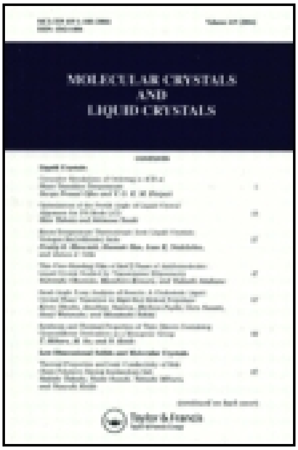

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

X-Ray Structural Analysis in the Crystalline Phase of a Nematogenic Fluoro-Phenyl Compound

S. Haldar [a] , S. Biswas [a] , P. K. Mandal [a] , K. Goubitz [b] , H. Schenk [b] & W. Haase [c]

[a] Physics Department, North Bengal University, Siliguri, India

[b] Crystallography Laboratory, University of Amsterdam, Amsterdam, The Netherlands

[c] Institute of Physical Chemistry, Darmstadt University of Technology, Darmstadt, Germany

Version of record first published: 22 Sep 2010

To cite this article: S. Haldar, S. Biswas, P. K. Mandal, K. Goubitz, H. Schenk & W. Haase (2008): X-Ray Structural Analysis in the Crystalline Phase of a Nematogenic Fluoro-Phenyl Compound, Molecular Crystals and Liquid Crystals, 490:1, 80-87

To link to this article: http://dx.doi.org/10.1080/15421400802305855

Mol. Cryst. Liq. Cryst., Vol. 490, pp. 80–87, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802305855

Taylor & Francis
Taylor & Francis Group

X-Ray Structural Analysis in the Crystalline Phase of a Nematogenic Fluoro-Phenyl Compound

S. Haldar[1], S. Biswas[1], P. K. Mandal[1], K. Goubitz[2], H. Schenk[2], and W. Haase[3]
[1]Physics Department, North Bengal University, Siliguri, India
[2]Crystallography Laboratory, University of Amsterdam, Amsterdam, The Netherlands
[3]Institute of Physical Chemistry, Darmstadt University of Technology, Darmstadt, Germany

Crystal and molecular structures of a nematogenic compound 4′-(3,4-difluoro phenyl)-4-propyl-bicyclohexyl (3ccp-ff) has been determined by direct methods using single crystal X-ray diffraction data. The compound ($C_{21}H_{30}F_2$) crystallizes in the monoclinic system with the space group $P2_1/n$ and $Z = 4$. The unit cell parameters are $a = 16.293(15)$ Å, $b = 6.278(7)$ Å, $c = 18.306(4)$ Å and $\beta - 96.84(6)^\circ$. The two cyclohexyl rings are almost coplanar, so also are the phenyl ring and the propyl chain. The cyclohexyl groups are in chair conformation. Imbricated mode of packing of the molecules is found in the crystalline state which is precursor to the nematic phase structure. Several close van der Waals interactions are found to exist between the neighbouring molecules. Short-range antiparallel type of association is found to exist between the neighbouring molecules in crystalline as well as in nematic phase.

Keywords: crystal structure, difluorophenyl, imbricated mode of packing, molecular association, nematogen

1. INTRODUCTION

Compounds of the homologous series 4′-(3,4-difluoro-phenyl)-4-alkyl-bicyclohexyl are wide-range nematic materials characterized by low viscosity, high chemical stability, large dielectric anisotropy, low optical anisotropy, and very good voltage holding ratio. Mixtures of the present compounds are found to exhibit mesomorphism at ambient temperatures and have high bulk resistivity and low current

Address correspondence to Prof. Pradip K. Mandal, Physics Department, North Bengal University, Siliguri 734013, India. E-mail: mandal_pradip@yahoo.com consumption. All these features are important for liquid crystal displays (LCDs) with large information contents as in portable color TVs and computer terminals. These materials are, therefore, expected to be useful in active matrix displays (AMDs) such as in thin-film-transistor (TFT) and metal-insulator-metal (MIM) systems [1–4]. Various physical properties of this series have, therefore, been investigated by many authors employing different experimental techniques, like phase transitions and thermal properties [1,5], X-ray diffraction and optical birefringence [6,7], order parameter [8], viscosity [9], spectroscopic [10], dielectric, and elastic properties [11–13]. However, the authors are not aware of any report about the crystal and molecular structures of these compounds. In this article, structural data of the 3rd member of the series, 3ccp-ff, determined from single crystals X-ray diffractometer data, have been reported, and an attempt has been made to find the effect of the molecular geometry and packing in the crystalline state on its phase behavior and different physical properties. An excellent review on crystal structures of many liquid crystal compounds and their effect on mesogenic behavior can be found in [14].

2. EXPERIMENTAL, STRUCTURE DETERMINATION AND REFINEMENT

Transparent plate-shaped crystals were grown from a solution of acetone and xylene by slow evaporation technique. A crystal with dimensions $0.05 \times 0.65 \times 0.75$ mm approximately was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite–monochromated CuKα radiation in ω-2θ scan mode. A total of 3657 unique reflections were measured within the range $0 \leq h \leq 20$, $-7 \leq k \leq 0$, $-22 \leq l \leq 22$. Of these, 2205 reflections were above the significance level of $4\sigma(F_{obs})$ and were treated as observed. The range of $(\sin \theta)/\lambda$ was 0.039–0.626 Å ($3.4 \leq \theta \leq 74.8°$). Two reference reflections (211, 004) were measured hourly and showed 8% decrease during the 79 h collecting time, necessary correction was made. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections within $36.11 \leq 2\theta \leq 42.72$. Corrections for Lorentz and polarization effects were applied. Absorption correction was performed with the program PLATON [15], following the method of North *et al.* [16] using Ψ-scans of five reflections, with coefficients in the range 0.703–0.968. The structure was solved by the Direct Methods using the program GENTAN from the XTAL3.7 program system [17].

The positions of the hydrogen atoms were calculated using the known geometry around the carbon atoms. Full-matrix least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.0 Å, converged to R = 0.072, Rw = 0.061, $(\Delta/\sigma)\max = 0.20$, S = 0.97. A weighting scheme $w = [1.0 + 0.01^{*}(\sigma(\text{Fobs}))^2 + 0.01/(\sigma(\text{Fobs}))]^{-1}$ was used. The secondary isotropic extinction coefficient [18,19] refined to g = 707(29). Final difference Fourier map revealed a residual electron density between −0.37 and 0.28 e $Å^{-3}$. Scattering factors were taken from Cromer and Mann [20] and Tables for X-ray Crystallography [21]. The anomalous scattering of S was taken into account [22]. All calculations were performed with XTAL3.7, unless stated otherwise. Important crystallographic data and refinement parameters are given in Table 1. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 652602.

3. RESULTS AND DISCUSSION

A perspective drawing of the molecule with the atom numbering scheme is shown in Fig. 1. Selected bond lengths and bond angles of the selected atoms are listed in Tables 2 and 3. The average aromatic bond length in the phenyl ring is 1.377(6) Å (maximum and minimum values being 1.393(5) and 1.364(6) Å), and the bond angle is 120.0(4)°

TABLE 1 Important Crystallographic Data

Formula	$C_{21}H_{30}F_2$
Formula weight	320.51 g/mol
T (K)	293(2)
Radiation, $\lambda(CuK_\alpha)$	1.5418 (Å)
Crystal system	monoclinic
Space group	P2/n
a	16.293(15), Å
b	6.2777(7)
c	18.306(4) Å
β	96.84(6)°
V	1859.1(2) $Å^3$
Z	4
D_{cal}	1.145g/cc
μ (CuK_α)	0.63/mm
F(000)	696
Crystal size	$0.75 \times 0.65 \times 0.05\,mm^3$
Independent reflections	3657
No. of observed reflections	2205 $[F_{obs} > 4\sigma(F_{obs})]$
Refinement method	full-matrix least-squares on F
R	0.072
Rw	0.061

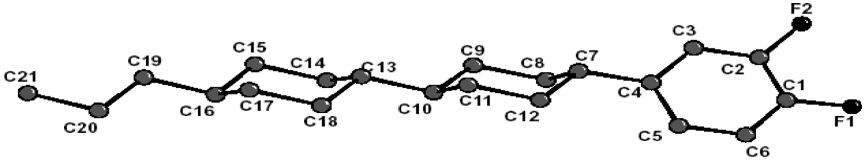

FIGURE 1 Perspective view of 3ccp-ff molecule with atom numbering scheme.

(maximum and minimum values being 122.3(4) and 117.2(3)°). These values are in agreement with the geometry of the other phenyl moieties reported in literature. In particular, the geometry of the phenyl fragment of 3ccp-ff agrees well with that of the 4-cyano-4′-n-propylbiphenyl (CB3) [23];

4-cyanophenyl-4′-hexylbiphenyl carboxylate (6CBB) [24]; cholesteryl 6[4-(4-pentyloxyphenylethynyl) phenoxy] hexanoate [25]; 3-[4-(4′-ethylbiphenyl)]-1-propene [26] and 4-(*trans*-4-undecylcyclohexyl) isothiocyanatobenzene (11CHBT) [27] (average aromatic bond distances are 1.383(8) Å, 1.387(5) Å, 1.373(12) Å, 1.368(2) Å, and 1.376 Å, respectively, and average aromatic bond angles are 120.4(1.4)°, 120.0(3)°, 120.0(10)°, 119.9(15)°, and 120.0(3)°, respectively). The cyclohexyl groups are in chair conformation as was observed in other mesogenic molecules [28–32]. The alkyl chain is in all-trans conformation with mean bond distance 1.519(8) Å and bond angle 113.7(5)° as found in other mesogenic compounds [24,31,33–35]. Length of the bonds (C_1-F_1 and C_2-F_2), by which the fluorine atoms are connected to the phenyl ring, are found to be 1.351(4) Å and 1.353(5) Å close to the reported C-F bond lengths *viz.* 1.347(3), in 4-ethyl-2′-fluoro-4′-(4″-pentylcyclohexyl)-biphenyl (BCH52F) [36] and 1.363(3), in 1-(4-fluorophenyl)-3-(3,4,5-trimethoxyphenyl)-2-propen-1-one [37]. The phenyl ring is found to be highly planar, and the two fluorine atoms are in the same plane.

TABLE 2 Selected Bond Lengths (Å) with Standard Deviation in Parentheses

Atom	Atom	Bond length
C1	F1	1.351(4)
C1	C6	1.364(6)
C1	C2	1.369(6)
C2	F2	1.353(5)
C2	C3	1.365(6)
C4	C7	1.507(5)
C10	C13	1.535(5)
C16	C19	1.528(6)

TABLE 3 Selected Bond Angles (°) with Standard Deviations in Parentheses

Atom	Atom	Atom	Angle
F1	C1	C6	121.4(4)
F1	C1	C2	119.3(4)
C6	C1	C2	119.3(4)
F2	C2	C3	120.7(4)
F2	C2	C1	117.2(4)
C3	C2	C1	122.1(4)
C5	C4	C7	123.8(3)
C3	C4	C7	119.0(3)
C4	C7	C8	111.9(3)
C4	C7	C12	114.6(3)
C9	C10	C13	112.9(3)
C11	C10	C13	112.6(3)
C17	C16	C19	113.1(4)
C19	C16	C15	110.9(4)

Geometry of the 3ccp-ff molecule may be described in terms of four planes: the phenyl ring (**1**), the two cyclohexyl rings (**2 & 3**), and the plane of the alkyl chain (**4**). The phenyl ring is highly planar, highest displacement of C2 from the plane being 0.010 Å. The fluoride atoms are displaced upward from it by 0.041 Å (F1) and 0.008 Å (F2). The dihedral angles between the planes (**1 & 2**), (**1 & 3**), (**1 & 4**), (**2 & 3**), (**2 & 4**), and (**3 & 4**) are, respectively, 122.1°, 123.5°, 8.8°, 3.4°, 127.8°, and 128.7°. Thus the two bicyclohexyl rings are almost coplanar as was observed in CCHs [28]. However, nearly perpendicular bicyclohexyl rings were also reported in CCNs [29]. The phenyl ring and the propyl chain are also almost coplanar. In one crystalline modification of PCH8 and PCH9 such situation was observed [38], although a dihedral angle of about 90° was found in other crystalline modifications of the same compounds. Dihedral angles between the cyclohexyl rings and the alkyl chain are very large compared to those reported for PCHs [38].

The length of the 3ccp-ff molecule [F1-H213] in the crystalline state is found to be 17.30 Å whereas the model length in the most extended conformation form is 17.6 Å. Thus the molecules are in most extended conformation.

Preliminary molecular modeling calculations using the software Hyperchem 6.03 for windows [39] have been carried out using the semi-empirical PM3 method. Almost similar molecular conformation with molecular length of 17.53 Å was obtained when the geometry of the molecule, as extracted from the crystal, was optimized assuming it as if *in vacuo*. A single point calculation on an isolated molecule as extracted from the crystal data yields a dipole moment (μ) of 3.54 D with direction cosines -0.43, -0.73, and 0.53. Optimized geometry resulted in a slightly modified dipole moment of 3.21 D with same direction cosines. Thus in both cases the orientation of dipole is markedly different from the molecular backbone. Previously reported theoretical values were 3.32 D and 3.20 D [40] consistent with the present calculation. From the dielectric study, μ was found to be 2.64 D inclined at an angle of 29.8° with molecular axis [8].

Projection of the crystal structure along the b axis is shown in Fig. 2. It is seen that the molecules run almost parallel to the crystallographic

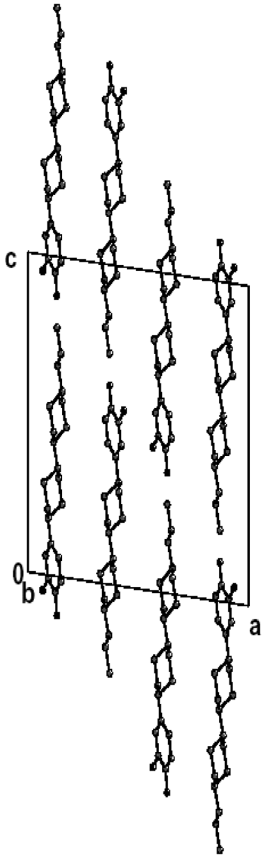

FIGURE 2 Crystal structure of 3ccp-ff projected along b-axis.

c-axis. It is also evident that the molecules are packed in interpenetrating layers with various degrees of overlap of the neighboring molecules. This type of imbricated mode of packing is usually observed in crystalline phase as a precursor to nematic phase [14,41].

To get an idea about the nature of molecular associations, we calculated intermolecular distances between the neighboring molecules, and it reveals existence of several close van der Waals interactions. Five different types of molecular associations are observed.

(i) Pair of parallel molecules in head-to-head configuration overlaps completely (related by symmetry operation x, y − 1, z having pair length 19.75 Å). (ii) Pair of parallel molecules in head-to-tail configuration overlap almost completely (related by symmetry operation −x + 2, −y, −z + 1 having associated length 19.95 Å and related by symmetry operation –x + 2, −y + 1, −z + 1 having associated length 21.245 Å). (iii) Pair of nonparallel molecules in head-to-tail configuration overlaps only in the alkyl group (related by symmetry operation −x + 3/2, −y + 1/2, −z + 1/2 having associated length 29 Å. (iv) Pair of non-parallel molecules in head-to-tail configuration with almost complete overlap of the rigid part (related by symmetry operation −x + 3/2, −y + 1/2, −z + 3/2 having associated length 23.76 Å). (v) Pair of two translated molecules with no overlap at all (related by symmetry operation x, y + 1, z − 1 having associated length 36.61 Å).

ACKNOWLEDGMENT

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

REFERENCES

[1] Goto, Y., Ogawa, T., Swada, S., & Sugimori, S. (1991). *Mol. Cryst. Liq. Cryst.*, *209*, 1.

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

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

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

[5] Bartmann, E., Dorsch, D., Finkenzeller, U., Kurmeier, H. A., & Poetsch, E. (1990). *Freiburger Arbeitstagung Flüssigkristalle*, *19*, P8.

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

[7] Finkenzeller, U., Kurmeier, A., & Poetsch, E. (1989). *Freiburger Arbeitstagung Flüssigkristalle*, *18*, P17.

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

[9] Kirsch, P., Naemura, S., & Tarumi, K. (1998). *Freiburger Arbeitstagung Flüssigkristalle*, *27*, P45.

[10] Tabayashi, K. & Akasaka, K. (1999). *Liq. Cryst.*, *26*, 127.

[11] Ishikawa, H., Toda, A., Matsubara, A., Nishi, T., Okada, H., Onnagawa, H., Sugimori, S., & Miyashita, K. (1994). *20th Jpn. Symp. Liq. Cryst.*, Nagoya 1G505.

[12] Dunmur, D. A., Hanson, R., Okada, H., Onnagawa, H., Sugimori, S., & Toriyama, K. (1995). Asia Display'95 Proceedings S22-2 (p. 563).

[13] Klasen, M., Bremer, M., Götz, A., Manabe, A., Naemura, S., & Tarumi, K. (1998). *Jpn. J. Appl. Phys., Part 2*(37), L945-L948.

[14] Haase, W. & Athanassopoulou, M. A. (1999). *Structure and Bonding, Volume: Liquid Crystals I*, Mingos, M. (Ed.), Springer: Berlin, 139–197.

[15] Spek, A. L., PLATON (1990). *Acta Cryst.*, *A46*, C-34.

[16] North, A. C. T., Phillips, D. C., & Scott Mathews. F. (1968). *Acta Cryst.*, *A26*, 351.

[17] Hall, S. R., Boulay, D. J. du., & Olthof-Hazekamp, R. Eds. (2000). *XTAL3.7 System*, University of Western Australia: Lamb, Perth.

[18] Larson, A. C. (1969). *Crystallographic Computing*, Ahmed, F. R., Hall, S. R., & Huber, C. P. (Eds.), Munksgaard: Copenhagen, 291.

[19] Zachariasen, W. H. (1967). *Acta Cryst.*, *A23*, 558.

[20] Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.*, *A24*, 321.

[21] International Tables for X-ray Crystallography. (1974). Kynoch Press: Birmingham, Vol. 4, 55.

[22] Cromer, D. T. & Liberman. D. J. (1970). *Chem. Phys.*, *53*, 1891.

[23] Haase, W., Paulus, H., & Pendzialek, R. (1983). *Mol. Cryst. Liq. Cryst.*, *100*, 211.

[24] Jaishi, B. R., Mandal, P. K., Goubitz, K., Schenk, H., Dabrowski, R., & Czuprynski, K. (2003). *Liq. Cryst.*, *30*, 1327.

[25] Sridhar, M. A., Lokanath, N. K., Shashidhara Prasad, J., Yelammagad, C. V., & Varshney, S. K. (2000). *Liq. Cryst.*, *28*, 45.

[26] Gupta, S., Chang-Chien, Gou-Ping, Lee, Wei-Shan., Centore, R., & SenGupta, S. P. (2002). *Liq. Cryst.*, *29*, 657.

[27] Biswas, S., Haldar, S., Mandal, P. K., Goubitz, K., Schenk, H., & Dabrowski, R. (2007). *Cryst. Res. Technol.*, *42*, 1029.

[28] Haase, W. & Paulus, H. (1983). *Mol. Cryst. Liq. Cryst.*, *100*, 111.

[29] Walz, L., Haase, W., & Eidenschink, R. (1989). *Mol. Cryst. Liq. Cryst.*, *168*, 169.

[30] Mandal, P., Majumdar, B., Paul, S., Schenk, H., & Goubitz, K. (1989). *Mol. Cryst. Liq. Cryst.*, *168*, 135.

[31] Gupta, S., Mandal, P., Paul, S., Goubitz, K., Wit, M. de., & Schenk, H. (1991). *Mol. Cryst. Liq.Cryst.*, *195*, 149.

[32] Nath, A., Mandal, P., Paul, S., & Schenk, H. (1996). *Liq. Cryst.*, *20*, 765.

[33] Mandal, P., Paul, S., Schenk, H., & Goubitz, K. (1992). *Mol. Cryst. Liq. Cryst.*, *210*, 21.

[34] Mandal, P., Paul, S., Schenk, H., & Goubitz, K. (1986). *Mol. Cryst. Liq. Cryst.*, *135*, 35.

[35] Mandal, P. & Paul, S. (1985). *Mol. Cryst. Liq. Cryst.*, *131*, 223.

[36] Walz, L., Nepveu, F., & Haase, W. (1987). *Mol. Cryst. Liq. Cryst.*, *148*, 111.

[37] Patil, P. S., Shettigar, V., Dharmaprakash, S. M., Naveen, S., Sridhar, M. A., & Shashidhara Prasad, J. (2007). *Mol. Cryst. Liq. Cryst.*, *461*, 123.

[38] Haase, W., Loub, J., Paulus, H., Mokhles, M. A., & Ibrahim, I. H. (1991). *Mol. Cryst. Liq. Cryst.*, *197*, 57.

[39] Hypercube Inc., Gainesville, Florida, USA, http://www.hyper.com.

[40] Klasen, M., Bremer, M., Gotz, A., Manabe, A., Naemura, S., & Tarumi, K. (1998). *Jpn. J. Appl. Phys.*, *2*(37), L 945.

[41] Bryan, R. F. & Forcier. P. G. (1980). *Mol. Cryst. Liq. Cryst.*, *60*, 133.