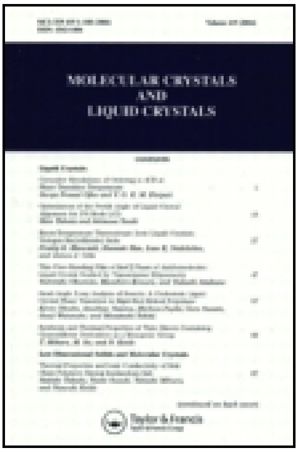

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New Fluorine Substituted Liquid Crystal Containing Bicyclo[2.2.2]Octane Unit

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New Fluorine Substituted Liquid Crystal Containing Bicyclo[2.2.2]Octane Unit

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We have designed and synthesized a new series of liquid crystalline compounds with hybridized three-ring system based on bicyclo[2.2.2]octane unit together with fluorine substituted phenyl and biphenyl fragments. The key stages of the synthesis are alkylation of substituted benzene in concentrated sulfuric acid by bicyclo[2.2.2] octanoles and further cross-coupling between 3,4-difluorophenylboronic acid and the alkylation product. The influence of bicyclo[2.2.2]octane unit position in mesogenic core and fluorine substituents onto a phase transitions of the liquid crystals is discussed.

Keywords Bicyclo[2.2.2]octane; biphenyles; fluoro-substituted benzenes; liquid crystals

1. Introduction

Phenyls and biphenyls in conjunction with bicycle[2.2.2]octane unit are known as excellent cores for generating of liquid crystals [1–4]. Linearly connected bicyclo[2.2.2]octane unit creates rigid rotationally symmetric systems [2]. On the other hand, fluoro-substitution is known as one of the most useful modification ways for corresponding aromatic cores [5–8].

Fluorine's value as lateral substituent consists of its small atom size and high electronegativity and these two characteristic properties lead to a subtle modification of physical properties, often reducing melting without total elimination of liquid crystal phase [7].

In present work we report our recent results on synthesis, characterization and LC properties of a range of novel liquid crystals, whose molecular architecture composed of some fluorine-substituted benzenes and bicyclo[2.2.2]octane moiety incorporated in different positions of mesogenic core. The influence of mentioned structural changes on mesomorphic properties of typical LC molecules is discussed.

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2. Results and Discussion

The bicyclo[2.2.2]octyl unit has been placed at the end and in the centre of three-ring mesogenic core.

2.1. *Synthesis of Target Intermediates and Liquid Crystals*

The synthetic route for the preparation of liquid crystal compounds is shown in Schemes 1–4. According to Scheme 1, the first key stage is alkylation of substituted bromobenzenes **2a-c** in concentrated sulfuric acid by 4-n-pentyl bicyclo[2.2.2]octanol **1** at room temperature [9]. The second key stage is the cross-coupling of 3,4-difluoro-phenylboronic acid **4** with fluoro-substituted phenyl n-pentyl bicyclo[2.2.2]octanes **3a-c** in the presence of palladium catalyst. The coupling reaction leads to new liquid crystalline products **5a-c**.

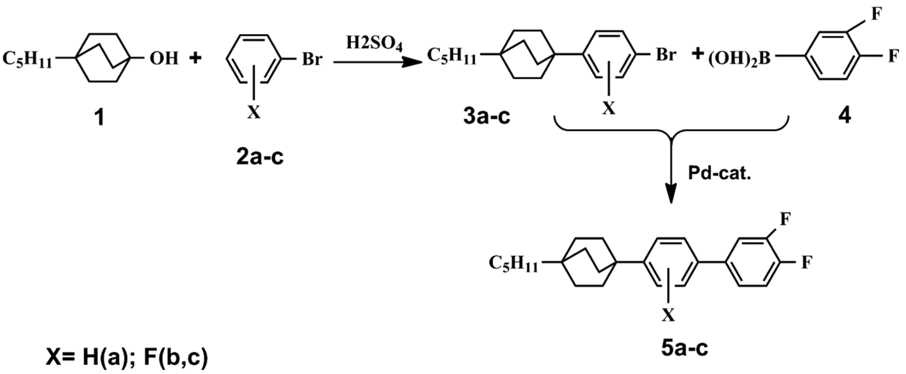
Another group of liquid crystals **16–18** has been prepared through alkylation of n-propylbenzene (**13**) and fluoro-substituted n-propylbenzene (**14, 15**) in concentrated sulfuric acid with bicyclooctanoles according to the Scheme 4.

The key intermediate in Scheme 4 is 3,4-difluorophenyl bicyclo[2.2.2]octanol **12**, which have been prepared using Scheme 2.

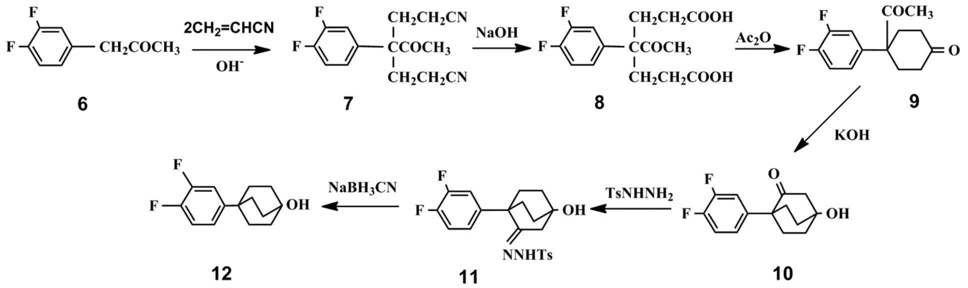
The reaction of 3,4-difluorophenylpropan-2-one **6** with acrylonitrile in the presence of 40% triethylbenzylammonium hydroxyde in methanol afforded 87% yield of dinitrile **7**, which after subsequent treatment with sodium hydroxide yielded 90% of diacid **8**. The cyclization of compound **8** in acetic anhydride solution led to diketone **9** in 42% yield. The diketone **9** was converted into hydroxyketone **10** in 85% yield by treatment potassium hydroxide solution in ethanol.

In order to avoid an exchange of fluorine atoms for hydroxy-groups under conditions of Kizhner-Wolf reaction, we have approached reduction of carbonyl group via its conversion into tosylhydrazone with further application of sodium borohydride [10]. The initial experiments using this technique showed bad results. The reduction of tosylhydrazone **11** by sodium borohydride resulted in a mixture of bicyclooctanols with total yield of 35%.

It was established that the best option for reduction of tosylhydrazone **11** is a sodium cyanoborohydride in accordance with Hutchins method [11]. The yield of 3,4-difluorophenyl-bicyclo[2.2.2]-octan-1-ol **12** in this case was 84%.



Scheme 1. Synthesis of liquid crystals **5a-c** by cross-coupling reaction.



Scheme 2. Synthesis of 3,4-difluorophenyl bicyclo[2.2.2]octanol (**12**).

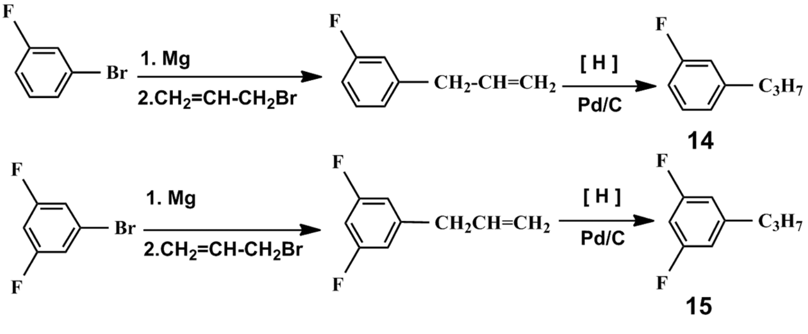
Fluoro-substituted n-propylbenzenes (**14, 15**) have been prepared according to known methods by Scheme 3.

2.2. *Liquid Crystal Properties*

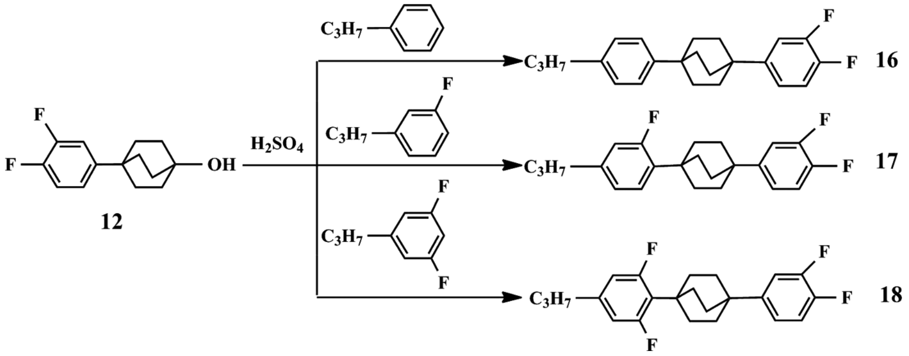
Table 1 presents compounds **5a-c** with a bicyclo[2.2.2]octyl unit attached directly to the end of the mesogenic core and compounds **16–18** with a bicyclo[2.2.2]octyl unit in the centre of LC core.

It is known, that the LC molecules are packed as dimers in “head-to-tail” manner and the lateral substituent in biphenyls influences the ability of the molecules to create associates [13–15].

We have two factors contributing into the LC phase formation. Firstly, the twisting of the planes of two aromatic rings in molecule caused by steric effect of the fluorine atoms is presumably responsible for a decrease of melting point values and decrease of the clearing point to some extent [7,8]. The dispersion interactions responsible for LC phases may have been diminished due to the reduced conjugation possibilities between the rings. Secondly, the packing of bicyclo[2.2.2]octane LC molecules is secured by introduction of phenyl rings of one molecule in a cavity of the bicyclo[2.2.2]octane system of the another molecule, which results in a denser packing and accordingly leads to increase of melting and clearing points. All the synthesized compounds (**5a**, **5c**, **16–18**, except of **5b)** exhibit nematic LC phase. In the compound **5c** one can observe how the introduction of the third fluorine atom



Scheme 3. Synthesis of fluoro-substituted n-propylbenzene (**14**, **15**).

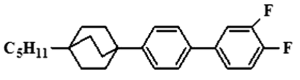
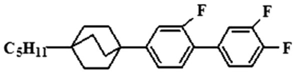
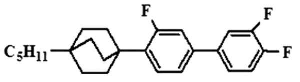
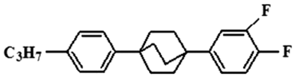
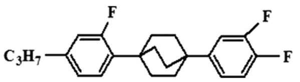
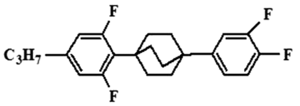


Scheme 4. Synthesis of liquid crystals (**16–18**) by cross-coupling reaction.

to the compound **5a** decreases the melting temperature and clearing point. As one can see on the example of compound **5b**, the presence of the third fluorine atom in the second position of the biphenyl ring leads to complete disappearance of the LC properties.

In the second group of LC compounds (**16–18**), the fluorine atoms play less important role in determination of mesogenic properties. The phase transition temperatures depending on the location and number of fluorine atoms in the benzene rings connected with bicyclo[2.2.2]octane system do not undergo a significant change. Here the bicyclo[2.2.2]octane system is a primary factor influencing the molecular packing and LC phase.

Table 1. Transition temperatures (°C) for fluoro-substituted bicyclo[2.2.2]octane derivatives

Compound	Molecular structure	Cr	S	N	I
5a		110	–	.	151
5b		oil	–	–	.
5c		92	–	.	137
16		75	–	.	115
17		58	–	.	97
18		60	–	.	80

3. Experimental

All commercially available substances were purchased from Aldrich, Merck, Acros, Fluka or Lancaster and were used without further purification. Solvents were purified and dried if necessary according to standard procedures. All reactions were monitored by thin-layer chromatography on silica gel (Merck, Kieselgel 60, F254). UV-light with wavelength of $\lambda = 254$ nm was used for detection. The 1-Hydroxy-4-penthylbicyclo[2.2.2]octane (**1**) was obtained by previously developed method [1,12].

Melting and Clearing Points. The temperatures of phase transitions and liquid crystalline phases were observed with Mettler FP 90 coupled with a polarizing Olympus BH-2 microscope. Temperatures measured using the polarizing microscope method have been corrected by calibration with standard materials.

NMR Spectroscopy. Confirmations of the intermediate and final product structures were accomplished by ^{1}H, ^{13}C, ^{19}F, NMR spectroscopy (Bruker AM-300 and Bruker Avance II 300 spectrometers) at ambient temperature. Chemical shifts values (δ) are relative to Me_4Si and are given in ppm (references solvents are $CDCl_3$ and DMSO-d6).

Mass Spectrometry. Mass-spectra were obtained directly using Finningan MAT INCOS 50 spectrometer (EI, 70 eV).

General procedure for alkylation of bromobenezene (**2a**), *1-bromo-2-fluorobenezene* (**2b**) *and 1-bromo-3-fluorobenezene* (**2c**) *by 1-hydroxy-4-penthylbicyclo[2.2.2] octane* (**1**)

Bromobenzene **2a** or 1-bromo-2-fluorobenezene (**2b**) or 1-bromo-3-fluorobenezene (**2c**) (0,02 mol) was added slowly to vigorously stirred solution of compound **1** (0,01 mol) in 98% sulfuric acid (20 ml). The mixture was stirred for 2 hr at the temperature of 20–25°C. The cooled mixture was added to the ice, and the resulted mixture was shaken with ether (3 × 50 ml). The combined ether extracts were washed with sodium bicarbonate, with water and dried over the magnesium sulphate. The solvent was removed in vacuo and the crude compound **3a** was crystallized from ethanol.

1-(4-Bromophenyl)-4-pentylbicyclo[2.2.2]-octane (**3a**). Yield 96%; mp 94–96°C. (lit. [12]: mp 95–96°C).

1-(4-Bromo-3-fluorophenyl)-4-pentylbicyclo[2.2.2]octane (**3b**). Yield 92%; mp. 27–29°C; ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t), 1.27 (8H, m), 1.48 (6H, q), 1.75 (6H, q), 7.02 (1H, t), 7.23 (1H,oct), 7.46 (1H,dd). ms m/z 353 (M^+).

1-(4-Bromo-2-fluorophenyl)-4-pentylbicyclo[2.2.2]octane (**3c**). Yield 90%; mp. 75–77°C; ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t), 1.27 (8H, m), 1.48 (6H, q), 1.75 (6H, q), 7.17 (3H, sec); ms m/z 353 (M^+).

General procedure for cross-coupling reaction of 1-(4-bromophenyl)-4-pentylbicyclo-[2.2.2]-octane (**3a**). *1-(4-Bromo-3-fluorophenyl)-4-pentylbicyclo[2.2.2]octane* (**3b**) and *1-(4-Bromo-2-fluorophenyl)-4-pentylbicyclo[2.2.2]octane* (**3c**) *with 3,4-difluorophenylboronic acid* (**4**).

Compound **3a** or **3b** or **3c** (0.0015 mol) in DMF (3 ml) was added to the mixture of 3,4-difluorophenylboronic acid **4** (0.00225 mol) in DMF (6.3 ml) solution containing water (2.5 ml), 2 M sodium carbonate (3.5 ml), dichlorobis(triphenylphosphine) palladium (II) (0.04 g) under nitrogen atmosphere. The resulting mixture was stirred and heated under (100°C) for 5 h. The product was extracted into ether and the combined ether extracts were washed with brine and dried over magnesium sulfate. The solvent was removed in vacuo and the crude product was purified by column chromatography (silicagel/pentane).

3,4-Difluoro-4′-(4-pentylbicyclo[2.2.2]oct-1-yl)biphenyl (**5a**). Yield 54%; transitions (°C) Cr 110 N 151 I; ^{1}H NMR($CDCl_3$) δ 0.91 (3H, t), 1.26 (8H, m), 1.54 (6H, q), 1.84 (6H, q), 7.27 (2H,d), 7.39 (1H,t), 7.50 (4H,q); ^{19}F NMR($CDCl_3$) δ 137.57 (1 F, d; $^2J_{CF}$9.4), 140.59 (1 F, d; $^2J_{CF}$9.4); ms m/z 368 (M^+).

2,3′,4′-Trifluoro-4-(4-pentylbicyclo[2.2.2]oct-1-yl)biphenyl (**5b**). Yield 44%; colorless oil; ^{1}H NMR($CDCl_3$) δ 0.91 (3H, t), 1.20 (8H, m), 1.52 (6H, m), 1.81 (6H, m), 7.24 (6H, m). ^{19}F NMR($CDCl_3$) δ 123.10 (1 F, s), 137.68 (1 F, d), 139.32 (1 F, d); ms m/z 386 (M^+).

3,3′,4-Trifluoro-4′-(4-pentylbicyclo[2.2.2]oct-1-yl)biphenyl (**5c**). Yield 48%; transitions (°C) Cr 92 N 137 I; ^{1}H NMR($CDCl_3$) δ 0.91 (3H, t), 1.23 (8H, m), 1.50 (6H, q), 1.92 (6H, q), 7.24 (6H,m); ^{19}F NMR($CDCl_3$) δ 107.43 (1 F, s), 137.1 (1 F, d), 139.46 (1 F, d); ms m/z 386 (M^+).

3,4-Difluorophenylpropan-2-one (**6**). An ethereal solution of methyl lithium (Aldrich, 1,6 M in ether) (50 ml, 0.016 mol) was added to 3,4-difluorophenylacetic acid (Aldrich, mp 45°C) (0.004 mol) dissolved in dry ether (100 ml). This mixture was refluxed for 3 h and the excess of methyl lithium was quenched by brine. The dried ethereal phase ($MgSO_4$) was evaporated in vacuo to give a liquid ketone **6**. Yield 38%; bp 72–74°C at 1.0 mm Hg; n_D^{20} 1.4800; mp 24°C; ^{1}H NMR ($CDCl_3$) δ 2.2 (s, 3H, CH_3), 3.7 (s, 2H,CH_2).

3-Acetyl-1,5-dicyano-3-(3,4-difluorophenyl)lpentane (**7**). Acrylonitrile (0.04 mol) was added slowly to vigorously stirred solution of 3,4-difluorophenylpropan-2-one **6** (0.02 mol) in t-butanole (5 ml) containing 0.28 g of 40% triethylbenzylammonium hydroxyde in methanol. The solution was stirred 2 hr at 20–25°C temperature, then added into 8 ml of water and shaken with ether (3 × 5 ml). Combined ether extracts were washed by water and dried with magnesium sulfate. The solvent was evaporated under the reduced pressure, the crude product was rectified under reduced pressure to yield compound **7**. Yield 87%; mp 114–117°C (methanol); ^{1}H NMR ($CDCl_3$) δ 1.58 – 2.43 (m, 11H,), 6.9–7.0 (m, 2H,); 7.21–7.35 (m, 1H); ms m/z 276 (M^+).

3-Acetyl-3-(3,4-difluorophenyl)pentane-1,5-dicarboxylic acid (**8**). A mixture of sodium hydroxide (0.05 mol) and compound **7** (0,01 mol) in 20 ml of water was boiled under reflux for 30 hours. The solution was treated with "Norite", filtered, and acidified with concentrated hydrochloric acid. The product (**8**) was separated as a white crystalline mass. Yield 90%; mp 168–172°C.

4-Acetyl-4-(3,4-difluorophenyl)cyclohexanone (**9**). A mixture of compound **8** (0.01 mol) and acetic anhydride (8,5 ml) was heated for 4 hour in anhydrous conditions. The acetic acid formed in this reaction and an excess of acetic anhydride were continuously distilled from the mixture at 125–180°C, then at 290°C. The resulted mixture was distillated in vacuo giving rise to compound **9**. Yield 42%; bp 162–164°C at 1.0 mm Hg; ms m/z 252 (M^+).

1-Hydroxy-4-(3,4-difluorophenyl) bicyclo[2.2.2]-octan-3-one (**10**). A mixture of compound **9** (0.005 mol) and potassium hydroxide (0,027 mol) in ethanol (7 ml) was stirred for 17 hrs at 20°C. of water (5 ml) were added in this solution, the product was extracted with ether (3 × 5 ml), the combined ether extracts were washed with brine (2 × 5 ml) and dried over magnesium sulfate. The crude compound **10** was crystallized from benzene. Yield 82%; mp 120–123°C. ^{1}H NMR ($CDCl_3$) δ 1.88 – 2.21 (m, 8H,), 2.61 (s, 2H), 6.87–7.27 (m, 3H); ^{13}C-NMR 210.28 (C=O), 152.4, 151.36, 146.70, 123.4, 116.7, 69.63, 67.58, 51.78, 49.25, 33.17, 29.50, 23.7; ms m/z 252 (M^+).

Tosylhydrazone of hydroxy-4-(3,4 difluorophenyl) bicyclo[2.2.2]-octan-3-one (**11**). Compound **10** (0.00214 mol), toluenesulfonhydrazine (0.00215 mol) and ethanol (4,5 ml) containing 2 drops of HCl were refluxed for 0.5 h and then cooled. The solid was filtered off and recrystallized from ethanol to give hydrazone **11**. Yield 89%; mp 275–278°C.

4-(3,4-Difluorophenyl) bicyclo[2.2.2]-octan-1-ol (**12**). Toluene (3 ml) was added to a 10 mL round bottom flask charged with a solution of the tosylhydrazone **11** (0.62 g, 0.00148 mol) in DMF (6.5 ml), and the resulting solution was heated up to 100–105°C. A mixture of sodium cyanoborohydride (0.378 g, 0.006 mol) and *p*-toluenesulfonic acid monohydrate (0.076 g, 0.0004 mol) was added to the reaction mixture. After stirring at 110°C for 2 h, additional equal portion of sodium cyanoborohydride and *p*-toluenesulfonic acid monohydrate was added and the process was repeated after another 2 h. After 6 h total, the reaction mixture was cooled and poured into water (40 ml), then extracted with ether (5 × 10 mL). The combined extract was washed with water (3 × 10 mL), dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was columned (ether/benzene, 95/5) on silica to give pure product. Yield 84%; mp 116–118°C; ^{1}H-NMR($CDCl_3$) δ 1.25 (s, 1H,), 1.8 (d, 6H), 1.95 (d, 6H), 7.0–7.27 (m, 3H,); ^{19}F-NMR (DMSO) δ 142.24 and 138.12 (s, 2 F). ms m/z 238(M^+).

1-Fluoro-3-propylbenzene (**14**). *Stage 1.* 3-Difluorophenylmagnesium bromide was prepared from reaction of the 3-fluoro-bromobenzene (0.05 mol) with magnesium (0.05 mol) in anhydrous diethyl ether (20 ml), then it was added dropwise to a solution of allyl bromide (0.55 mol) in ether (10 ml) over 30 min. The resulting mixture was refluxed for 2 h, cooled, and was then poured into iced dilute sulfuric acid. The product was extracted from the aqueous phase by ether (3 × 50 ml) and the combined extracts were washed with brine (50 ml) and dried over $MgSO_4$. The removal of solvent in vacuo and further distillation afforded the desired product. Yield of 1-allyl-3-fluorobenzene is 70%; bp 157–160°C; n_D^{20} 1.4920; ms m/z 136(M^+).

Stage 2. 10% Palladium on carbon (0.02 g) was suspended in 1-allyl-3-fluorobenzene (0.02 mol), and mixture was stirred until absorption of theoretically designated hydrogen volume. The catalyst was filtered off and washed with ethanol. The removal of solvent in vacuo and further distillation afforded the desired product **14**. Yield 92%; bp 162–164°C; n_D^{20} 1.4745; ms m/z 138(M^+).

1,3-Difluoro-5-propylbenzene (**15**). *Stage 1.* 3,5-Difluorophenylmagnesium bromide was prepared from reaction of the 3,5-difluorobromo benzene (0.05 mol) with magnesium (0.05 mol) in anhydrous diethyl ether (20 ml), then it was added dropwise to solution of the allyl bromide (0.55 mol) in 10 ml ether over 30 min. The resulting mixture was refluxed for 2 h, cooled, and was then poured into iced dilute sulfuric acid. The product was extracted from the aqueous phase into ether (3 × 50 ml) and the combined extracts were washed with brine (50 ml) and dried over $MgSO_4$), The removal of solvent in vacuo and further distillation afforded the desired product. Yield of 1-allyl-3,5-difluorobenzene is 73%; bp 168–170°C; n_D^{20} 1.4930; ms m/z 154(M^+).

Stage 2. 10% Palladium on carbon (0.75 g) was suspended in (0.1 mol) 1-allyl-3,5-difluorobenzene, and mixture was stirred until absorption of the theoretically designated hydrogen volume. The catalyst was filtered off and washed with ethanol. The removal of solvent in vacuo and further distillation afforded the desired product **15**. Yield 90%; bp 167–170°C; n_D^{20} 1.4920; ms m/z 156 (M^+).

General procedure for alkylation of propylbenezene (**13**), *1-fluoro-3-propylbenzene* (**14**) *and 1,3-difluoro-5-propylbenzene* (**15**) *by 4-(3,4-difluorophenyl) bicyclo[2.2.2] octan-1-ol* (**12**).

Propylbenzene **(13)** (Acros) or 1-fluoro-3-propylbenzene (**14**) or 1,3-difluoro-5-propylbenzene (**15**) (0.001 mol) was added slowly to vigorously stirred solution of 4-(3,4-difluorophenyl) bicyclo[2.2.2]octan-1-ol **12** (0.001 mol) in 98% sulfuric acid (6 ml). The mixture was stirred 2 hr at the temperature 20–25°C. The cooled mixture was poured into ice, and the resulted mixture was shaken with ether (3 × 50 ml). The combined ether extracts were washed with sodium bicarbonate, with water and dried over the magnesium sulfate. The solvent was removed in vacuo.

1-(3,4-Difluorophenyl)-4-(4′-propylphenyl)bicyclo[2.2.2]octane (**16**). Yield 73%; transitions (°C) Cr 75 N 115 I; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, 3H, CH_3), 1.55–1.75 (m, 2H, CH_2), 2.05 (s, 12H, BCO), 2.6 (t, 2H, CH_2), 7.0–7.35 (m, 7H,); ^{19}F-NMR (DMSO): δ 138.22 and 142.69 (s, 2 F); ms m/z 340 (M^+).

1-(3,4-Difluorophenyl)-4-(2-fluoro-4-propylphenyl)bicyclo[2.2.2]octane (**17**). Yield 43%; transitions (°C) Cr 58 N 97 I. ^{1}H NMR ($CDCl_3$) δ 0.95(t, 3H, CH_3), 1.65 (m, 2H, CH_2), 1.95 (q, 6H, BCO), 2.1 (q,6H,), 2.55 (t, 2H, CH_2), 6.85 (t, 3H), 7.15 (m, 3H,); ^{19}F-NMR (DMSO) δ 109.25 (s, 1 F), 138.25 and 142.58 (s, 2 F); ms m/z 358 (M^+).

1-(3,4-Difluorophenyl)-4-(2,6-difluoro-4-propylphenyl)bicyclo[2.2.2]octane (**18**). Yield 34%; transitions (°C) Cr 60 N 80 I. ^{1}H NMR ($CDCl_3$): 0.95 (t, 3H, CH_3), 1.6 (m, 2H, CH_2), 1.9 (q, 6H, BCO), 2.2 (q,6H,), 2.5 (t, 2H, CH_2), 6.65 (d, 2H), 7.22 (m, 3H,); ^{19}F-NMR (DMSO) δ 106.61 (s, 1 F), 138.4 and 142.78 (s, 2 F); ms m/z 376 (M^+).

4. Conclusions

The introduction of fluorine atoms in aromatic part of three-ring mesogenic structures, containing bicyclo [2.2.2] octane unit at the end or in the middle of the mesogenic core, leads to decrease of melting and clearing points values, reduces the interval of the mesophase or even removes the LC phase completely depending on location and number of fluorine atoms.

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