Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Influence of chloro substituent on mesomorphism of unsymmetrical achiral four-ring bent-core compounds: synthesis and characterization

Rahul Kanti Nath, Rahul Deb, Nirmalangshu Chakraborty, Golam Mohiuddin, Doddamane S. Shankar Rao[#] and Nandiraju V S Rao*

Chemistry Department, Assam University, Silchar-788011, India

[#]Centre for Soft Matter Research, Jalahalli, Bangalore 560013, India

*Corresponding author, Tel:91-3842270943, FAX: 91-3842-270802, E-mail: nandirajuv@gmail.com

Supporting Information

Synthesis

4′-nitrophenyl 2-chloro-5-nitrobenzoate:

2-chloro-5-nitrobenzoic acid (3g; 15mmol) was dissolved in dichloromethane in a two neck round bottomed flask with a teflon coated magnetic stirrer and the reaction flask was flushed with N_2, sealed with a rubber septum and cooled in an ice bath. Thionylchloride (2.0 ml, 16.5 mmol) was added drop wise slowly to the cooled reaction mixture. The ice bath was removed and the reaction mixture was vigorously stirred and refluxed for 1h. The solvent and excess thionyl chloride was evaporated under reduced pressure and the resulting compound was dried under vacuum. To the resulting acyl chloride dissolved in dichloromethane (30ml), an aqueous solution of 4-nitro phenol (2.08g; 15mmol) and K_2CO_3 (4.14g; 30mmol) were added. The resulting solution was vigorously stirred for 24 h after adding a catalytic amount of tetra butyl ammonium bromide (TBAB). After the stirring was complete, the organic layer was separated, washed several times with the alkaline solution and water and then dried over sodium sulphate. Evaporation of the solvent gave the crude product which was then purified by column chromatography (silica gel, eluent petroleum ether/ ethyl acetate, 97:3 v/v) followed by recrystallization from ethanol to obtain the pure product as white solid. Yield = 4 g, (78 %), m. p. = 160^{o}C.

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 8.91 (d, 1H, J = 6 Hz, Ar**H**); 8.41 (d, 1H, J = 9.2 Hz, Ar**H**); 8.38 (d, 2H, J = 8.0 Hz, Ar**H**); 7.79 (d, 1H, J = 8.4 Hz, Ar**H**); 7.50 (d, 2H, J = 8.6 Hz, Ar**H**). Elemental analysis calculated for $C_{13}H_7ClN_2O_6$: C, 48.39; H, 2.19; N, 8.68 % Found: C, 48.09; H = 2.02; N = 8.09 %.

4′-nitrophenyl 4-chloro-3-nitrobenzoate:

4′-nitrophenyl 4-chloro-3-nitrobenzoate was synthesized following the same procedure described for the synthesis of 4′-nitrophenyl 2-chloro-5-nitrobenzoate. From the starting material 4-chloro-3-nitrobenzoic acid (3g; 15mmol), thionylchloride (2.0 ml, 16.5 mmol), 4-nitro phenol (2.08g; 15mmol) and K_2CO_3 (4.14g; 30mmol), 4.7 g crude product was

obtained, which was then purified by column chromatography (silica gel, eluent petroleum ether/ ethyl acetate, 97:3 v/v) followed by recrystallization from ethanol to obtain the pure product as white solid. Yield: 4.1 g, (80%).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 8.94 (s, 1H, Ar**H**); 8.38 (d, 2H, J = 8.0 Hz, Ar**H**); 8.21 (d, 1H, J = 8.8 Hz, Ar**H**); 7.78 (d, 1H, J = 8.4 Hz, Ar**H**); 7.48 (d, 2H, J = 8.4 Hz, Ar**H**). Elemental analysis calculated (theoretical) for $C_{13}H_7ClN_2O_6$: C = 48.39; H = 2.19; N= 8.68 % Found C = 48.17; H = 2.11; N = 8.03 %.

4′-Aminophenyl-5-amino-2-chlorobenzoate:

4′-nitrophenyl-2-chloro-5-nitrobenzoate (3.2 g, 10 mmol) was dissolved in ethyl acetate in a two neck round bottom flask to it 10% Pd-C (0.28g). The reaction mixture is stirred for 15hrs under balloon pressure filled with hydrogen gas. On completion of the reaction the crude product was collected by evaporating the solvent under reduced pressure. The crude product was then purified by column chromatography (silica gel 60-120 mesh, using dichloromethane/ethanol, (99.5:0.5::V/V) as eluent to give pure product. Yield: 2.2 g (77 %),

5.4. 4′-Aminophenyl-3-amino-4-chlorobenzoate:

The synthesis of 4′-Aminophenyl-3-amino-4-chlorobenzoate was carried out following the same procedure adopted for 4′-aminophenyl-5-amino-2-chlorobenzoate. Starting material 4′-nitrophenyl-4-chloro-3-nitrobenzoate (3.2 g; 10mmol) was reduced with H_2 and 10% Pd-C (0.28g) to give 4′-aminophenyl-3-amino-4-chlorobenzoate in quantitative yield. Yield: 2.3 g (78%).

4-n-decyloxysalicylaldehyde 6-10:

The synthesis of 4-n-alkoxy-2-hydroxy benzaldehyde, (**Scheme 1**) viz., mono alkylation was performed by using a modification of the literature procedure to improve the product yield. 2,4-dihydroxybenzaldehyde (10 g, 72.4 mmol), 1-bromodecane (17.7 ml, 75 mmol), $NaHCO_3$ (6.30 g, 75 mmol) and KI (catalytic amount) were mixed in dry acetone (250ml) and then the mixture was refluxed for 48 hours at 50 ^oC. The hot solution was then filtered to remove the insoluble solids. To neutralize the warm solution dilute HCl was added, which was then extracted twice with $CHCl_3$ (100ml). The combined extracts were concentrated to give a purple solid. The product was purified by column chromatography using silica gel (60-120 mesh) eluting with a mixture of chloroform and hexane (V/V; 1/1) followed by evaporation of solvent. The product a white solid was obtained. Yield = 13.5g, (67 %), m. p. 32 ^oC.

IR ν_{max} in cm^{-1}: 1668 ($\nu_{C=O}$, aldehyde), 3443 (ν_{O-H}, H-bonded);

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.39 (s, 1H, **-OH**); 9.71 (s, 1H, **-CH**=O); 7.44 (d, 1H, J = 8.9 Hz, Ar**H**); 6.51 (d, 1H, J = 8.8 Hz, Ar**H**); 6.41 (d, 1H, J = 8.7 Hz, Ar**H**); 4.05 (t, 2H, J = 6.3 Hz, -O-**CH_2**-); 1.66 (q, 2H, J = 6.6 Hz, - CH_2-**CH_2**-); 1.41-1.25 (m, 14H, -**$(CH_2)_7$**-); 0.86 (t, 3H, J = 6.6 Hz, -**CH_3**). Elemental analysis calculated for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41%; Found C, 73.39%; H, 9.40%.

The other required 4-n-alkyloxysalicyladehydes (**n = 12, 14** and **16**) were prepared following the above procedure with appropriate amount of 1-bromoalkanes. The required 1-bromoalkanes, respective yields of the aldehydes, spectroscopic and analytical data are presented below.

4-n-dodecyloxysalicylaldehyde, 6-12: 1-bromododecane (18.8 ml, 75 mmol). 16.9 g of white solid was obtained which was subjected to column chromatography to obtain **6-12** in pure form. Yield = 15.2g, (68 %), m. p. 41^{o}C.

IR ν_{max} in cm^{-1}: 1666 ($\nu_{C=O}$, aldehyde), 3442 (ν_{O-H}, H-bonded);

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.21 (s, 1H, **-OH**); 9.71 (s, 1H, **-CH**=O); 7.45 (d, 1H, J = 8.7 Hz, Ar**H**); 6.55 (d, 1H, J = 8.6 Hz, Ar**H**); 6.33 (d, 1H, J = 8.9 Hz, Ar**H**); 4.09 (t, 2H, J = 6.3 Hz, -O-**CH_2**-); 1.63 (q, 2H, J = 6.7 Hz, - OCH_2-**CH_2**-); 1.45-1.27 (m, 18H, -**$(CH_2)_9$**-); 0.86 (t, 3H, J = 6.6 Hz, -**CH_3**). Elemental analysis calculated for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87 %; Found C, 74.34; H, 9.79%

4-n-tetradecyloxysalicylaldehyde, 6-14:

1-bromotetradecane (20.7 ml, 75 mmol), 18 g of white solid was obtained which was subjected to column chromatography to obtain **6-14** in pure form. Yield = 17.2g, (71 %), m. p. 48^{o}C.

IR ν_{max} in cm^{-1}: 1663 ($\nu_{C=O}$, aldehyde), 3448 (ν_{O-H}, H-bonded);

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.30 (s, 1H, **-OH**); 9.71 (s, 1H, **-CH**=O); 7.55 (d, 1H, J = 8.7 Hz, Ar**H**); 6.50 (d, 1H, J = 8.7 Hz, Ar**H**); 6.33 (d, 1H, J = 8.9 Hz, Ar**H**); 4.11 (t, 2H, J = 6.8 Hz, -O-**CH_2**-); 1.63 (q, 2H, J = 6.7 Hz, - OCH_2-**CH_2**-); 1.34-1.27 (m, 22H, -**$(CH_2)_{11}$**-); 0.88 (t, 3H, J = 6.8 Hz, -**CH_3**). Elemental analysis calculated for $C_{21}H_{34}O_3$: C, 75.41; H, 10.25 %; Found C, 75.14; H, 10.22%.

4-n-hexadecyloxysalicylaldehyde, 6-16:

1-bromohexadecane (22.8 ml, 75 mmol), 21 g of white solid was obtained which was subjected to column chromatography to obtain **6-16** in pure form. Yield = 20.2g, (77%), m. p. 50^{o}C.

IR ν_{max} in cm^{-1}: 1665 ($\nu_{C=O}$, aldehyde), 3440 (ν_{O-H}, H-bonded);

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.25 (s, 1H, -**OH**); 9.55 (s, 1H, -**CH**=O); 7.70 (d, 1H, J = 8.7 Hz, Ar**H**); 6.55 (d, 1H, J = 8.8 Hz, Ar**H**); 6.41 (d, 1H, J = 8.8 Hz, Ar**H**); 4.11 (t, 2H, J = 6.8 Hz, -O-**CH_2**-); 1.58 (q, 2H, J = 6.7 Hz, - OCH_2-**CH_2**-); 1.36-1.28 (m, 26H, -**$(CH_2)_{13}$**-); 0.86 (t, 3H, J = 6.8 Hz, -**CH_3**). Elemental analysis calculated for $C_{23}H_{38}O_3$: C, 76.20; H, 10.56 %; Found C, 76.08; H = 10.53%.

4-(N-4′-n-tetradecyloxysalicylidene)aminophenyl [2-chloro-5-(N-4′-n-tetradecyloxy-salicylidene) aminobenzoate]: (14R-2Cl)

An ethanolic solution of 4-aminophenyl 5-amino-2-chlorobenzoate, **4a**, (0.65 g, 2.5 mmol) was added drop wise to an ethanolic solution (20 ml) of 4-n-tetradecyloxysalicylaldehyde (1.67 g, 5 mmol). The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the yellow colored Schiff's base 4-(N-4′-n-tetradecyloxysalicylidene)aminophenyl [2-chloro-5-(N-4′-n-tetradecyloxysalicylidene) aminobenzoate], (**14R-2Cl**). The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure compound. Yield = 1.3 g, (60%).

IR ν_{max} in cm^{-1}: 1622 ($\nu_{CH=N}$, imine); 1725 ($\nu_{C=O}$, ester), 3430(ν_{O-H}, H-bonded); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 13.62 & 13.46 (s, 2H, -**OH**); 8.62 & 8.54 (s, 2H, -**CH**=N-); 8.01 (d, 1H, J = 8.0Hz, Ar**H**); 7.54 (t, 2H, J = 7.6 Hz, Ar**H**); 7.34-7.32 (m, 4H, Ar**H**); 7.29 (d, 2H, J = 8.8 Hz, Ar**H**); 6.50 (m, 4H, Ar**H**); 4.00 (t, 4H, J = 6.0Hz, -O-**CH_2**-); 1.81 (q, 4H, J = 6.2Hz, - OCH_2-**CH_2**-); 1.44 (m, 4H, - CH_2-**CH_2**-); 1.46-1.26 (m, 40H, -**$(CH_2)_{10}$**-); 0.88 (t, 6H, J = 6.4 Hz, -**CH_3**). Elemental analysis calculated (theoretical) for $C_{55}H_{75}ClN_2O_6$: C, 73.76, H, 8.44, N, 3.13 %; Found C, 73.51, H, 8.36, N, 3.01 %.

4-(N-4′-n-decyloxysalicylidene)aminophenyl [4-chloro-3-(N-4′-n-decyloxysalicylidene)-aminobenzoate]: (10R-4Cl)

An ethanolic solution of 4-aminophenyl 3-amino-4-chlorobenzoate, **4b**, (0.65 g, 2.5 mmol) was added drop wise to an ethanolic solution (20 ml) of 4-n-decyloxysalicylaldehyde (1.39 g, 5 mmol). The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hours to yield the Schiff's base 4-(N-4′-n-decyloxysalicylidene)aminophenyl [4-chloro-3-(N-4′-n-decyloxysalicylidene) aminobenzoate], (**10R-4Cl**). The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure compound. Yield = 1.1 g, (60%).

IR ν_{max} in cm^{-1}: 1625 ($\nu_{CH=N}$, imine); 1733 ($\nu_{C=O}$, ester); 3437 (ν_{O-H}, H-bonded); ^{1}H NMR (400MHz, $CDCl_3$), δ(ppm): 13.54 (s, -**OH**, 1H), 13.41 (s, -**OH**, 1H); 8.55(s, **HC**=N, 1H), 8.45(s, **HC**=N, 1H), 7.98 (d, Ar-**H**, 2H), 7.47(d, Ar-**H**, 1H), 7.31(d, Ar-**H**, 2H), 7.17 (s, Ar-

H, 4H), 6.45 (d, Ar-**H**, 4H), 3.93 (t, -O**CH$_2$**-, 4H), 1.73 (m, OCH$_2$-**CH$_2$**-, 4H), 1.39-1.27 (m, -(**CH$_2$**)$_7$-, 28H), 0.82 (t, -**CH$_3$**-, 6H),; Elemental analysis calculated (theoretical) for $C_{47}H_{59}ClN_2O_6$: C, 72.05, H, 7.59 %; Found C, 71.95, H, 7.53 %.

The other homologues were also synthesized following the above procedure. The IR, NMR and CHN data of other compounds of the homologous series are presented below.

4-(N-4$^/$-n-dodecyloxysalicylidene)aminophenyl [4-chloro-3-(N-4$^/$-n-dodecyloxy-salicylidene) aminobenzoate]: (12R-4Cl)

IR ν_{max} in cm^{-1}: 1621 ($\nu_{CH=N}$, imine); 1739 ($\nu_{C=O}$, ester); 3430 (ν_{O-H}, H-bonded); ^{1}H NMR (400MHz, $CDCl_3$), δ(ppm): 13.54(s, -**OH**, 1H), 13.39(s, -**OH**, 1H); 8.54(s, **HC**=N, 1H), 8.47(s, **HC**=N, 1H), 8.01(d, Ar-**H**, 2H), 7.47(d, Ar-**H**, 1H), 7.25(d, Ar-**H**, 2H), 7.19(s, Ar-**H**, 4H), 6.44(d, Ar-**H**, 4H), 3.93(t, -O**CH$_2$**-, 4H), 1.73(m, OCH$_2$-**CH$_2$**-, 4H), 1.39-1.26 (m, -(**CH$_2$**)$_9$-, 36H), 0.82(t, -**CH$_3$**-, 6H),; Yield = 1.30 g, (62%). Elemental analysis calculated (theoretical) for $C_{51}H_{67}ClN_2O_6$: C, 72.96, H, 8.04%; Found C, 72.79, H, 8.01 %.

4-(N-4$^/$-n-tetradecyloxysalicylidene)aminophenyl [4-chloro-3-(N-4$^/$-n-tetradecyloxy salicylidene) aminobenzoate]: (14R-4Cl)

IR ν_{max} in cm^{-1}: 1624 ($\nu_{CH=N}$, imine); 1739 ($\nu_{C=O}$, ester); 3439 (ν_{O-H}, H-bonded); ^{1}H NMR (400MHz, $CDCl_3$), δ(ppm): 13.54 and 13.39(s, -**OH**, 2H); 8.55 and 8.47(s, **HC**=N, 2H), 8.01 (d, Ar-**H**, 2H), 7.47 (d, Ar-**H**, 1H), 7.25 (d, Ar-**H**, 2H), 7.19 (s, Ar-**H**, 4H), 6.44 (d, Ar-**H**, 4H), 3.93 (t, -O**CH$_2$**-, 4H), 1.73 (m, OCH$_2$-**CH$_2$**-, 4H), 1.39-1.25 (m, -(**CH$_2$**)$_{11}$-, 44H), 0.81(t, -**CH$_3$**-, 6H),; Yield = 1.45 g, (65%). Elemental analysis calculated (theoretical) for $C_{55}H_{75}ClN_2O_6$: C, 73.76, H, 8.44 %; Found C = 73.59, H = 8.36%.

4-(N-4$^/$-n-hexadecyloxysalicylidene)aminophenyl [4-chloro-3-(N-4$^/$-n-hexadecyloxy salicylidene) aminobenzoate]: (16R-4Cl)

IR ν_{max} in cm^{-1}: 1625 ($\nu_{CH=N}$, imine); 1728 ($\nu_{C=O}$, ester); 3437 (ν_{O-H}, H-bonded); ^{1}H NMR (400MHz, $CDCl_3$), δ(ppm): 13.54(s, -**OH**, 1H), 13.49 (s, -**OH**, 1H); 8.55(s, **HC**=N, 1H), 8.37(s, **HC**=N, 1H), 8.11(d, Ar-**H**, 2H), 7.49 (d, Ar-**H**, 1H), 7.24 (d, Ar-**H**, 2H), 7.19 (s, Ar-**H**, 4H), 6.49 (d, Ar-**H**, 4H), 3.99 (t, -O**CH$_2$**-, 4H), 1.73 (m, OCH$_2$-**CH$_2$**-, 4H), 1.38-1.26 (m, -(**CH$_2$**)$_{13}$-, 52H), 0.88(t, -**CH$_3$**-, 6H),; Yield = 1.68 g, (71%). Elemental analysis calculated (theoretical) for $C_{59}H_{83}ClN_2O_6$: C, 74.46, H = 8.79 %; Found C, 74.29, H, 8.71 %.