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Synthesis and Liquid-Crystalline Properties of Novel Compounds with 3-Fluoro-4-cyanophenoxy Group

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Facile and convenient synthesis of four series of novel compounds with 3-fluoro-4-cyanophenoxy group were performed by using 2-fluoro-4-hydroxyphenyl as intermediate. The structures of these compounds were characterized by means of elemental analysis, infrared (IR), nuclear magnetic resonance (^{1}H NMR) and mass spectra (MS). One of these compounds was found to exhibit potential liquid-crystalline properties.

Key Words: 3-Fluoro-4-cyanophenoxy, Synthesis, Liquid crystalline properties.

INTRODUCTION

During the last few years much attention and efforts have been devoted to the development of new liquid crystalline compounds which possess low melting points, high clear points and suitable mesophase ranges. Fluoro-substituted liquid crystals became a hot topic because these liquid crystals generally exhibit excellent properties[1-9] compared with the corresponding unsubstitued compounds, such as low viscosity, high voltage mean retension, high specific resistance, *etc*. A number of compounds, which are synthesized from 2-fluoro-4-hydroxybenzonitrile, have been used widely in LCDs all over the world and exhibit excellent properties[10,11]. In contrast, only a small number of compounds bearing a terminal CN-function and a lateral substituent have been reported[12,13]. To study the effect of lateral substitution on liquid crystals incorporating F and CN groups in a terminal position, we synthesized four series of derivatives of 2-fluoro-4-hydroxybenzonitrile. The F atom was chosen as the lateral substituent, because F-substituted liquid crystals generally exhibit nematic-isotropic transition temperature only a little below those of the corresponding compounds with a H atom in place of the F atom[14].

EXPERIMENTAL

General procedure for synthesis of substituted phenoxyacetic acid esters of 2-fluoro-4-hydroxy-benzonitrile (1a-j, 2a-j, 3a-j): A mixture of the corresponding phenol (0.10 mol), 2-chloro acetic acid (0.20 mol), sodium hydroxide (0.4 mol) and water (100 mL) was stirred vigorously and refluxed for 8 h. After cooling, the mixture was poured into a mixture of concentrated hydrochloric acid (50 mL) and ice-cold water (100 mL) and stirred for 0.5 h. The precipitate was filtered off, washed with water, dried and recrystallisted from 99 % ethyl alcohol to give the title compound **1**. To a solution of **1** (0.01 mol) in $CHCl_3$ (20 mL) was added sulfuryl dichloride (20 mL). The mixture was then heated and refluxed for 4 h. After reaction, the extra sulfuryl dichloride was removed to give the title compound **2**. A mixture of 2-fluoro-4-hydroxybenzonitrile (0.05 mol), triethylamine (1.5 mL) and chloroform (20 mL) was added dropwise into the **2** in $CHCl_3$ (15 mL) with an ice bath. The mixture was then heated and refluxed for 4 h. After cooling to room temperature, the mixture was washed with H_2O (30 mL), 4 % HCl (30 mL), 4 % Na_2CO_3 (30 mL) and H_2O (30 mL) in turn. Removing of solvent afforded the crude product **3**. The crude product was purified by column chromatography (silica gel, petroleum ether/ EtOAc, 1/4) to give a solid with constant melting point.

3a: Colourless powder. Yield 43 %. Anal. calcd: C, 70.59; H, 3.92; N, 5.49. Found: C, 70.41; H, 4.23; N, 5.16. IR (ν_{max}, cm^{-1}): 2234 (C≡N); 1788 (C=O); 1076, 1164 (C-O-C); 1495, 1583, 1618 (phenyl ring). ^1H NMR: δ 4.88 (s, 2H, CH_2); 6.80-7.70 (m, 8H, Ar-H).

3b: Colourless powder. Yield 56 %. Anal. calcd: C, 62.18; H, 3.11; N, 4.84. Found: C, 61.73; H, 3.58; N, 5.21. IR (ν_{max}, cm^{-1}): 2234 (C≡N); 1788 (C=O); 1091, 1167 (C-O-C); 1496, 1583, 1618 (phenyl ring). ^1H NMR: δ 5.13 (s, 2H, CH_2), 7.08-8.09 (7H, Ar-H).

3c: Colourless powder. Yield 45 %. Anal. calcd: C, 71.38; H, 4.46; N, 5.20. Found: C, 71.18; H, 4.58; N, 5.27. IR (ν_{max}, cm^{-1}): 2237 (C≡N); 1791 (C=O); 1079, 1148 (C-O-C); 1513, 1584, 1615 (phenyl ring). ^1H NMR: δ 2.31 (s, 3H, CH_3), 4.87 (s, 2H, CH_2), 6.86-7.68 (7H, Ar-H).

3d: Colourless powder. Yield 38 %. Anal. calcd: C, 67.37; H, 4.21; N, 4.91. Found: C, 67.79; H, 4.19; N, 4.41. IR (ν_{max}, cm^{-1}): 2235 (C≡N); 1789 (C=O); 1078, 1151 (C-O-C); 1507, 1583, 1614 (phenyl ring). ^1H NMR: δ 2.31(s, 3H, CH_3), 4.87 (s, 2H, CH_2), 6.86-7.68 (7H, Ar-H).

3e: Light yellow powder. Yield 54 %. Anal. calcd: C, 60.00; H, 3.00; N, 9.33. Found: C, 59.45; H, 2.79; N, 9.97. IR (ν_{max}, cm^{-1}): 2241 (C≡N); 1784 (C=O); 1072, 1169 (C-O-C); 1516, 1596, 1614 (phenyl ring). ^1H NMR: δ 5.03 (s, 2H, CH_2), 7.01-8.30 (7H, Ar-H).

3f: Colourless powder. Yield 60 %. Anal. calcd: C, 71.38; H, 4.46; N, 5.20. Found: C, 71.21; H, 4.63; N, 5.31. IR (ν_{max}, cm^{-1}): 2237 (C≡N); 1788 (C=O); 1098, 1169 (C-O-C); 1491, 1591, 1620 (phenyl ring). ^1H NMR: δ 2.37 (s, 3H, CH_3), 4.93 (s, 2H, CH_2), 6.60-7.60 (7H, Ar-H).

3g: Light yellow powder. Yield 35 %. Anal. calcd: C, 62.18; H, 3.11; N, 4.84. Found: C, 61.73; H, 3.67; N, 5.36. IR (ν_{max}, cm^{-1}): 2236 (C≡N); 1774 (C=O); 1082, 1167 (C-O-C); 1484, 1586, 1616 (phenyl ring). ^1H NMR: δ 4.96 (s, 2H, CH_2), 6.88-7.76 (7H, Ar-H).

3h: Light yellow powder. Yield 42 %. Anal. calcd: C, 60.00; H, 3.00; N, 9.33. Found: C, 60.53; H, 3.17; N, 9.01. IR (ν_{max}, cm^{-1}): 2234 (C≡N); 1770 (C=O); 1070, 1164 (C-O-C); 1516, 1593, 1611 (phenyl ring). ^{1}H NMR: δ 4.90 (s, 2H, CH_2), 6.83-8.18 (7H, Ar-H).

3i: Colourless powder. Yield 32 %. Anal. calcd: C, 55.56; H, 2.47; N, 4.32. Found: C, 55.07; H, 2.36; N, 4.79. IR (ν_{max}, cm^{-1}): 2237 (C≡N); 2237 (C=O); 1087, 1171 (C-O-C); 1506, 1591, 1615 (phenyl ring). ^{1}H NMR: δ 4.85 (s, 2H, CH_2), 6.61-7.56 (6H, Ar-H).

3j: Light yellow powder. Yield 30 %. Anal. calcd: C, 67.37; H, 4.21; N, 4.91. Found: C, 67.86; H, 3.68; N, 4.12. IR (ν_{max}, cm^{-1}): 2234 (C≡N); 1770 (C=O); 1054, 1158 (C-O-C); 1503, 1590, 1614 (phenyl ring). ^{1}H NMR: δ 3.65 (s, 3H, OCH_3), 4.82 (s, 2H, CH_2), 6.73-7.86 (7H, Ar-H).

General procedure for synthesis of 2-(4-cyano-3-fluorophenyl)-N-substituted phenlyactamide (4a-l): A mixture of 2-chloro-N-substituted phenylacetamide (5 mmol), 2-fluoro-4-hydroxybenzonitrile (5 mmol), potassium carbonate (7 mmol), acetone (30 mL) and a catalytic amount of KI was refluxed for 4 h. After cooling, the precipitate was filtered off. The solvent was removed from filtrate to give a yellowish powder. The crude product was purified by column chromatography (silica gel, petroleum ether/EtOAc, 1/7) to give a solid with constant melting point.

4a: Colourless powder. Yield 67 %. m.p. 150.7-152.5 ºC. Anal. calcd: C, 64.00; H, 4.33; N, 9.33. Found: C, 63.72; H, 4.69; N, 9.01. IR (ν_{max}, cm^{-1}): 3101, 3397 (N-H); 2228 (C≡N); 1693 (C=O); 1510, 1545, 1575, 1602 (phenyl ring). ^{1}H NMR: δ 3.72 (s, 3H, OCH_3), 4.85 (s, 2H, CH_2), 6.89-7.89 (7H, Ar-H); 10.03 (s, 1H, NH).

4b: Colourless powder. Yield 71 %. m.p. 160.4-161.6 ºC. Anal. calcd: C, 67.61; H, 4.58; N, 9.86. Found: C, 67.58; H, 4.31; N, 10.17. IR (ν_{max}, cm^{-1}): 3096, 3424 (N-H); 2224 (C=N); 1702 (C=O); 1506, 1546, 1576, 1591 (phenyl ring). ^{1}H NMR: δ 2.19 (s, 3H, CH_3),4.92 (s, 2H, CH_2), 7.05-8.00 (7H, Ar-H); 9.61 (s,1H, NH).

4c: Colourless powder. Yield 79 %. m.p. 134.0-135.1 ºC. Anal. calcd: C, 67.61; H, 4.58; N, 9.86. Found: C, 67.73; H, 4.62; N, 9.61. IR (ν_{max}, cm^{-1}): 3096, 3351 (N-H); 2231 (C≡N); 1687 (C=O); 1505, 1545, 1577, 1596 (phenyl ring). ^{1}H NMR: δ 2.28 (s, 3H, CH_3), 4.88 (s, 2H, CH_2), 6.90-7.90 (7H, Ar-H); 10.09 (s, 1H, NH).

4d: Colourless powder. Yield 81 %. m.p. 168.0-169.8 ºC. Anal. calcd: C, 67.61; H, 4.58; N, 9.86. Found: C, 67.33; H, 4.25; N, 10.27. IR (ν_{max}, cm^{-1}): 3095, 3393 (N-H); 2225 (C≡N); 1688 (C=O); 1500, 1578, 1538, 1597 (phenyl ring). ^{1}H NMR: δ 2.26 (s, 3H, CH_3), 4.86 (s, 2H, CH_2), 7.03-7.89 (7H, Ar-H), 10.08 (s, 1H, NH).

4e: Light yellow powder. Yield 85 %. m.p. 126.3-127.7 ºC. Anal. calcd: C, 66.67; H, 4.07; N, 10.37. Found: C, 66.19; H, 4.00; N, 10.58. IR (ν_{max}, cm^{-1}): 3103, 3346 (N-H); 2229 (C≡N); 1684 (C=O); 1507, 1545, 1579, 1601 (phenyl ring). ^{1}H NMR: δ 4.89 (s, 2H, CH_2), 7.03-7.90 (8H, Ar-H), 10.08 (s, 1H, NH).

4f: Colourless powder. Yield 57 %. m.p. 172.7-173.6 ºC. Anal. Calcd: C, 64.00; H, 4.33; N, 9.33. Found: C, 63.91; H, 4.37; N, 9.29. IR (ν_{max}, cm^{-1}): 3095, 3404 (N-H); 2231 (C≡N); 1686 (C=O); 1494, 1541, 1576, 1603 (phenyl ring). ^{1}H NMR: δ 3.87 (s, 3H, OCH_3), 4.96 (s, 2H, CH_2), 6.90-8.00 (7H, Ar-H), 9.39 (s, 1H, NH).

4g: Light yellow powder. Yield 63 %. m.p. 116.2-117.0 ºC. Anal. calcd: C, 64.97; H, 4.78; N, 8.92. Found: C, 64.57; H, 4.48; N, 9.25. IR (ν_{max}, cm^{-1}): 3095, 3392 (N-H); 2222 (C≡N); 1693 (C=O); 1493, 1510, 1591, 1602 (phenyl ring). ^{1}H NMR: δ 1.25-1.28 (t, 3H, CH_3), 4.05-4.09 (q, 2H, CH_2CH_3), 4.76 (s, 2H, $COCH_2O$), 6.58-7.57 (7H, Ar-H), 8.66 (s, 1H, NH).

4h: Colourless powder. Yield 77 %. m.p. 122.2-122.7 ºC. Anal. calcd: C, 64.97; H, 4.78; N, 8.92. Found: C, 64.63; H, 4.59; N, 9.17. IR (ν_{max}, cm^{-1}): 3096, 3384 (N-H); 2231 (C≡N); 1695 (C=O); 1491, 1517, 1598, 1605 (phenyl ring). ^{1}H NMR: δ 1.31-1.34 (t, 3H, CH_3), 3.99-4.02 (q, 2H, CH_2CH_3), 4.91 (s, 2H, $COCH_2O$), 6.60-7.57 (7H, Ar-H), 9.00 (s, 1H, NH).

4i: Light yellow crystal. Yield 73 %. m.p. 175.5-177.5 ºC. Anal. calcd: C, 61.76; H, 4.04; N, 15.44. Found: C, 61.33; H, 4.35; N, 15.26. IR (ν_{max}, cm^{-1}): 3098, 3401 (N-H); 2232 (C≡N); 1697 (C=O); 1463, 1525, 1579 (phenyl ring). ^{1}H NMR: δ 1.31-1.34 (t, 3H, CH_3), 99-4.02 (q, 2H, CH_2CH_3), 4.91 (s, 2H, $COCH_2O$), 6.60-7.57 (7H, Ar-H), 9.00 (s, 1H, NH).

4j: Light yellow crystal. Yield 70 %. m.p. 137.3-138.2 ºC. Anal. calcd: C, 71.47; H, 3.76; N, 8.78. Found: C, 71.34; H, 3.83; N, 8.62. IR (ν_{max}, cm^{-1}): 3099, 3434 (N-H); 2230 (C≡N); 1674 (C=O); 1494, 1578, 1596 (phenyl ring). ^{1}H NMR: δ 4.78 (s, 2H, CH_2), 6.90-7.82 (7H, Ar-H), 9.57 (s, 1H, NH).

4k: Light yellow powder. Yield 62 %. m.p. 250.1-251.9 ºC. Anal. calcd: C, 57.14; H, 3.17; N, 13.33. Found: C, 57.53; H, 3.46; N, 12.98. IR (ν_{max}, cm^{-1}): 3109, 3377 (N-H); 2229 (C≡N); 1705 (C=O); 1509, 1542, 1596 (phenyl ring). ^{1}H NMR: δ 4.99 (s, 2H, CH_2), 7.05-8.27 (7H, Ar-H), 10.80 (s, 1H, NH).

4l: Light yellow powder. Yield 64 %. m.p. 217.2-218.0 ºC. Anal. calcd: C, 57.14; H, 3.17; N, 13.33. Found: C, 57.31; H, 3.25; N, 13.07. IR (ν_{max}, cm^{-1}): 3097, 3298 (N-H); 2234 (C≡N); 1701 (C=O); 1447, 1512, 1549, 1586 (phenyl ring). ^{1}H NMR: δ 4.92 (s, 2H, CH_2), 6.72-8.23 (7H, Ar-H), 9.64 (s, 1H, NH).

General procedure for synthesis of N'-(substitutedbenzylidene)-2-(4-cyano-3-fluorophenoxy)acetohydrazide (5a-h, 6a-h, 7a-h): Ethyl chloroacetate (30 mmol) was added dropwise at 60 ºC to a mixture of 2-fluoro-4-hydroxybenzonitrile (20 mmol), potassium carbonate (15 mmol), KI (7 mmol) and DMF (20 mL). After the complete addition, the reaction mixture was stirred at 120 ºC for 7 h. The precipitate was filtered off and the solvent was removed from filtrate to give **5** as a oily substance. 80 % Hydrazine (30 mmol) was added to the oily substance and the resulting mixture was stirred vigorously to afford solid. After filtration, the filter cake was washed with water and dried. The crude product was recrystallisted from 95 % ethyl alcohol to give **6**, yield 80 %. To a solution of **6** (2 mmol) in EtOH (20 mL) was added aldehyde (3 mmol), the mixture was heated and refluxed for 12 h. After cooling, the resulting mixture was evaporated *in vacuo* to give colourless solid **7**. The crude product was purified by column chromatography (silica gel, petroleum ether/EtOAc, 1/6) to give a solid with constant melting point.

7a: Colourless crystal. Yield 65 %. m.p. 209.1-209.8 ºC. Anal. calcd: C, 61.34; H, 3.83; N, 13.42. Found: C, 61.96; H, 3.12; N, 13.05. IR (ν_{max}, cm^{-1}): 3055, 3450 (N-H); 2229 (C≡N); 1701 (C=O); 1492, 1506, 1536, 1576,1620 (C=N, C=C). ^1H NMR: δ 4.87 (s, 2H, CH_2), 5.33 (s, 1H, OH), 6.89-7.90 (m, 7H, Ar-H), 8.31 (s, 1H, NH), 8.54 (s, 1H, =CH).

7b: Colourless powder. Yield 67 %. m.p. 173.1-174.3 ºC. Anal. calcd: C, 58.54; H, 3.48; N, 14.63. Found: C, 58.09; H, 3.97; N, 14.95. IR (ν_{max}, cm^{-1}): 3100 3432 (N-H); 2235 (C≡N); 1686 (C=O); 1507 1542 1578 1622 (C=N, C=C). ^1H NMR: δ 4.83 (s, 2H, CH_2), 6.63-7.85 (m, 7H, Ar-H), 7.90 (s, 1H, NH), 8.18 (s, 1H, =CH).

7c: Light yellow powder. Yield 73 %. m.p. 207.6-209.3 ºC. Anal. calcd: C, 52.46; H, 2.73; N, 11.48. Found: C, 52.06; H, 2.36; N, 11.74. IR (ν_{max}, cm^{-1}): 3094 3436 (N-H); 2229 (C≡N); 1695 (C=O); 1438 1468 1506 1576 1621 (C=N, C=C).

7d: Colourless powder. Yield 69 %. m.p. 177.5-178.8 ºC. Anal. calcd: C, 64.65; H, 4.04; N, 12.12. Found: C, 64.12; H, 4.17; N, 12.36. IR (ν_{max}, cm^{-1}): 3095 3461 (N-H); 2223 (C≡N); 1686 (C=O); 1442 1505 1577 1622 (C=N, C=C). ^1H NMR: δ 4.85 (s, 2H, CH_2), 7.00-7.90 (m, 7H, Ar-H), 8.01 (s, 1H, NH), 8.30 (s, 1H, =CH).

7e: Light yellow powder. Yield 71 %. m.p. 208.0-210.0 ºC. Anal. calcd: C, 56.14; H, 3.22; N, 16.37. Found: C, 56.82; H, 3.37; N, 15.82. IR (ν_{max}, cm^{-1}): 3109 3379 (N-H); 2231 (C≡N); 1706 (C=O); 1509 1543 1595 1621 (C=N, C=C).

7f: Colourless powder. Yield 76 %. m.p. 245.0-247.0 ºC. Anal. calcd: C, 61.34; H, 3.83; N, 13.42. Found: C, 60.89; H, 3.07; N, 13.11. IR (ν_{max}, cm^{-1}): 3103 3411 (N-H); 2229 (C≡N); 1688 (C=O); 1510 1545 1580 1605 (C=N, C=C).

7g: Colourless powder. Yield 68 %. m.p. 194.0-195.7 ºC. Anal. calcd: C, 62.39; H, 4.28; N, 12.14. Found: C, 61.85; H, 5.18; N, 11.67. IR (ν_{max}, cm^{-1}): 3096 3435 (N-H); 2236 (C≡N); 1681 (C=O); 1506 1576 1608 1622 (C=N, C=C). ^1H NMR: δ 3.80 (s, 3H, OCH_3), 4.82 (s, 2H, CH_2), 6.90-7.90 (m, 7H, Ar-H), 7.95 (s, 1H, NH), 8.23 (s, 1H, =CH).

7h: Light yellow powder. Yield 63 %. Anal. calcd: C, 60.47; H, 3.49; N, 16.28. Found: C, 59.86; H, 3.07; N, 3.07. IR (ν_{max}, cm^{-1}): 3101 3435 (N-H); 2231 (C≡N); 1684 (C=O); 1505 1547 1576 1621 (C=N, C=C).

General procedure for 4-cyano-3-fluoro-phenyl dialkoxyl phosphate (8a-c, 9a-c): A mixture of anhydrous ethyl alcohol (0.75 mol), phosphoryl trichloride (0.25 mol) and toluene (250 mL) was stirred at 8-10 ºC overnight. Sulfuryl dichloride (0.25 mol) was added dropwise to the mixture. After the complete addition, the mixture was stirred at 8-10 ºC for 1 h. The volatiles were removed *in vacuo* to afford **8**. A mixture of 2-fluoro-4-hydroxybenzonitrile (2 mmol), Et_3N (3 mmol) and $CHCl_3$ (30 mL) was stirred in an ice bath. After dissolution, **8** (2 mmol) in $CHCl_3$ (10 mL) was added. The reaction mixture was warmed to room temperature and stirred until the reaction was completed. The mixture was washed with water (30 mL), 4 % HCl (30 mL), 4 % Na_2CO_3 (30 mL) and H_2O (30 mL) and dried ($MgSO_4$). The solvent was removed to obtain a yellowish powder **9**. The crude product was purified by column chromatography (silica gel, petroleum ether/EtOAc, 1/8) to give a colourless crystal with constant melting point.

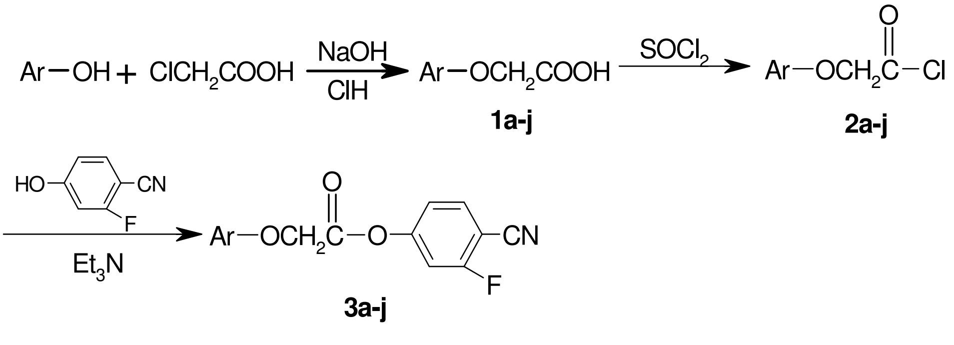
9a: Colourless crystal. Yield 56 %. Anal. calcd: C, 44.08; H, 3.67; N, 5.71. Found: C, 44.62; H, 3.76; N, 5.02. IR (ν_{max}, cm^{-1}): 1246 (P=O); 1099 (P-O-C); 2221 (C≡N); 1477, 1539, 1596 (phenyl ring). ^{1}H NMR: δ 3.46 (s, 6H, CH$_3$), 6.60-7.49 (m, 3H, Ar-H).

9b: Colourless crystal. Yield 52 %. Anal. calcd: C, 48.35; H, 4.76; N, 5.13. Found: C, 47.83; H, 4.19; N, 5.72. IR (ν_{max}, cm^{-1}): 1237 (P=O); 1046 (P-O-C); 2227 (C≡N); 1469, 1507, 1594 (phenyl ring). ^{1}H NMR: δ 1.25-1.32 (t, 6H, CH$_3$), 3.02-3.15 (q, 4H, CH$_2$), 6.43-7.45 (m, 3H, Ar-H).

9c: Colourless crystal. Yield 41 %. Anal. calcd: C, 51.38; H, 5.65; N, 4.65. Found: C, 51.95; H, 4.96; N, 4.97. IR (ν_{max}, cm^{-1}): 1270 (P=O); 1036 (P-O-C); 2235 (C≡N); 1435, 1476, 1578 (phenyl ring). ^{1}H NMR: δ 0.91-1.07 (t, 6H, CH$_3$), 1.49-1.63 (m, 4H, CH$_2$), 3.61-3.73 (t, 4H, O-CH$_2$), 6.49-7.78 (m, 3H, Ar-H).

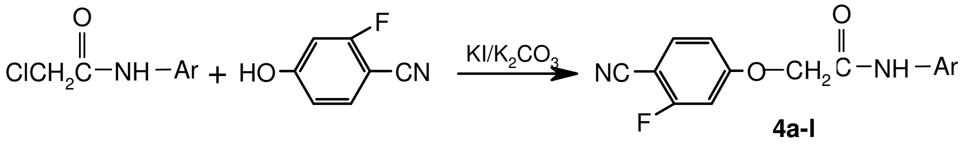
RESULTS AND DISCUSSION

Melting points were measured on a WRR melting point apparatus, with the thermometer uncorrected. Infrared (IR) spectra were recorded on a Nicolet 510P FT-IR spectrophotometer with KBr tablets. ^{1}H NMR spectra were recorded on a Rigaku JNM-ECP 600 spectrometer using DMSO-d_6 as solvent and internal standard used was TMS. Phase transition temperatures were measured using a NETZCH DSC-204 differential scanning calorimetry (DSC) with a heating rate of 5 ºC/min and a cooling rate of -5 ºC/min. The temperatures at the maximum in DSC enthalpic peaks were taken as the phase transition temperatures. Four series of noval compounds with 2-fluoro-4-hydrobenzonitrile side group were synthesized (**Schemes I** to **IV**).



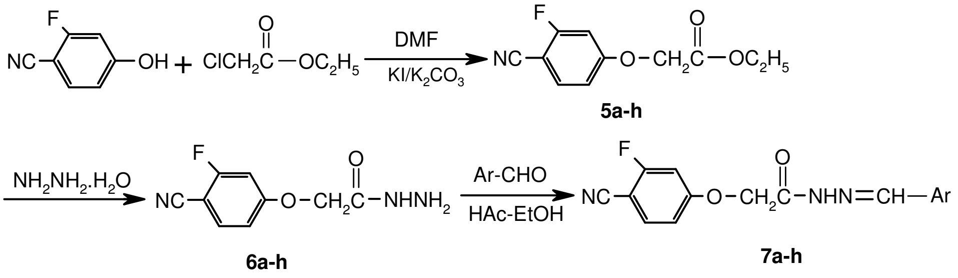
a, R = phenyl; **b**, R = *p*-chlorophenyl; **c**, R = *p*-methylphenyl;
d, R = *p*-methoxyphenyl; **e**, R = *p*-nitrophenyl; **f**, R = *o*-methylphenyl;
g, R = *o*-chlorophenyl; **h**, R = *o*-nitrophenyl; **i**, R = 2,4-dichlorophenyl;
j, R = *o*-methoxyphenyl.

Scheme-I: Synthesis of substituted phenoxyacetic acid esters of 2-fluoro-4-hydroxybenzonitrile

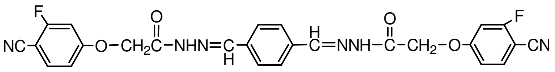


a, R = *p*-methoxyphenyl; **b**, R = *o*-methylphenyl; **c**, R = *m*-methylphenyl;
d, R = *p*-methoxyphenyl; **e**, R = phenyl; **f**, R = *o*-methoxylphenyl;
g, R = *o*-ethoxyphenyl; **h**, R = *p*-ethoxyphenyl; **i**, R = 2-pyridyl;
j, R = 2-naphthyl; **k**, R = *p*-nitrophenyl; **l**, R = *o*-nitrophenyl.

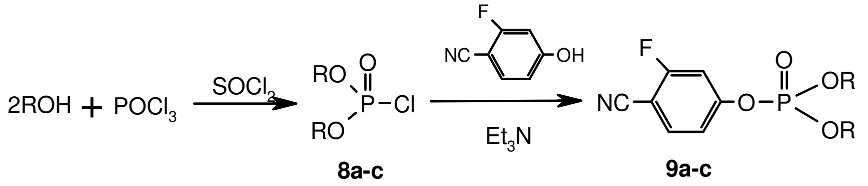
Scheme-II: Synthesis of 2-(4-cyano-3-fluorophenyl)-N-substituted phenlyactamides



a, R = *o*-hydroxyphenyl; **b**, R = 2-furfuryl; c, R = 2,4-dichlorophenyl;
d, R = phenyl; **e**, R = *p*-nitrophenyl; **f**, R = *p*-hydroxyphenyl;
g, R = p-methoxyphenyl; 7h,



Scheme-III: Synthesis of N'-(substitutedbenzylidene)-2-(4-cyano-3-fluorophenoxy)-acetohydrazides



a, R = Me; **b**, R = Et; **c**, R = Pr.

Scheme-IV: Synthesis of 4-cyano-3-fluoro-phenyl dialkoxyl phosphates

Differential scanning calorimeter (DSC) spectra of compound **3d** is shown in Fig. 1. The 3-fluoro-4-cyanophenol ester of 2'-(4-methyloxy)phenyloxy acetic acid, exhibits three endotherm peaks. The first peak at 72.7 ºC stands for the transformation from crystal to liquid crystal and the second peak at 79.9 ºC is due to the transformation from liquid crystal to normal liquid. At 286.1 ºC, the compound decomposes. From Fig. 1, the conclusion can be drawn that the compound **3d** exhibits the properties of liquid-crystal compounds.

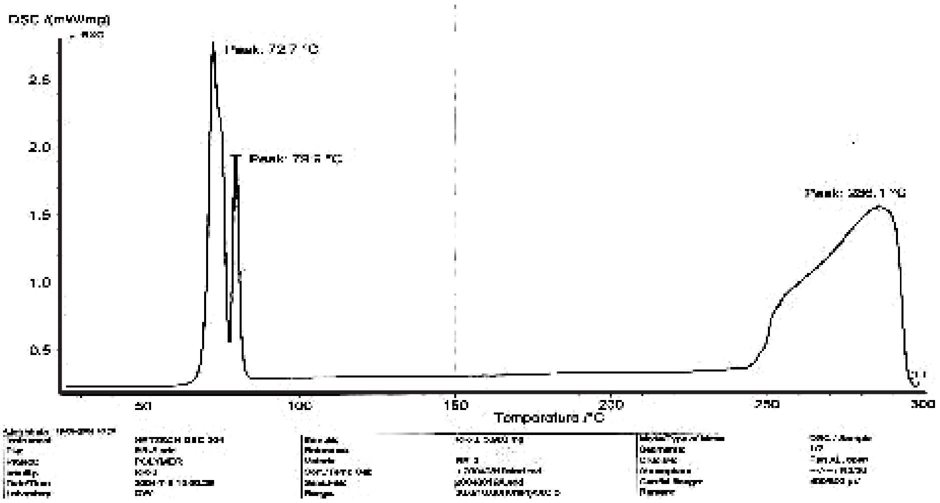


Fig. 1. DSC spectra of compound **3d**

Conclusion

Four series of novel compounds with 3-fluoro-4-cyanophenoxy group by using 2-fluoro-4-hydroxyphenyl as intermediate were synthesized. One of these compounds was found to exhibit potential liquid-crystalline properties.

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REFERENCES

1. R.D. Schnebeck, E. Freisinger and B. Lippert, *Angew. Chem.*, **111**, 235 (1999).
2. P.N.W. Baxter, J.-M. Lehn, G. Baum and D. Ferske, *Chem. Eur. J.*, **5**, 102 (1999).
3. S.-T. Wu, C.-S. Hsu and Y.-N. Chen, *Appl. Phys. Lett.*, **61**, 2275 (1992).
4. D.A. Mcmorran and P.J. Steel, *Angew. Chem. Int. Ed.*, **37**, 3295 (1998).
5. M. Ozaki, K. Yoshino, T. Sakurai and N. Mikami, *J. Chem. Phys.*, **86**, 3648 (1987).
6. S.J. Sung, K.Y. Cho and J.K. Park, *Mater. Sci. Eng. C*, **24**, 181 (2004).
7. P.N.W. Baxter, J.-M. Lehn, B.O. Kneisel, G. Baum and D. Ferske, *Chem. Eur. J.*, **5**, 113 (1999).
8. D.A. Mcmorran and P.J. Steel, *Angew. Chem.*, **110**, 3495 (1998).
9. T.B. Patrik and S. Nadji, *J. Fluorine Chem.*, **49**, 147 (1990).
10. R. Buchecker and A. Villiger, *Eur. Pat. Appl. EP.*, 789,067 (1997).
11. A. Fujita, N. Tamura, H. Takeuchi and F. Takeshita, *PCT. Int. Appl. WO.* 0031,019. (2000).
12. M.A. Osman, *Helv. Chim. Acta*, **65**, 2450 (1982).
13. S.M. Kelly, *J. Chem. Soc., Chem. Commun.*, 366 (1983).
14. S.M. Kelly, *Helv. Chim. Acta*, **67**, 1572 (1984).

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