms of four planes: the phenyl ring (**1**), the two cyclohexyl rings (**2** and **3**) and the plane of the alkyl chain (**4**). The phenyl ring is highly planar and the three fluorine atoms are almost in the same plane. An almost similar phenyl ring geometry was observed in 3ccp-ff. The dihedral angles between the planes (**1** and **2**), (**1** and **3**), (**1** and **4**), (**2** and **3**), (**2** and **4**) and (**3** and **4**) are, respectively, 83.2°, 83.4°, 51.3°, 0.8°, 35.9° and 36.4°. In 3ccp-ff the dihedral angle between the two cyclohexyl groups was found to be 3.4° compared to 0.8° in 3ccp-fff. The phenyl ring and the propyl chain are at an angle 51.3°, whereas they were almost in the same plane in 3ccp-ff (dihedral angle 8.8°). Dihedral angles between the phenyl and nearby cyclohexyl rings are found to be 83.2° and 122.1° in 3ccp-fff and 3ccp-ff, respectively. Thus, introduction of another fluorine atom causes a nearly perpendicular orientation of the phenyl ring relative to the neighbouring cyclohexyl ring because of steric requirements.

Table 3. Fractional coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms, with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	U_{eq}/Å^2
C1	0.4175(8)	0.1380(3)	0.6080(2)	0.078
C2	0.6265(7)	0.1073(3)	0.5579(2)	0.075
C3	0.6526(6)	0.1646(3)	0.4839(2)	0.064
F1	0.3956(4)	0.0806(2)	0.6811(1)	0.118
F2	0.8110(4)	0.0179(2)	0.5845(1)	0.109
F3	0.0242(4)	0.2585(2)	0.6312(1)	0.112
C4	0.4639(6)	0.2562(3)	0.4570(2)	0.058
C5	0.2501(7)	0.2864(3)	0.5074(2)	0.069
C6	0.2313(7)	0.2282(3)	0.5811(2)	0.075
C7	0.4910(6)	0.3222(3)	0.3752(2)	0.063
C8	0.5147(8)	0.4629(3)	0.3787(2)	0.078
C9	0.5506(8)	0.5288(4)	0.2970(2)	0.079
C10	0.3412(6)	0.5151(3)	0.2435(2)	0.055
C11	0.3181(8)	0.3728(3)	0.2408(2)	0.074
C12	0.2838(8)	0.3065(4)	0.3227(2)	0.075
C13	0.3746(6)	0.5822(3)	0.1617(2)	0.056
C14	0.3976(8)	0.7239(3)	0.1639(2)	0.075
C15	0.4235(8)	0.7916(4)	0.0829(2)	0.078
C16	0.2144(6)	0.7788(3)	0.0309(2)	0.057
C17	0.1921(9)	0.6377(3)	0.0269(2)	0.073
C18	0.1666(7)	0.5695(4)	0.1082(2)	0.074
C19	0.2463(7)	0.8462(4)	−0.0509(2)	0.072
C20	0.0323(9)	0.8516(5)	−0.1038(3)	0.089
C21	0.0726(15)	0.9243(6)	−0.1827(3)	0.110

The length of the 3ccp-fff molecule in the crystalline state is found to be 17.27 Å (F1–H21c), whereas the model length in the all-trans conformation is 17.6 Å. Thus, the molecules are in the most extended conformation, as was observed in 3ccp-ff.

The packing of the molecules in the unit cell is shown in Figure 2, which shows that the molecules run almost parallel to each other but not parallel to any crystallographic axis. However, in 3ccp-ff molecules were found to be parallel to each other and also to one crystallographic axis. To describe the nature of the packing, the direction cosines of the molecular long axis, defined as the best fitted line through all the non-hydrogen atoms, have been calculated and are found to be 0.3825, −0.5230 and 0.7616. In other words, the molecules are inclined to the orthogonal *x*-, *y*- and *z*-axes at angles 67.5°, 121.5° and 40.4°, respectively.

The projections of the crystal structure along the crystal axis *a* is shown in Figures 3. It is evident that the molecules are packed with various degrees of overlap with the neighbouring molecules. Orientation of the molecules in adjacent layers is opposite to each other. Overlap of the molecules in neighbouring layers is in the phenylcyclohexyl groups on one side and in the cyclohexylalkyl chain part on the other side. This type of imbricated mode of packing is often observed in the crystalline phases of nematogens (*30, 31*).

Intermolecular distances between the neighbouring molecules were calculated and several van der Waals interactions were observed. Selected intermolecular distances, less than 3.5 Å, are shown in Table 4. Two different types of molecular overlaps are observed between associated neighbouring molecules (Figure 4): (i) a pair of parallel molecules in head-to-head configuration overlaps completely (related by symmetry operation 'a' having pair length

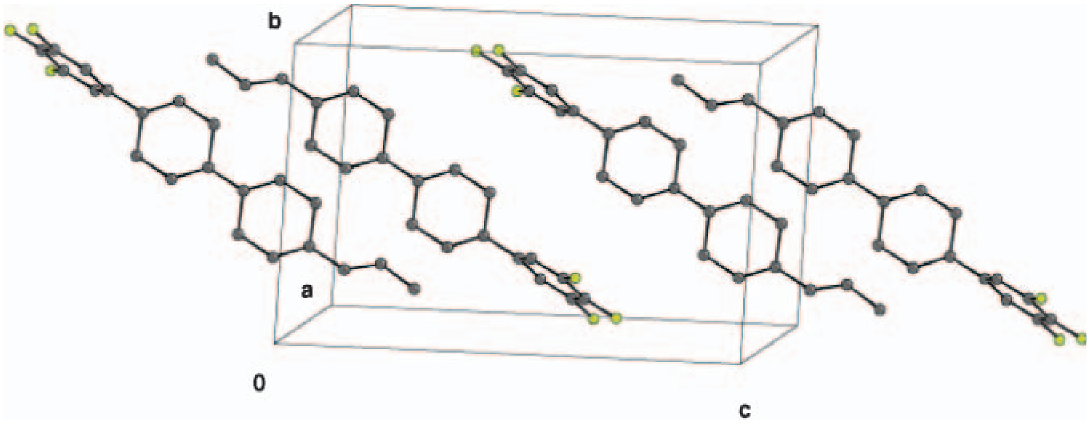

Figure 2. Partial packing of the 3ccp-fff molecule in the unit cell.

18.80 Å); (ii) a pair of parallel molecules in head-to-tail configuration overlap partially (related by symmetry operation 'b' having associated length 25.26 Å).

A preliminary molecular modelling calculation using the software Hyperchem 6.03 (*32*) has been carried out using the semi-empirical PM3 method. An almost similar molecular conformation with molecular length 17.03 Å was obtained when the geometry of the molecule, as extracted from the crystal, was optimised assuming that it was in vacuo. A single point calculation on an isolated molecule, as extracted from the crystal data, yields a dipole moment (μ) of 3.61 D with direction cosines -0.39, -0.77 and 0.51. Optimised geometry resulted in a slightly modified dipole moment of 3.72 D and direction cosines -0.08, -0.96 and 0.27. However, in both cases the orientation of the dipole is different from the molecular backbone, 40° and 16°, respectively. In the case of 3ccp-ff, on the other hand, single point energy calculation and optimised geometry revealed slightly different dipole moments (3.54 D and 3.21 D) but with same inclination angle (43°) in both cases. Thus, the molecular dipole moments of the two molecules in optimised geometry differ by about 0.5 D.

The calculated density in the crystalline state of 3ccp-fff (1.19 g cm^{-3}) was found to be higher than that of 3ccp-ff (1.14 g cm^{-3}). The density measured in the nematic state near Cr–N transition temperature was also found to be higher in 3ccp-fff (1.08 g cm^{-3}) than in 3ccp-ff (1.03 g cm^{-3}).

The average intermolecular distance (*D*) and apparent molecular length or fluctuation length (*l*) were measured throughout the nematic phase from a small-angle X-ray diffraction study on magnetically aligned samples. An exemplary X-ray diffraction photograph is shown in Figure 5. Near the Cr–N transition temperature, both *D* and *l* values are found to be more in 3ccp-fff (5.55 Å, 24.9 Å) than in 3ccp-ff (5.35 Å and 22.8 Å) (*10*). Therefore, *l* values are, respectively, 1.41 and 1.30 times greater than the length of the molecules in the most extended conformation (*L*).

We also studied the variation of *l* with temperature, as shown in Figure 6. An average value of 1.4 is observed for *l*/*L*, whereas in 3ccp-ff it is found to be 1.27. This suggests the existence of some sort of molecular associations in both cases; however,

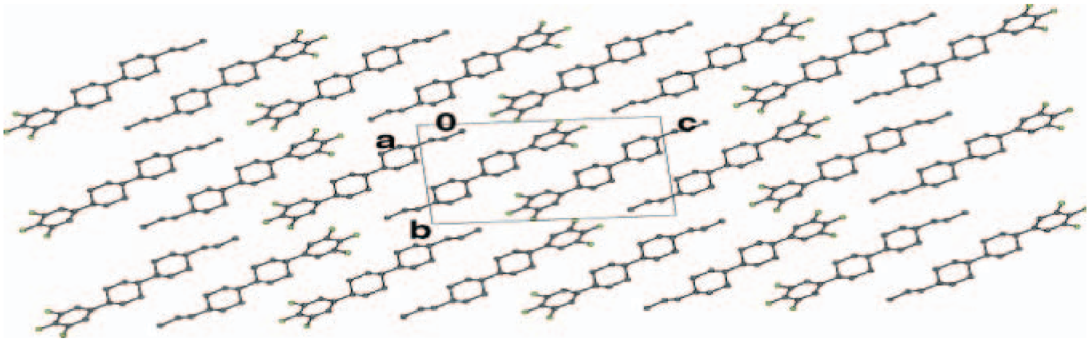

Figure 3. Crystal structure of 3ccp-fff projected along the *a*-axis.

Table 4. Selected intermolecular short contact distances less than 3.5 Å.

Atom	Atom	Distance/Å
C1	F3(a)	3.443
C2	F3(a)	2.688
C2	C6(a)	3.435
C3	F3(a)	3.097
C3	C5(a)	3.399
C3	C6(a)	3.496
F2	C1(a)	3.442
F2	F3(a)	2.379
F2	C6(a)	2.922
F3	C10(b)	3.222
F3	C14(b)	3.437

Symmetry-related atoms are at (a) *x*+1, *y*, *z*, (b) −x, −y+1, −z+1.

overlapping of the associated molecules in 3ccp-fff is less than in 3ccp-ff. Existence of such associations in nematic phase has recently been reported by us in three other similar molecules (*10*) from X-ray scattering results. The same is supported by results of crystal structure analysis. Partially overlapped pair of molecules in head-to-tail configuration having length of 25.26 Å may give rise to a fluctuation length of 24.9 Å on melting, as was observed in other systems with axial dipole moments (*12–14*).

Since the magnitudes of the dipole moments, estimated from molecular modelling, differ by only 0.5 D in 3ccp-fff and 3ccp-ff molecules but the inclination angles with the molecular long axes differ by about 27°, it may also be inferred that overlapping of the associated molecules depends more on the orientations of the molecular dipole than on their strength. In general, it may be qualitatively stated that the difference in molecular geometry and conformation, values of the molecular dipole moments and their orientations, and packing in the crystalline state are probable causes for the observed difference in melting points and nematic ranges of the two compounds.

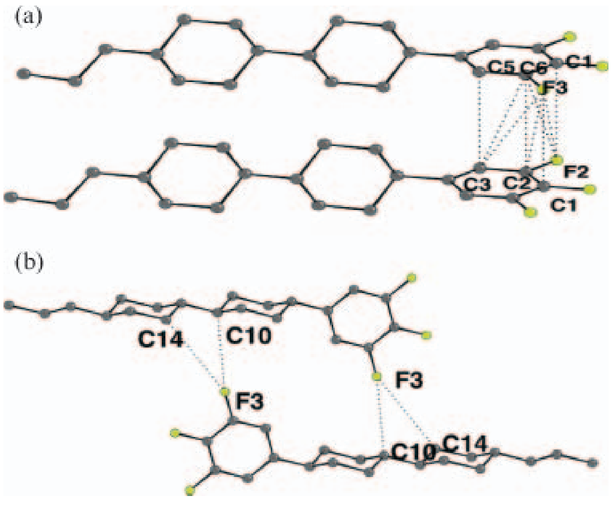

Figure 4. Two types of molecular close contacts observed in the crystal structure of 3ccp-fff. Values of relevant interatomic distances and meaning of the symmetry relations a and b are given in Table 4.

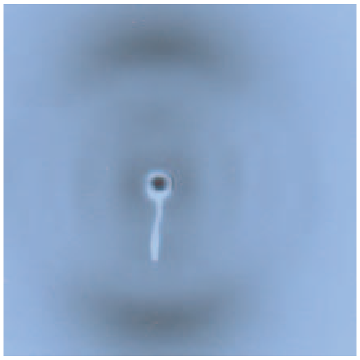

Figure 5. X-ray diffraction photograph of 3ccp-fff at 55°C in the nematic phase.

4. Conclusions

A fluorophenyl compound, 4′-(3,4,5-trifluorophenyl)-4-propylbicyclohexyl (3ccp-fff), useful for AMLCD applications, has been studied in crystalline as well as in nematic phases by X-ray diffraction methods in continuation of our previous works on such systems (*10, 11*). From 3D X-ray structural analysis and molecular modelling it is found that molecular geometry and conformation, values of molecular dipole moments and their inclination with long axes and packing in the crystalline state differ from those in a related difluorinated compound (3ccp-ff). These differences may be responsible for the substantial difference in the melting points. Although introduction of another fluorine atom increases the molecular volume it simultaneously makes the molecular geometry more symmetrical. This results in better and efficient packing of the molecules both in crystalline and nematic phase, which is evident from the fact that the density in both the phases is less in 3ccp-fff than in 3ccp-ff. Possibly this explains the

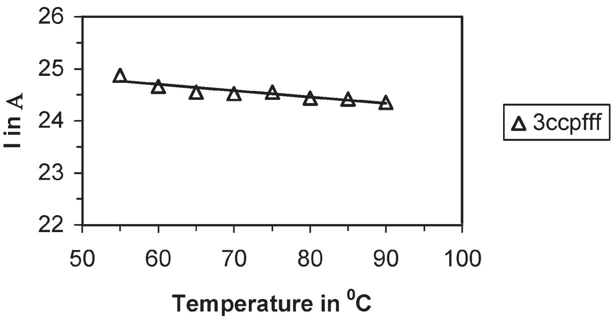

Figure 6. Temperature variation of average fluctuation length (*l*) in the nematic phase of 3ccp-fff.

higher crystal–nematic transition in the former than the later.

Calculation of intermolecular distances strongly suggests existence of molecular packings in a head-to-tail configuration. From small-angle X-ray photographs of magnetically aligned samples, the fluctuation length is found to be about 1.4 times the molecular length. This might result from the molecular organisations due presumably to strong dipole moments; however, the extent of overlap is found to depend more on the orientations of the molecular dipoles than on their magnitudes. This may be the result of steric factors. Whatever might be the reason, conclusive evidence of existence of antiparallel packings both in the crystalline and nematic phases for fluorobenzene systems has been reported for the first time. For cyanobiphenyls and isothiocyanates the existence of such molecular associations is well established (12–14).

Moreover, the existence of overlapping cores in the nematic phase is expected to increase T_{NI}. Since overlapping is less in 3ccp-fff than that in 3ccp-ff and the clearing temperature of the former is found to be less than the later. It may thus be concluded that increased melting point due to more efficient packing in the crystalline state and decreased clearing point due to less overlapping cores in the nematic state is the reason for substantially lower nematic range in 3ccp-fff than its bifluorinated analogue.

Acknowledgement

This work was supported by Indo-German Joint Research Project No. IND/02/007. The authors are also thankful to Dr. E. Poetsch, Merck, Germany, for supplying the compound.

References

(1) Goto Y.; Ogawa T.; Swada S.; Sugimori S. *Mol. Cryst. Liq. Cryst.* **1991**, *209*, 1–7.

(2) Demus D.; Goto Y.; Sawada S.; Nakagawa E.; Saito H.; Tarao R. *Mol. Cryst. Liq. Cryst.* **1995**, *260*, 1–21.

(3) Nishi T.; Matsubara A.; Okada H.; Onnagawa H.; Sugimori S.; Miyashita K. *Jap. J. Appl. Phys.* **1995**, *34*, 236–237.

(4) Petrov V.F. *Liq. Cryst.* **1995**, *19*, 729–741.

(5) Saito H.; Sawada A.; Manabe A.; Naemura S. *Mol. Cryst. Liq. Cryst. A* **2001**, *366*, 313–320.

(6) Ishikawa H.; Toda A.; Okada H.; Onnagawa H.; Sugimori S. *Liq. Cryst.* **1997**, *22*, 743–747.

(7) Tabayashi K.; Akasaka K. *Liq. Cryst.* **1999**, *26*, 127–129.

(8) Klasen M.; Bremer M.; Götz A.; Manabe A.; Naemura S.; Tarumi K. *Jap. J. Appl. Phys., Pt 2* **1998**, *37*, L945–L948.

(9) Vill V. *Liquid Crystal Database V4.4*; LCI Publisher: Hamburg, 2003, and references therein.

(10) Biswas S.; Haldar S.; Mandal P.K.; Haase W. *Liq. Cryst.* **2007**, *34*, 365–372.

(11) Haldar S.; Mandal P.K.; Goubitz K.; Schenk H.; Haase W., *Mol. Cryst. Liq. Cryst.* submitted for publication. **2008**, *490*, 80–87.

(12) Leadbetter A.J.; Richardson R.M.; Colling C.N. *J. Phys., Paris* **1975**, *36*, C1-37–43.

(13) Mandal P.; Paul S. *Mol. Cryst. Liq. Cryst.* **1985**, *131*, 223–232.

(14) Sarkar P.; Mandal P.; Paul S.; Paul R.; Dabrowski R.; Czuprinski K. *Liq. Cryst.* **2003**, *30*, 507–527.

(15) SMART (ver. 5.054), Bruker AXS Inc. Madison, WI, 1998; SAINT (ver. 6.02a) and SADABS (ver. 2.03), Bruker AXS Inc., Madison, WI, 2000.

(16) Sheldrick G.M. *SHELXS86 and SHELXL97*; University of Göttingen: Germany.

(17) Walkin D.M.; Pearce L.; Prout C.K. *CAMERON*; a molecular graphics package, University of Oxford: Oxford, 1993.

(18) Haase W.; Paulus H.; Pendzialek R. *Mol. Cryst. Liq. Cryst.* **1983**, *100*, 211–221.

(19) Jaishi B.R.; Mandal P.K.; Goubitz K.; Schenk H.; Dabrowski R.; Czuprynski K. *Liq. Cryst.* **2003**, *30*, 1327–1333.

(20) Biswas S.; Haldar S.; Mandal P.K.; Goubitz K.; Schenk H.; Dabrowski R. *Cryst. Res. Technol.* **2007**, *42*, 1029–1035.

(21) Haase W.; Paulus H. *Mol. Cryst. Liq. Cryst.* **1983**, *100*, 111–126.

(22) Walz L.; Haase W.; Eidenschink R. *Mol. Cryst. Liq. Cryst.* **1989**, *168*, 169–182.

(23) Gupta S.; Mandal P.; Paul S.; Goubitz K.; de Wit M.; Schenk H. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 149–159.

(24) Nath A.; Gupta S.; Mandal P.; Paul S.; Schenk H. *Liq. Cryst.* **1996**, *20*, 765–770.

(25) Mandal P.; Paul S.; Schenk H.; Goubitz K. *Mol. Cryst. Liq. Cryst.* **1992**, *210*, 21–30.

(26) Mandal P.; Paul S.; Schenk H.; Goubitz K. *Mol. Cryst. Liq. Cryst.* **1986**, *135*, 35–48.

(27) Mandal P.; Paul S. *Mol. Cryst. Liq. Cryst.* **1985**, *131*, 223–235.

(28) Walz L.; Nepveu F.; Haase W. *Mol. Cryst. Liq. Cryst.* **1987**, *148*, 111–121.

(29) Patil P.S.; Shettigar V.; Dharmaprakash S.M.; Naveen S.; Sridhar M.A.; Prasad J.S. *Mol. Cryst. Liq. Cryst.* **2007**, *461*, 123–130.

(30) Haase W.; Athanassopoulou M.A. In *Structure and Bonding. Volume I: Liquid Crystals*; Mingos M. (Ed.), Springer: Berlin, 1999. p. 139–197.

(31) Bryan R.F.; Forcier P.G. *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 133–152.

(32) *Hyperchem 6.03*; Hypercube Inc: Gainesville, FL.