Molecular Structure and Packing Analysis of Two Nematogenic Fluoro-Phenyl Compounds in the Crystalline Phase

Sripada Haldar, Pradip Kumar Mandal and Wolfgang Haase

Abstract The crystal and molecular structures of two nematogenic compounds 4′-(3, 4-difluoro-phenyl)-4-propyl-bicyclohexyl(3ccp-ff) and 4′-(3,4,5-trifluoro-phenyl)-4-propyl-bicyclohexyl(3ccp-fff) have been determined by direct methods using single crystal X-ray diffraction data. The compounds ($C_{21}H_{30}F_2$) and ($C_{21}H_{29}F_3$) crystallize in the monoclinic system with the space group $P2_1/n$ and $Z = 4$ and in the triclinic system with the space group $P\overline{1}$ and $Z = 2$ respectively. The fluorine atoms are in the plane of phenyl ring. Both the cyclohexyl groups are found to be in chair conformation. Parallel imbricated mode of packing of the molecules are found in the crystalline state which is precursor to the nematic phase. Several van der Waals interactions are observed between the neighbouring molecules. Results of crystal structure have been compared with that obtained from molecular modelling.

Keywords Nematogen · Fluorophenyl · X-ray diffraction · Imbricated mode of packing · Molecular association · Molecular modelling

1 Introduction

Gathering knowledge about the crystal structures of molecules is one of the fundamental aims of scientists. From the determined structures one may get idea about the relative positions of the atoms or ions which make up the substance under study and hence a geometrical description and pictorial representation of chemical structures in terms of bond lengths and angles, torsion angles, non-bonded distances

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J.K. Mandal et al. (eds.), *Information Systems Design and Intelligent Applications*,
Advances in Intelligent Systems and Computing 340,
DOI 10.1007/978-81-322-2247-7_8

and other quantities of interest are possible. One may then try to correlate the structural properties of the material with its physical properties. It might be of interest to point out here that in 1956, the British chemist, Dorothy Hodgkin, described the structure of vitamin B12 for which she received the Nobel Prize for Chemistry in 1964 which led to the successful synthesis of the vitamin in 1971. Since liquid crystals may possess only long range orientational order, or long range one-dimensional or quasi-long range two dimensional translational symmetry, one expects that the molecular arrangement in the crystalline state will predetermine the molecular arrangement in the mesomorphic state [1]. Thus knowledge of molecular geometry and packing of the molecules in the crystalline state helps in explaining the observed phase behaviour that depends on the subtle balance of intermolecular interactions [1]. In a typical nematogen, the long narrow molecules lie more or less parallel and are interleaved giving what was described by Bernal and Crowfoot [2] as an *imbricated* packing and that the transformation from the solid to the nematic phase is characterised by the breakdown of the positional order of the molecules but not of the orientational order. We described various physical properties of a number of partially fluorinated phenyl-bicyclohexyl and biphenyl-cyclohexyl compounds and discussed influence of molecular core structure, chain length and fluorination on their properties [3, 4]. In order to investigate how the molecular structures of the two compounds differ in the crystalline state and their effect on observed phase behaviour, their crystal structures have been determined. We also wanted to probe whether antiparallel molecular association found to exist in the nematic phase are also present in the crystalline phases of the compounds.

2 Experimental, Structure Solution and Refinement

Transparent plate shaped crystals of 3ccp-ff was grown from a solution of acetone and p-xylene and that of 3ccp-fff was obtained from a solution of dichloromethane and methyl alcohol by slow evaporation technique. A crystal with suitable dimensions were used for data collection of 3ccp-ff and 3ccp-fff with the help of an Enraf-Nonius CAD-4 diffractometer and a Bruker SMART CCD single crystal diffractometer. The structures of 3ccp-ff was solved by the Direct Methods using the program GENTAN from the XTAL3.7 program system whereas 3ccp-fff was solved by direct methods and difference Fourier synthesis. The positions of the hydrogen atoms were calculated using the known geometry around the carbon atoms. All calculations were performed with XTAL3.7 for 3ccp-ff, unless stated otherwise. The details of the data collection and refinement were done using the following packages for 3ccp-fff: data collection and cell refinement: Bruker SMART; data reduction: SAINT; absorption correction: SADABS; structure solution: SHELXS-86; refinement: SHELXL97; molecular graphics: CAMERON. The crystal structures of the compounds have been deposited at the Crystallographic Data Centre and allocated the deposition numbers CCDC 652602 and CCDC 679992 respectively.

3 Results and Discussion

Important crystallographic data and refinement parameters are given in Table 1. A perspective drawing of the molecules with the atom numbering scheme are shown in Fig. 1. Final positional coordinates with equivalent temperature factors of the non-hydrogen atoms is listed in Table 2. The average aromatic bond length and the bond angle of 3ccp-ff in the phenyl ring are found to be 1.377(6)A and 120.0(4)°, corresponding values in 3ccp-fff are 1.368(6)A and 120.0(4)°. These values are in agreement with the geometry of the other phenyl moieties reported in literature [5]. The cyclohexyl groups in both the compounds are in chair conformation as was observed other mesogenic molecules [6]. The alkyl chains are in all-trans conformation with mean bond distance 1.519(8)A and bond angle 113.7(5)° in 3ccp-ff and 1.520(6)A and 111.6(4)° in 3ccp-fff respectively as found in other mesogenic compounds [1]. Geometry of the 3ccp-ff and 3ccp-fff molecules 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 rings are highly planar and the three fluorine atoms are almost in the same plane. In 3ccp-ff the dihedral angles between

Table 1 Summary of crystallographic data and refinement parameters

Parameter	3ccp-ff	3ccp-fff
Formula	$C_{21}H_{30}F_2$	$C_{21}H_{29}F_3$
Formula weight	320.51 g/mol	338.44 g/mol
T (K)	293(2)	293(2)
Radiation	1.5418(A)(CuK_α)	0.71073(A)(MoK_α)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a	16.293(15)A	5.3715(14)A
b	6.2777(7)A	10.559(3) A
c	18.306(4)A	16.891(4) A
α	90°	86.33(5)°
β	96.84(6)°	85.20(6)°
γ	90°	81.94(5)°
V	1859.1(2) A^3	943.9(4)A^3
Z	4	2
F(000)	696	364
Crystal size	0.75 × 0.65 × 0.05 mm^3	0.4 × 0.35 × 0.25 mm^3
Independent reflections	3,657	3,331
No. of observed reflections	2,205 [Fobs > $4\sigma(Fobs)$]	1,398 [I > $2\sigma(I)$]
Scan range	$36.11 \le 2\theta \le 42.72(6)^0$	$1.95 \le \theta \le 25.00(6)^0$
Refinement method	full-matrix least-squares on F	full-matrix least-squares on F2
R (observed reflection)	0.072	0.058
RW (observed reflection)	0.061	0.086

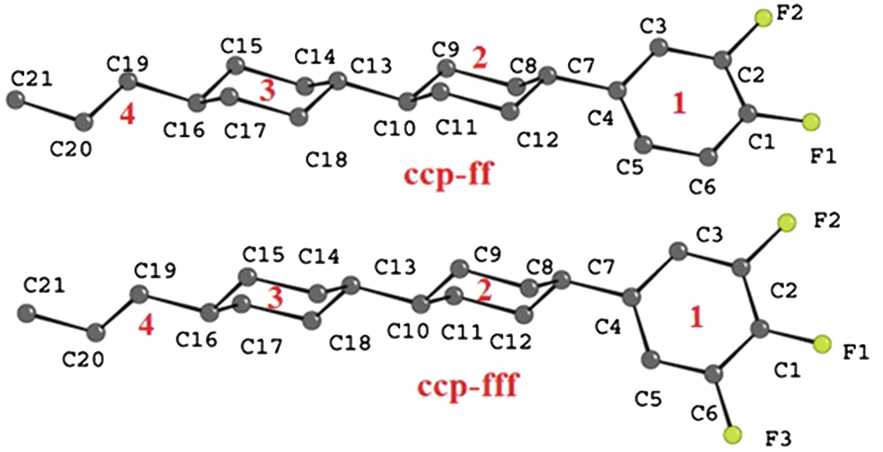
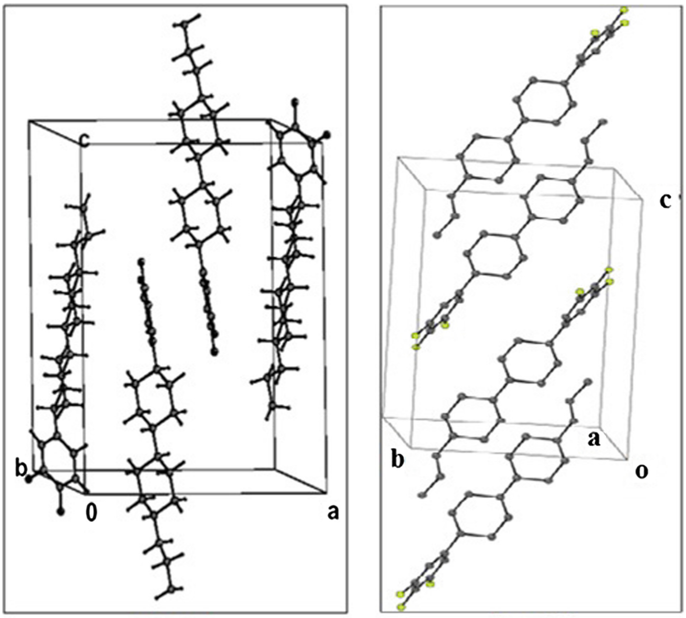


Fig. 1 Perspective view of 3ccp-ff and 3ccp-fff molecules with atom numbering scheme

Table 2 Fractional co-ordinates and equivalent isotropic thermal parameters of the non-Hydrogen atoms for 3ccp-ff (*left part*) and 3ccp-fff (*right part*)

Atom	X	Y	Z	Ueq(A^2)	Atom	X	Y	Z	Ueq(A^2)
C1	0.877	−0.061	1.050	0.063	C1	0.418	0.608	0.608	0.078
F1	0.870	−0.088	1.123	0.087	C2	0.627	0.558	0.558	0.075
C2	0.910	−0.222	1.012	0.070	C3	0.653	0.484	0.484	0.064
F2	0.934	−0.400	1.051	0.117	F1	0.396	0.681	0.681	0.118
C3	0.921	−0.201	0.940	0.065	F2	0.811	0.585	0.585	0.109
C4	0.897	−0.016	0.902	0.052	F3	0.024	0.631	0.631	0.112
C5	0.862	0.143	0.941	0.068	C4	0.464	0.457	0.457	0.058
C6	0.851	0.122	1.014	0.073	C5	0.250	0.507	0.507	0.069
C7	0.910	0.002	0.822	0.054	C6	0.231	0.581	0.581	0.075
C8	0.846	−0.124	0.772	0.063	C7	0.491	0.375	0.375	0.063
C9	0.862	−0.118	0.692	0.062	C8	0.515	0.379	0.379	0.078
C10	0.866	0.109	0.661	0.052	C9	0.551	0.297	0.297	0.079
C11	0.928	0.236	0.713	0.068	C10	0.341	0.244	0.244	0.055
C12	0.911	0.231	0.793	0.066	C11	0.318	0.241	0.241	0.074
C13	0.885	0.115	0.581	0.051	C12	0.284	0.323	0.323	0.075
C14	0.827	−0.022	0.530	0.069	C13	0.375	0.162	0.162	0.056
C15	0.847	−0.014	0.450	0.072	C14	0.398	0.164	0.164	0.075
C16	0.845	0.214	0.420	0.060	C15	0.424	0.083	0.083	0.078
C17	0.903	0.349	0.471	0.075	C16	0.214	0.031	0.031	0.057
C18	0.885	0.341	0.551	0.075	C17	0.192	0.027	0.027	0.073
C19	0.865	0.217	0.341	0.069	C18	0.167	0.108	0.108	0.074
C20	0.851	0.429	0.302	0.102	C19	0.246	−0.051	−0.051	0.072
C21	0.869	0.420	0.222	0.112	C20	0.032	−0.104	−0.104	0.089
					C21	0.073	−0.183	−0.183	0.110

the planes (1 and 2), (1 and 3), (1 and 4), (2 and 3), (2 and 4) and (3 and 4) are respectively 122.1°, 123.5°, 8.8°, 3.4°, 127.8° and 128.7°. In case of 3ccp-fff 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°. Thus the two bicyclohexyl rings are almost coplanar in both the compounds as was observed in CCHs [7]. However, nearly perpendicular bicyclohexyl rings were also reported in CCNs [8]. The phenyl ring (1) and the propyl chain (4) are almost in the same plane in 3ccp-ff (dihedral angle 8.8°) whereas they were at an angle 51.3° in 3ccp-fff. Dihedral angles between the phenyl and nearby cyclohexyl rings are found to be 122.1° and 83.2° in 3ccp-ff and 3ccp-fff respectively. Length of the 3ccp-ff and 3ccp-fff molecules in the crystalline state are found to be 17.30 A and 17.27 A respectively whereas the model length in all-trans conformation is 17.6 A. Thus both the molecules are in their most extended conformation. Packing of the molecules in the unit cells are shown in Fig. 2, which shows that in 3ccp-ff system molecules are found to be parallel to each other and also to one crystallographic axis. However in 3ccp-fff system molecules run almost parallel to each other but not parallel to any crystallographic axis. To get better idea about the nature of packing, the direction cosines of the molecular long axis, defined as the best fitted line through all the non-H atoms, have been calculated and are found to be 0.2435, −0.1570 and 0.9571 for 3ccp-ff system. In other words, the molecules are inclined to the orthogonal X, Y and Z axes at angles 75.9°, 99.0° and 16.8° respectively. For 3ccp-fff system the best



3ccp-ff 3ccp-fff

Fig. 2 Partial packing of 3ccp-ff molecule and 3ccp-fff molecule in the unit cell fitted line through all the non-H atoms, have also been calculated and are found to be 0.3825, −0.5230 and 0.7616. That is the molecules are inclined to the orthogonal crystallographic axes at angles 67.5°, 121.5° and 40.4° respectively. Projections of the crystal structures of the molecules along the **a** and **b** axes are seen. It is evident that the molecules are packed with various degrees of overlapping with the neighbouring ones. Orientation of the molecules in adjacent layers is opposite to each other. Overlaps of the molecules in the neighbouring layers are in the phenyl-cyclohexyl groups in one side and in the cyclohexyl-alkyl chain part on the other side. This type of imbricated mode of packing is usually observed in crystalline phase as a precursor to nematic phase [9]. Intermolecular distances between the neighbouring molecules have been calculated and several van der Waals interactions are observed. Selected intermolecular distances, less than 4.0 A, are shown in Tables 3 for the systems 3ccp-ff and 3cc-fff respectively. In 3ccp-ff six different types of molecular associations are observed: (1) Pair of parallel molecules in head-to-head configuration overlaps completely [related by symmetry operation ‘**a**’(x, y − 1, z) having pair length 19.75A]. (2) Pair of parallel molecules in head-to-tail configuration overlap almost completely [related by symmetry operation ‘**b**’(x + 2, −y, −z + 1) having associated length 19.95 A and related by symmetry operation ‘**c**’(x + 2, −y + 1, −z + 1) having associated length 21.25 A]. (3) Pair of nonparallel molecules in head-to-tail configuration overlaps only in the alkyl group [related by symmetry operation ‘**d**’ (x + 3/2, −y + 1/2, −z + 1/2) having associated length 29A]. (4) Pair of non parallel molecules in head-to-tail configuration with almost complete overlap of the rigid part [related by symmetry operation ‘**e**’(x + 3/2, −y + 1/2, −z + 3/2) having associated length 23.76 A] and (5) Pair of two translated molecules with no overlap at all [related by symmetry operation ‘**f**’(x, y + 1, z − 1) having associated length 36.61 A]. In 3ccp-fff also following five different types of molecular overlaps are observed between neighbouring molecules: (1) Pair of parallel molecules in head-to-head configuration overlaps

Table 3 Selected intermolecular short contact distances less than 4.0 A for 3ccp-ff (a-f) and 3ccp-fff (g-k)

Atom	Atom	Dist.	Atom	Atom	Dist.	Atom	Atom	Dist.	Atom	Atom	Dist.
F2	C5(a)	3.623	C20	C19(d)	3.856	C1	F2(g)	3.442	C10	F3(h)	3.222
F2	C6(a)	3.328	C21	C14(d)	3.298	F3	C2(g)	2.688	C13	F3(h)	3.745
F2	C21(b)	3.729	C21	C15(d)	3.349	C5	C2(g)	3.849	C14	F3(h)	3.437
C3	C21(b)	3.909	C21	C16(d)	3.838	C6	F2(g)	2.922	C19	C19(i)	3.942
C21	F2(b)	3.729	C5	C8(e)	3.556	F3	C8(h)	3.943	C19	C20(i)	3.625
C21	C3(b)	3.909	C5	C9(e)	3.868	F3	C9(h)	3.586	C19	C21(i)	3.828
C11	C17(c)	3.949	C6	C8(e)	3.935	F3	C10(h)	3.222	C20	C16(i)	3.979
C17	C11(c)	3.949	C6	C9(e)	3.935	F3	C13(h)	3.745	C20	C19(i)	3.625
C20	C14(d)	3.919	C18	F1(e)	3.971	F3	C14(h)	3.437	C20	C20(i)	3.91
C20	C15(d)	3.327	C21	F1(f)	3.589	C8	F3(h)	3.943	C21	C15(j)	3.843
C20	C16(d)	3.579	C21	F2(f)	3.619	C9	F3(h)	3.586	F1	C21(k)	3.738

completely [related by symmetry operation ‘**g**’(x − 1, y, z) having pair length 18.80 A]. (2) Pair of parallel molecules in head-to-tail configuration overlap partially [related by symmetry operation ‘**h**’(x, −y + 1, −z + 1) having associated length 25.26A]. (3) Pair of non parallel molecules in head-to-tail configuration overlaps only in the alkyl group [related by symmetry operation ‘**i**’(x, −y + 2, −z) having associated length 29.34 A and related by symmetry operation ‘**j**’(x + 1, −y + 2, −z) having associated length 29.20 A] and (4) Pair of two translated molecules with no overlap at all [related by symmetry operation ‘**k**’(x, y − 1, z) having associated length 36.50 A]. Two of these associated pairs of 3ccp-ff molecules (related to the symmetry **b** and **c**) and 3ccp-fff molecules (related to the symmetry **h** and **i**) have been shown in Fig. 3. It was also observed that apparent molecular lengths or fluctuation lengths (*l*) were 22.8 A and 24.9 A respectively in 3ccp-ff and 3ccp-fff systems near Cr-N transition temperature. On the average these were respectively 1.27 and 1.4 times greater than the length of the molecules in the most extended conformations (L). This was explained assuming the existence of some sort of antiparallel molecular associations in both cases as was done in other polar compounds [1]. However, overlapping of the associated molecules in 3ccp-ff is more than in 3ccp-fff. Existence of such association is supported by results of crystal structure analysis. In 3ccp-ff, the length of the pair related by symmetry **a** is 19.75 A, it is unlikely that such head-to-head parallel pair of polar molecules would persists in nematic phase. Rather it is more likely that on melting, shift of the molecules of antiparallel head-to-tail configurations (related by symmetry operations **b** and **c** having lengths 19.95 A and 21.25 A) along the molecular long axis may give rise to a fluctuation length of 22.8 A in the nematic phase. On the other hand in 3ccp-fff, out of different types of associated pairs the one having partial overlap in antiparallel head-to-tail configuration related by symmetry operation ‘**h**’ with length of 25.26A may give rise to a fluctuation length of 24.9A on melting.

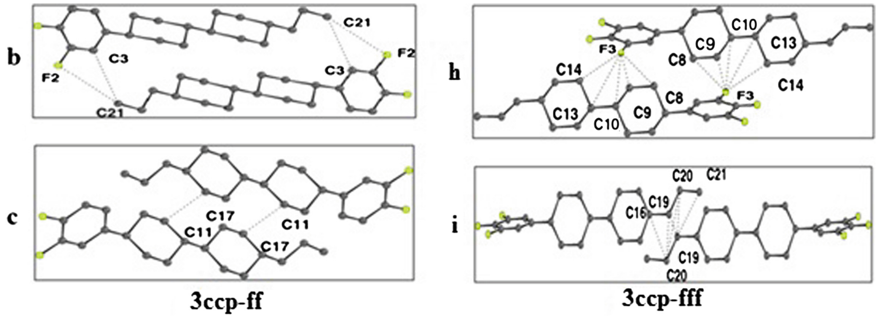


Fig. 3 molecular associations in the crystal structure of 3ccp-ff and 3ccp-fff

4 Conclusions

Crystal and molecular structures of two three ring fluorinated compounds 3ccp-ff and 3ccp-fff have been determined in order to probe structure-property relationship. All the crystal structures have been solved by direct methods using single crystal X-ray diffraction data at room temperature. It is observed that: While difluorinated 3ccp-ff crystallizes in monoclinic space group $P2_1/n$, trifluorinated 3ccp-fff crystallizes in triclinic system with space group $P\overline{1}$. All bond lengths and bond angles agree well with values reported in Cambridge Structural Database and in other mesogenic compounds. In 3ccp-ff and 3ccp-fff molecules are almost in their most extended conformations in crystalline state. All the phenyl rings are found to be planar and the cyclohexyl rings are in chair conformation. Dihedral angle between the phenyl and nearby cyclohexyl ring decreases (122.1° to 83.2°) on the introduction of additional fluorine atom in the phenyl ring (3ccp-ff to 3ccp-fff). Parallel imbricated mode of molecular packing is observed as precursor to nematic phase in 3ccp-ff and 3ccp-fff compounds. Calculation of intermolecular distances strongly suggests existence of molecular packing in a head-to-tail configuration in all cases. From X-ray study the apparent molecular lengths in nematic phase are found to be always greater than the molecular lengths in 3ccp-ff and 3ccp-fff. This might result from antiparallel molecular associations due to dipole-dipole interactions. Whatever might be the reason, conclusive evidence of existence of antiparallel bimolecular associations has been reported for the first time in both the crystalline and nematic phases for fluorobenzene systems.

Acknowledgments The authors would like to thank Dr. E. Poetsch, Merck, Germany for supplying the compounds. This work has been supported by the Research Project of North bengal University.

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