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Efficient and practical method for the synthesis of hydrophobic azines as liquid crystalline materials

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ABSTRACT

A series of hydrophobic symmetrical azines: 1,2-bis[4-(*n*-alkoxy) benzylidene]hydrazine (where, *n*-alkoxy: $O(CH_2)_nH$, $n = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 16,$ or 18) have been prepared following an efficient and practical method. These compounds have been synthesized via the condensation reaction of hydrazine hydrate and appropriately 4-(*n*-alkoxy) benzaldehydes in acidic medium under ambient conditions. The prepared organic compounds have been characterized and their structures were elucidated depending upon micro-elemental analysis and spectral data (IR, UV-Vis, ^{1}HNMR, ^{13}C{^{1}H}NMR, 2D ^{1}H-^{1}H-cozy, 2D ^{1}H-^{13}C-HSQC, and mass spectra). Liquid crystalline behavior of the prepared compounds was studied using polarized light optical microscopy and differential scanning calorimetry techniques. This study revealed that all the compounds displayed enantiotropic liquid crystal properties, exhibiting smectic and nematic mesophases.

KEYWORDS

Hydrophobic symmetrical azines; enantiotropic liquid crystal; mesogenic compounds

Introduction

Azines, N-N linked di-amines [1, 2], are extremely useful compounds, and recently they have received attention because of their utility in a number of interesting reactions and applications, specifically their biological properties [3, 4], the design of metal complexes [5, 6], potential application in bond formation, nonlinear optical materials [7], and their uses in the purification and characterization of carbonyl compounds [8]. Furthermore, azines are found to be intermediates for the preparation of several pharmacological compounds [9].

Liquid crystal (LC) or polymorphism is an intermediate state of matter – in-between liquid and crystals. It must possess some typical properties of a liquid (e.g., fluidity, inability to support shear formation, and coalescence of droplets) as well as some crystalline properties (anisotropy in optical, electrical, and magnetic properties, periodic arrangement of molecules in one spatial direction, etc.). Polymorphism can be classified in different ways. Thermotropic polymorphism (representing the most common polymorphisms) means that different polymorphs are obtained by the action of temperature (i.e., by heating or cooling). In other cases, different crystal phases can be obtained by the action of solvents [10–12]. If the transition from one form to another is reversible, the polymorphism is called enantiotropic;

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if it is irreversible, the polymorphism is classified as monotropic. Thermotropic nematic LCs represent the most technologically important LC compounds. It's usually composed of rigid rod-like or discal molecules [13], and widely used as operating fluid in LC displays (LCDs).

In 1959, a series of azine-type LCs were synthesized [14], which had high clearing points. Since then, many experimental and theoretical studies [15–21] were made on the synthesis of azine-type LCs using different synthetic approaches. In this work, we report the synthesis, characterization, and mesomorphic properties of a series of hydrophobic azine derivatives: 1,2-bis[4-(*n*-alkoxy)benzylidene]hydrazine (where *n*-alkoxy: $O(CH_2)_nH$, $n = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 16$, or 18) compounds with a very simple, efficient, and convenient method.

Experimental

Physical measurements

Electronic spectra were measured in the region (200–800 nm) for (5×10^{-5} M) in dichloromethane at (RT) by using a Varin Cary 100 Conc. spectrophotometer. Elemental analyses (C, H, and N) were carried out on a EuroEA 3000 Elemental Analyzer. Infrared (IR) spectra were preformed in the region (4000–600 cm^{-1}) using an 8400S-FTIR Shimadzu spectrophotometer. ^{1}HNMR, $^{13}C\{^1H\}$NMR, 2D ^1H-^1H-cozy, and 2D ^1H-^{13}C-HSQC spectra were recorded in $CDCl_3$ using a Brucker 400-MHz spectrometer. Mass spectra were obtained using a GC-DIMS QP 2010 Ultra spectrometer and Orbitrap LTQ XL-Thermo Fisher scientific mass spectrometer. Differential scanning calorimetry (DSC) thermograms were carried out in a nitrogen atmosphere at a heating and cooling rate of 5.0°C/min using Linseis STA PT-1000 equipment, which was pre-calibrated. The equipment was provided with an autocool system. Liquid crystalline mesophases of the compounds were obtained by PW-BK5000R microscope equipped with HS-400 (KER3100-08S) heating stage.

Materials

All the reagents were available commercially (Germany) and were used without further purification: 4-hydroxybenzaldehyde (98%, Fluka Co.), 1-iodomethane (98%, Aldrich Co.), 1-bromoethane (99%, Aldrich Co.), 1-bromopropane (99%, Aldrich Co.), 1-bromobutane (98%, CDH Co.), 1-bromopentane (99%, Aldrich Co.), 1-bromohexane (98%, Aldrich Co.), 1-bromoheptane (99%, Aldrich Co.), 1-bromooctane (99%, Aldrich Co.), 1-bromononane (99%, Aldrich Co.), 1-bromodecane (98%, Aldrich Co.), 1-bromododecane (97%, Aldrich Co.), 1-bromohexadecane (97%, Aldrich Co.), 1-bromooctadecane (97%, Aldrich Co.), potassium hydroxide (85%, SDFCL Co.), sodium sulfate anhydrous (99%, Aldrich Co.), hydrazine hydrate (80%, Sigma-Aldrich Co.), and acetic acid (100%, Aldrich Co.). Solvents used in the synthesis were distilled from appropriate drying agents immediately prior to use.

Preparation of 4-(n-alkoxy)benzaldehyde (general procedure) (A_1–A_{13})

These compounds were prepared according to the Williamson synthesis of ethers by a known method [22–24]. 4-hydroxybenzaldehyde (8.72 g, 71.5 mmol) was added to a solution of potassium hydroxide (4 g) in ethanol (60 mL). The mixture was treated with n-alkyl halide (71.5 mmol) (methyl iodide was used in the preparation of A_1, while *n*-alkylbromide used in the preparation of A_1–A_{13}) and heated under reflux. The reaction was monitored by thin-layer chromatography (TLC) using chloroform as eluent, and the optimal time of each reaction was

Table 1. Reaction conditions and quantities for the preparation of 4-(*n*-alkoxy)benzaldehyde compounds.

Compound	Alkylhalide weight (g)	Reaction time (h)	R_f	Yield (%)
A_1	10.40*	96	0.562	65
A_2	7.80	96	0.580	70
A_3	8.80	96	0.590	77
A_4	9.80	72	0.610	80
A_5	10.80	72	0.633	77
A_6	11.80	96	0.650	65
A_7	12.80	96	0.680	70
A_8	13.80	96	0.690	77
A_9	14.80	72	0.695	75
A_{10}	15.80	72	0.700	70
A_{11}	17.80	72	0.715	73
A_{12}	21.81	48	0.735	89
A_{13}	23.81	48	0.780	79

*Methyl iodide was used.

determined. The ethanol was evaporated and the residue was dissolved in diethyl ether. The ethereal was washed with an aqueous solution of potassium hydroxide (10%) followed by water until a pH = 7 was obtained. The organic layer was dried over sodium sulfate anhydrous and evaporated to give the desired product. The details of the reaction conditions for the preparation of each compound are described in Table 1.

4-methoxybenzaldehyde (A_1)

Yield = 65%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2970 (w, υ_{as}(C–H) of CH_3 group), 2870 (w, υ_s(C–H) of CH_3 group), 2922 (w, υ_{as}(C–H) of CH_2 group), 2841 (w, υ_s(C–H) of CH_2 group), 3070 (w, υ(C–H) aromatic), 2740 (w-m, υ(C–H) aldehydic), 1680 (s, υ(C=O)), 1599, 1575, and 1510 (s, m, m, υ(C=C) aromatic), 1255 (s, υ(C–O)), 1460 (m, δ (C–H)).

4-ethoxybenzaldehyde (A_2)

Yield = 70%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2981 (w, υ_{as}(C–H) of CH_3 group), 2869 (w, υ_s(C–H) of CH_3 group), 2933 (w-m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group), 3072 (w, υ(C–H) aromatic), 2729 (w-m, υ(C–H) aldehydic), 1681 (s, υ(C=O)), 1596, 1575 and 1508 (s, m, m, υ(C=C) aromatic), 1251 (s, υ(C–O)), 1475 (m, δ(C–H)).

4-propyloxybenzaldehyde (A_3)

Yield = 77%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2966 (w, υ_{as}(C–H) of CH_3 group), 2877 (w, υ_s(C–H) of CH_3 group), 2935 (m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group), 3076 (w, υ(C–H) aromatic), 2731 (w-m, υ(C–H) aldehydic), 1687 (s, υ(C=O)), 1597, 1575, and 1508 (s, m, m, υ(C=C) aromatic), 1253 (s, υ(C–O)), 1471 (m, δ(C–H)).

4-butyloxybenzaldehyde (A_4)

Yield = 80%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2976 (w, υ_{as}(C–H) of CH_3 group), 2938 (w-m, υ_s(C–H) of CH_3 group), 2959 (m, υ_{as}(C–H) of CH_2 group), 2872 (w,

υ_s(C–H) of CH_2 group), 3076 (w, υ(C–H) aromatic), 2731 (w-m, υ(C–H) aldehydic), 1688 (s, υ(C=O)), 1599, 1575, and 1508 (s, m, m, υ(C=C) aromatic), 1252 (s, υ(C–O)), 1468 (m, δ(C–H)).

4-pentoxybenzaldehyde (A_5)

Yield = 77%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2953 (w, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2933 (m, υ_{as}(C–H) of CH_2 group), 2862 (m, υ_s(C–H) of CH_2 group), 3070 (w, υ(C–H) aromatic), 2740 (w-m, υ(C–H) aldehydic), 1687 (s, υ(C=O)), 1599, 1577, and 1508 (s, m, m, υ(C=C) aromatic), 1252 (s, υ(C–O)), 1467 (m, δ(C–H)).

4-hexyloxybenzaldehyde (A_6)

Yield = 65%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2953 (w-m, υ_{as}(C–H) of CH_3 group), 2870 (w, υ_s(C–H) of CH_3 group), 2930 (m, υ_{as}(C–H) of CH_2 group), 2859 (m, υ_s(C–H) of CH_2 group), 3073 (w, υ(C–H) aromatic), 2733 (w, υ(C–H) aldehydic), 1692 (s, υ(C=O)), 1599, 1576, and 1508 (s, m, m, υ(C=C) aromatic), 1252 (s, υ(C–O)), 1470 (m, δ(C–H)).

4-heptyloxybenzaldehyde (A_7)

Yield = 70%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2956 (w-m, υ_{as}(C–H) of CH_3 group), 2867 (w, υ_s(C–H) of CH_3 group), 2928 (m, υ_{as}(C–H) of CH_2 group), 2857 (m, υ_s(C–H) of CH_2 group), 3075 (w, υ(C–H) aromatic), 2733 (w, υ(C–H) aldehydic), 1692 (s, υ(C=O)), 1599, 1576, and 1508 (s, m, m, υ(C=C) aromatic), 1254 (s, υ(C–O)), 1468 (m, δ(C–H)).

4-octyloxybenzaldehyde (A_8)

Yield = 77%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2953 (w-m, υ_{as}(C–H) of CH_3 group), 2869 (w, υ_s(C–H) of CH_3 group), 2926 (m, υ_{as}(C–H) of CH_2 group), 2855 (m, υ_s(C–H) of CH_2 group), 3073 (w, υ(C–H) aromatic), 2733 (w, υ(C–H) aldehydic), 1692 (s, υ(C=O)), 1599, 1576, and 1508 (s, m, m, υ(C=C) aromatic), 1254 (s, υ(C–O)), 1468 (m, δ(C–H)).

4-nonyloxybenzaldehyde (A_9)

Yield = 75%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2952 (w, υ_{as}(C–H) of CH_3 group), 2870 (w, υ_s(C–H) of CH_3 group), 2926 (s, υ_{as}(C–H) of CH_2 group), 2852 (m, υ_s(C–H) of CH_2 group), 3074 (w, υ(C–H) aromatic), 2733 (w-m, υ(C–H) aldehydic), 1693 (s, υ(C=O)), 1599, 1575, and 1508 (s, m, m, υ(C=C) aromatic), 1252 (s, υ(C–O)), 1467 (m, δ(C–H)).

4-decyloxybenzaldehyde (A_{10})

Yield = 70%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2956 (w, υ_{as}(C–H) of CH_3 group), 2869 (w, υ_s(C–H) of CH_3 group), 2923 (s, υ_{as}(C–H) of CH_2 group), 2852 (m, υ_s(C–H) of CH_2 group), 3075 (w, υ(C–H) aromatic), 2733(w, υ(C–H) aldehydic), 1694 (s, υ(C=O)), 1599, 1576, and 1507 (s, m, m, υ(C=C) aromatic), 1251 (s, υ(C–O)), 1463 (m, δ(C–H)).

4-dodecyloxybenzaldehyde (A_{11})

Yield = 73%. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2953 (w, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2927 (s, υ_{as}(C–H) of CH_2 group), 2850 (m, υ_s(C–H) of CH_2 group), 3060 (w, υ(C–H) aromatic), 2732 (w, υ(C–H) aldehydic), 1693 (s, υ(C=O)), 1599, 1576, and 1507 (s, m, m, υ(C=C) aromatic), 1252 (s, υ(C–O)), 1463 (m, δ(C–H)).

4-hexadecyloxybenzaldehyde (A_{12})

Yield = 89%, m.p. = 33–39°C. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2948 (w, υ_{as}(C–H) of CH_3 group), 2868 (w, υ_s(C–H) of CH_3 group), 2916 (s, υ_{as}(C–H) of CH_2 group), 2849 (s, υ_s(C–H) of CH_2 group), 3076 (w, υ(C–H) aromatic), 2733 (w, υ(C–H) aldehydic), 1688 (s, υ(C=O)), 1601, 1576, and 1507 (s, m, m, υ(C=C) aromatic), 1250 (s, υ(C–O)), 1471 (m, δ(C–H)).

4-octadecyloxybenzaldehyde (A_{13})

Yield = 79%, m.p. = 36–41°C. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2960 (w, υ_{as}(C–H) of CH_3 group), 2864 (w, υ_s(C–H) of CH_3 group), 2914 (s, υ_{as}(C–H) of CH_2 group), 2850 (s, υ_s(C–H) of CH_2 group), 3064 (w, υ(C–H) aromatic), 2732 (w, υ(C–H) aldehydic), 1692 (s, υ(C=O)), 1601, 1576, and 1507 (s, m, m, υ(C=C) aromatic),1254 (s, υ(C–O)), 1470 (m, δ(C–H)).

Synthesis of 1,2-bis[4-(n-alkoxy)benzylidene]hydrazine (general procedure) (B_1–B_{13})

Hydrazine hydrate (0.125 g, 2.5 mmol) was added to a solution of appropriate 4-(*n*-alkoxy)benzaldehyde (5 mmol) in ethanol (30 mL). Glacial acetic acid (0.1 mL) was then added to the mixture. The reaction mixture was stirred for 1 h, during which a precipitate was formed. This was removed by filtration, washed with cold water, recrystallized from a proper solvent, and dried to give a pure compound. The purity of the compound was checked by TLC using n-hexane: ethyl acetate (15:1) as eluents. The details of reaction conditions for the preparation of each compound are summarized in Table 2.

1,2-bis(4-methoxybenzylidene)hydrazine (B_1)

Yield = 62%. Elemental analysis (%) calc.: C 71.6, N 10.4, H 6.0; found: C 71.4, N 10.3, H 5.9. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2987 (w, υ_{as}(C–H) of CH_3 group), 2878 (w, υ_s(C–H) of CH_3 group), 2922 (w, υ_{as}(C–H) of CH_2 group), 2837 (m, υ_s(C–H) of CH_2 group), 3022 (w, υ(C–H) aromatic), 1620 (w, υ(C=N)), 1600, 1575, and 1508 (s, m, m, υ(C=C) aromatic), 1249 (s, υ(C–O)), 1470 (m, δ(C–H)). UV-Vis (λ/nm): 230 (n–σ^*), 326 (π–π^*).^{1}HNMR (δ/ppm): 3.73 (6H, t, OCH_3), 6.97 (4H, d, $J = 6.2$ Hz, aromatic protons), 7.80 (4H, d, $J = 6.2$ Hz, aromatic protons), 8.63 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 56.11 (OCH_3), 114.20 (aromatic C–H), 126.87 (aromatic C), 130.02 (aromatic C–H), 160.70 (CH=N), 162.30 (aromatic C–O). Mass spect. (m/z): 268.

Table 2. Reaction conditions and quantities for the preparation of 1,2-bis[4-(*n*-alkoxy)benzylidene] hydrazine compounds.

Compound	4-(*n*-alkoxy)benzaldehyde weight (g)	Recrystalizationnn solvent	R_f	Yield (%)
B_1	0.68	Ethanol	0.266	62
B_2	0.75	Ethanol	0.292	64
B_3	0.82	Ethanol	0.307	60
B_4	0.89	Ethanol	0.316	61
B_5	096	Ethanol	0.335	66
B_6	1.03	Ethanol	0.366	62
B_7	1.10	Ethanol	0.400	64
B_8	1.17	Ethanol	0.413	60
B_9	1.24	Dichloromethane	0.435	62
B_{10}	1.31	Dichloromethane	0.453	61
B_{11}	1.45	Dichloromethane	0.486	66
B_{12}	1.73	Chloroform	0.543	64
B_{13}	1.87	Chloroform	0.586	66

1,2-bis(4-ethoxybenzylidene)hydrazine (B_2)

Yield = 64%. Elemental analysis (%) calc.: C 73.0, N 9.5, H 6.8; found: C 72.8, N 9.4, H 6.7. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2981 (s, υ_{as}(C–H) of CH_3 group), 2896 (w-m, υ_s(C–H) of CH_3 group), 2929 (s, υ_{as}(C–H) of CH_2 group), 2852 (m, υ_s(C–H) of CH_2 group), 3030 (w, υ(C–H) aromatic), 1620 (w, υ(C=N)), 1600, 1577, and 1508 (s, m, m, υ(C=C) aromatic), 1247 (s, υ(C–O)), 1473 (m, δ(C–H)). UV-Vis (λ/nm): 230 (n–σ^*), 330 (π–π^*). ^{1}HNMR (δ/ppm): 1.45 (6H, t, CH_3), 4.11 (4H, q, J = 4.0, OCH_2), 6.96 (4H, d, J = 6.1 Hz, aromatic protons), 7.78 (4H, d, J = 6.1 Hz, aromatic protons), 8.61 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.65 (CH_3), 63.64 (OCH_2), 114.84 (aromatic C–H), 127.11 (aromatic C), 130.05 (aromatic C–H), 160.66 (CH=N), 161.44 (aromatic C–O). Mass spect. (m/z): 296.

1,2-bis(4-propyloxybenzylidene)hydrazine (B_3)

Yield = 60%. Elemental analysis (%) calc.: C 74.0, N 8.6, H 7.5; found: C 73.4, N 8.4, H 7.5. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2965 (w-m, υ_{as}(C–H) of CH_3 group), 2882 (w, υ_s(C–H) of CH_3 group), 2934 (w-m, υ_{as}(C–H) of CH_2 group), 2876 (w-m, υ_s(C–H) of CH_2 group), 3069 (w, υ(C–H) aromatic), 1622 (m, υ(C=N)), 1597, 1572, and 1505 (s, m, s, υ(C=C) aromatic), 1238 (s, υ(C–O)), 1460 (m, δ(C–H)). UV-Vis (λ/nm): 242 (n–σ^*), 331 (π–π^*). ^{1}HNMR (δ/ppm): 1.08 (6H, t, CH_3), 1.85 (4H, m, CH_2), 4.00 (4H, t, OCH_2), 6.97 (4H, d, J = 8.8 Hz, aromatic protons), 7.79 (4H, d, J = 9.1 Hz, aromatic protons), 8.63 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 10.52 (CH_3), 22.54 (CH_2), 69.64 (OCH_2), 114.75 (aromatic C–H), 126.80 (aromatic C), 130.12 (aromatic C–H), 161.11 (CH=N), 161.62 (aromatic C–O). Mass spect. (m/z): 324.

1,2-bis(4-butyloxybenzylidene)hydrazine (B_4)

Yield = 61%. Elemental analysis (%) calc.: C 75.0, N 8.0, H 8.0; found: C 74.9, N 7.9, H 8.0. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2958 (s, υ_{as}(C–H) of CH_3 group), 2875 (w-m, υ_s(C–H) of CH_3 group), 2931 (m, υ_{as}(C–H) of CH_2 group), 2855 (m, υ_s(C–H) of CH_2 group), 3025 (w, υ(C–H) aromatic), 1622 (w, υ(C=N)), 1599, 1567, and 1506 (s, m, m, υ(C=C) aromatic), 1247 (s, υ(C–O)), 1465 (m, δ(C–H)). UV-Vis (λ/nm): 241 (n–σ^*), 332 (π–π^*). ^{1}HNMR (δ/ppm): 0.97 (6H, t, CH_3), 1.41 (4H, m, CH_2), 1.85 (4H, m, CH_2), 4.01 (4H, t, OCH_2), 6.93 (4H, d, J = 9.0 Hz, aromatic protons), 7.75 (4H, d, J = 9.0 Hz, aromatic protons), 8.61 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.41 (CH_3), 21.40 (CH_2), 30.84 (CH_2)

68.94 (OCH_2), 114.30 (aromatic C–H), 127.20 (aromatic C), 130.33 (aromatic C–H), 161.10 (CH=N), 161.72 (aromatic C–O). Mass spect. (*m*/*z*): 352.

1,2-bis(4-pentyloxybenzylidene)hydrazine (B_5)

Yield = 66%. Elemental analysis (%) calc.: C 75.8, N 7.4, H 8.5; found: C 75.5, N 7.2, H 8.4. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2951 (w-m, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2934 (m, υ_{as}(C–H) of CH_2 group), 2854 (m, υ_s(C–H) of CH_2 group), 3066 (w, υ(C–H) aromatic), 1622 (m, υ(C=N)), 1599, 1568, and 1506 (m, s, s, υ(C=C) aromatic), 1248 (s, υ(C–O)), 1466 (m, δ(C-H)). UV-Vis (λ/nm): 241 (n–σ^*), 331 (π–π^*). ^{1}HNMR (δ/ppm): 0.97 (6H, t, CH_3), 1.27–1.55 (8H, m, CH_2), 1.84 (4H, m, CH_2), 4.02 (4H, t, OCH_2), 6.97 (4H, d, J = 9.1 Hz, aromatic protons), 7.80 (4H, d, J = 9.1 Hz, aromatic protons), 8.64 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.04 (CH_3), 22.48 (CH_2), 28.19 (CH_2), 28.90 (CH_2), 68.15 (OCH_2), 161.08 (CH=N), 114.76 (aromatic C–H), 126.79 (aromatic C), 130.13 (aromatic C–H), 161.08 (CH=N), 161.64 (aromatic C–O). Mass spect. (*m*/*z*): 380.

1,2-bis(4-hexyloxybenzylidene)hydrazine (B_6)

Yield = 62%. Elemental analysis (%) calc.: C 76.4, N 6.9, H 8.9; found: C 76.3, N 6.8, H 8.8. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2954 (w, υ_{as}(C–H) of CH_3 group), 2924 (m, υ_s(C–H) of CH_3 group), 2940 (w, υ_{as}(C–H) of CH_2 group), 2857 (m, υ_s(C–H) of CH_2 group), 3050 (w, υ(C–H) aromatic), 1618 (s, υ(C=N)), 1605, 1572, and 1508 (s, m, m, υ(C=C) aromatic), 1242 (s, υ(C–O)), 1466 (m, δ(C–H)). UV-Vis (λ/nm): 229 (n–σ^*), 329 (π–π^*). ^{1}HNMR (δ/ppm): 0.90 (6H, t, CH_3), 1.37–1.46 (12H, m, CH_2), 1.84 (4H, m, CH_2), 4.0 (4H, t, OCH_2), 6.94 (4H, d, J = 8.9 Hz, aromatic protons), 7.76 (4H, d, J = 8.8 Hz, aromatic protons), 8.60 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.16 (CH_3), 22.72 (CH_2), 25.82 (CH_2), 29.28 (CH_2), 31.70 (CH_2), 68.28 (OCH_2), 114.86 (aromatic C–H), 126.91 (aromatic C), 130.22 (aromatic C–H), 161.21 (CH=N), 161.74 (aromatic C–O). Mass spect. (*m*/*z*): 408.

1,2-bis(4-heptyloxybenzylidene)hydrazine (B_7)

Yield = 64%. Elemental analysis (%) calc.: C 77.0, N 6.4, H 9.2; found: C 77.1, N 6.3, H 9.1. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2953 (m, υ_{as}(C–H) of CH_3 group), 2874 (w-m, υ_s(C–H) of CH_3 group), 2922 (m, υ_{as}(C–H) of CH_2 group), 2857 (m, υ_s(C–H) of CH_2 group), 3055 (w, υ(C–H) aromatic), 1622 (s, υ(C=N)), 1602, 1574, and 1508 (s, m, m, υ(C=C) aromatic), 1246 (s, υ(C–O)), 1466 (m, δ(C-H)). UV-Vis (λ/nm): 229 (n–σ^*), 330 (π–π^*). ^{1}HNMR (δ/ppm): 0.96 (6H, t, CH_3), 1.29–1.49 (16H, m, CH_2), 1.83 (4H, m, CH_2), 4.0 (4H, t, OCH_2), 6.94 (4H, d, J = 8.9 Hz, aromatic protons), 7.81 (4H, d, J = 8.9 Hz, aromatic protons), 8.59 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.01 (CH_3), 23.10 (CH_2), 26.60 (CH_2), 30.0 (CH_2), 32.50 (CH_2), 69.11 (OCH_2), 114.30 (aromatic C–H), 127.21 (aromatic C), 130.02 (aromatic C–H), 161.10 (CH=N), 161.66 (aromatic C–O). Mass spect. (*m*/*z*): 436.

1,2-bis(4-octyloxybenzylidene)hydrazine (B_8)

Yield = 60%. Elemental analysis (%) calc.: C 77.5, N 6.0, H 9.5; found: C 77.4, N 5.9, H 9.4. Characteristic spectroscopic data: FTIR (U/cm^{-1}):2938 (w-m, υ_{as}(C–H) of CH_3 group), 2862 (w-m, υ_s(C–H) of CH_3 group), 2920 (m, υ_{as}(C–H) of CH_2 group), 2847 (m, υ_s(C–H) of CH_2 group), 3051 (w, υ(C–H) aromatic), 1616 (s, υ(C=N)), 1603, 1570, and 1508 (s, m, s, υ(C=C)

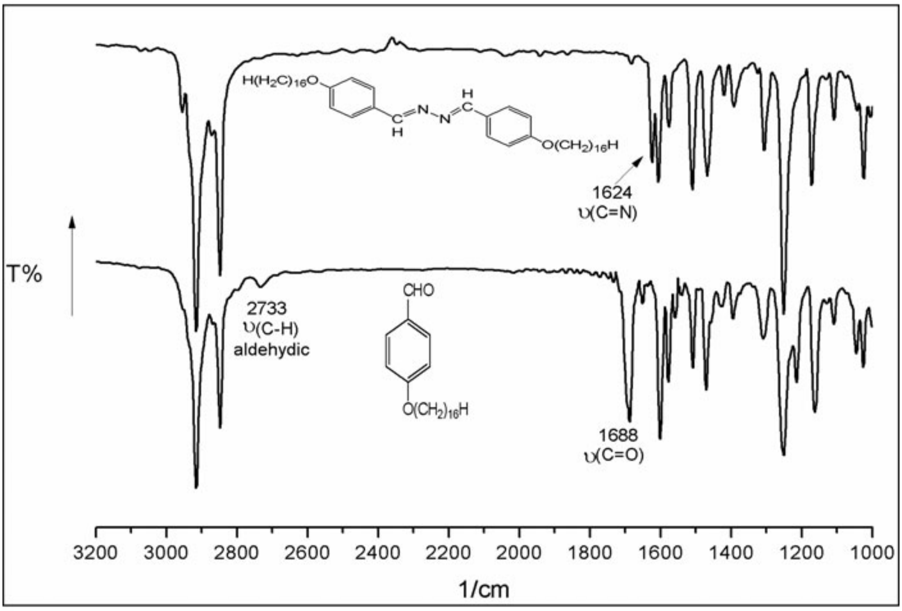


Figure 1. FTIR spectra of (A_{12}) and (B_{12}).

aromatic), 1246 (s, υ(C–O)), 1470 (m, δ(C–H)). UV-Vis (λ/nm): 229 (n–σ^*), 332 (π–π^*). ^{1}HNMR (δ/ppm): 0.90 (6H, t, CH_3), 1.28–1.45 (20H, m, CH_2), 1.84 (4H, m, CH_2), 4.0 (4H, t, OCH_2), 6.95 (4H, d, $J = 8.8$ Hz, aromatic protons), 7.80 (4H, d, $J = 8.8$ Hz, aromatic protons), 8.61 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.24 (CH_3), 22.79 (CH_2), 26.15 (CH_2), 29.32 (CH_2), 29.48 (CH_2), 31.95 (CH_2), 68.29 (OCH_2), 114.87 (aromatic C–H), 126.91 (aromatic C), 130.22 (aromatic C–H), 161.21 (CH=N), 161.74 (aromatic C–O). Mass spect. (*m*/*z*): 464.

1,2-bis(4-nonyloxybenzylidene)hydrazine (B_9)

Yield = 64%. Elemental analysis (%) calc.: C 78.0, N 5.7, H 9.8; found: C 77.8, N 5.6, H 9.7. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2953 (m, υ_{as}(C–H) of CH_3 group), 2860 (w, υ_s(C–H) of CH_3 group), 2922 (s, υ_{as}(C–H) of CH_2 group), 2848 (m, υ_s(C–H) of CH_2 group), 3070 (w, υ(C–H) aromatic), 1622 (s, υ(C=N)), 1600, 1574, and 1508 (s, m, s, υ(C=C) aromatic), 1250 (s, υ(C–O)), 1470 (m, δ(C–H)). UV-Vis (λ/nm): 229 (n–σ^*), 332 (π–π^*). ^{1}HNMR (δ/ppm): 0.91 (6H, t, CH_3), 1.31–1.49 (24H, m, CH_2), 1.83 (4H, m, CH_2), 4.03 (4H, t, OCH_2), 6.97 (4H, d, $J = 8.8$ Hz, aromatic protons), 7.79 (4H, d, $J = 8.8$ Hz, aromatic protons), 8.64 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.13 (CH_3), 22.69 (CH_2), 26.03 (CH_2), 29.28 (CH_2), 29.54 (CH_2), 31.89 (CH_2), 68.19 (OCH_2), 114.76 (aromatic C–H), 126.73 (aromatic C), 130.14 (aromatic C–H), 161.11 (CH=N), 161.67 (aromatic C–O). Mass spect. (m/z): 492.

1,2-bis(4-decyloxybenzylidene)hydrazine (B_{10})

Yield = 61%. Elemental analysis (%) calc.: C 78.4, N 5.4, H 10.1; found: C 78.1, N 5.3, H 10.1. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2955 (w-m, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2918 (s, υ_{as}(C–H) of CH_2 group), 2851 (m, υ_s(C–H) of CH_2 group), 3069 (w, υ(C–H) aromatic), 1624 (m, υ(C=N)), 1605, 1575, and 1508 (m, m, m,

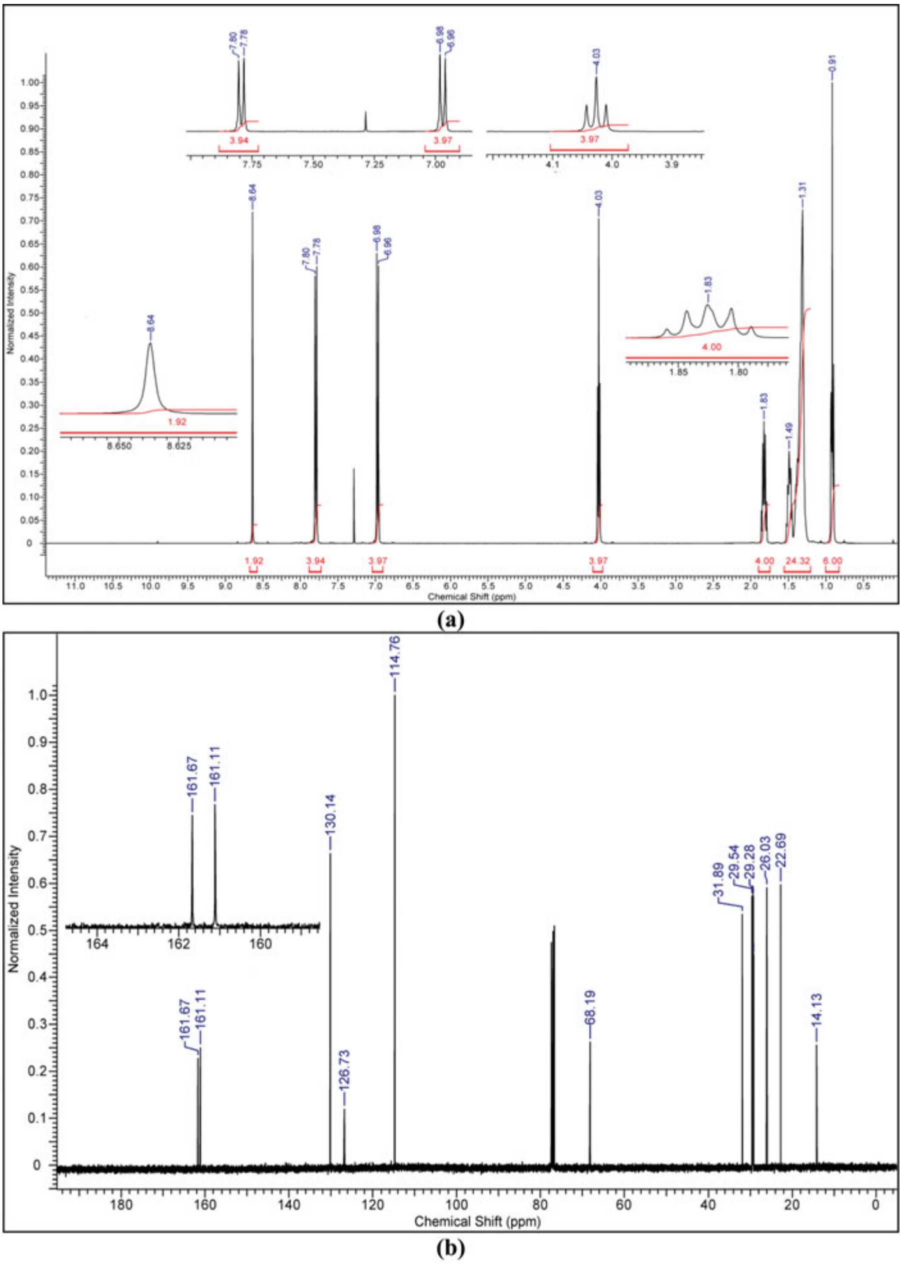


Figure 2. NMR spectra of (B_9): (a) ^{1}HNMR spectrum, (b) ^{13}CNMR spectrum.

υ(C=C) aromatic), 1248 (s,υ(C–O)), 1464 (m, δ(C–H)). UV-Vis (λ/nm): 230 (n–σ^*), 330 ($\pi-\pi^*$).^{1}HNMR (δ/ppm): 0.98 (6H, t, CH_3), 1.30–1.48 (28H, m, CH_2), 1.81 (4H, m, CH_2), 4.03 (4H, t, OCH_2), 6.95 (4H, d, $J = 8.9$ Hz, aromatic protons), 7.80 (4H, d, $J = 8.9$ Hz, aromatic protons), 8.63 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.07 (CH_3), 23.28 (CH_2), 26.66 (CH_2), 29.47 (CH_2), 30.14 (CH_2), 31.94 (CH_2), 68.08 (OCH_2), 114.44 (aromatic C–H), 126.89 (aromatic C), 129.81 (aromatic C–H), 161.24 (CH=N), 161.69 (aromatic C–O). Mass spect. (m/z): 520.

Table 3. Phase transition temperatures and thermodynamic data for 1,2-bis[4-(*n*-alkoxy)benzylidene] hydrazine compounds determined by DSC.

Compound	*n*	Phase transitions T°C (ΔH/KJ.mol^{-1}) (ΔS/J.mole^{-1}.K^{-1}) on first heating	Phase transitions T°C (ΔH/KJ.mol^{-1}) (ΔS/J.mole^{-1}.K^{-1}) on first cooling
B_2	2	Cr–N 173.2 (34.59) [77.52] N–I 195.7 (1.95) [4.16]	I–N 192.2 (−2.06) [−4.42] N–Cr 144.8 (−32.81) [−78.53]
B_3	3	Cr_1–Cr_2 103.8 (6.73) [17.8] Cr_2–N–I 157.9 (28.58) [66.32]	I–N 158.2 (−1.48) [−4.43] N–Cr_2–Cr_1 144.6 (−25.88) [−61.99]
B_4	4	Cr_1–Cr_2 98.4 (9.98) [26.87] Cr_2-N 145.1 (21.83) [52.21] N-I 166 (1.14) [2.60]	I–N 161.6 (−1.52) [−3.50] N–Cr_2 127.9 (−21.64) [−53.98] Cr_2–Cr_1 78.8 (−8.89) [−25.27]
B_5	5	Cr_1–Cr_2–N 129 (34.65) [86.19] N–I 148.8 (0.59) [1.40]	I–N 144.7 (−0.88) [−2.11] N–Cr_2 117.4 (−13.93) [−35.69] Cr_2–Cr_1 110.4 (−16.43) [−42.85]
B_9	9	Cr_1–Cr_2–Cr_3 82.2 (23.80) [67.00] Cr_3–SmC–N 124.2 (28.89) [72.73] N–I 132.3 (0.89) [2.20]	I–N 127.7 (−0.97) [−2.42] N–SmC–Cr_3 115.6 (−29.37) [−75.58] Cr_3–Cr_2–Cr_1 63.0 (−24.31) [72.35]
B_{10}	10	Cr_1–Cr_2–Cr_3 77.4 (22.71) [64.81] Cr_3–SmC–N 122 (33.08) [83.75] N–I 131.4 (2.04) [5.04]	I–N_D 127.7 (−2.80) [−6.99] N_D–N_{Th} 117.2 (−1.08) [−2.77] N_{Th}–SmC–Cr_3 114.6 (−24.80) [−63.98] Cr_3–Cr_2–Cr_1 62.7 (−21.81) [−64.97]
B_{11}	12	Cr_1–Cr_2–Cr_3 89.3 (26.16) [72.21] Cr_3– Cr_4–SmA 116.2 (18.39) [47.25] SmA–N–I 125.6 (4.79) [12.02]	I–N–SmA 118.2 (−9.33) [−23.85] SmA–Cr_4–Cr_3 107.3 (−27.11) [−71.29] Cr_3–Cr_2–Cr_1 73.7 (−28.09) [−81.02]
B_{12}	16	Cr_1-Cr_2-Cr_3 99.0 (13.29) [35.73] Cr_3-$Cr_4$108.8 (7.84) [20.53] Cr_4–SmA–N–I 116.9 (31.22) [80.07]	I–N–SmA 115.5 (−11.42) [−29.40] SmA–Cr_4–Cr_3 108.9 (−35.85) [−93.87] Cr_3–Cr_2–Cr_1 96.8 (−24.25) [−65.58]
B_{13}	18	Cr_1–Cr_2–Cr_3-Cr_3 103.4 (20.22) [53.72] Cr_3–SmA–N–I 116.2(70.63) [181.47]	I–N_D 114.2 (−5.29) [−13.66] N_D–N_{Th} 110.9 (−1.96) [−5.11] N_{Th}–SmA–Cr_4 109.6 (−19.73) [−51.57] Cr_4-Cr_3–Cr_2–Cr_1 103.8 (−22.81) [−60.54]

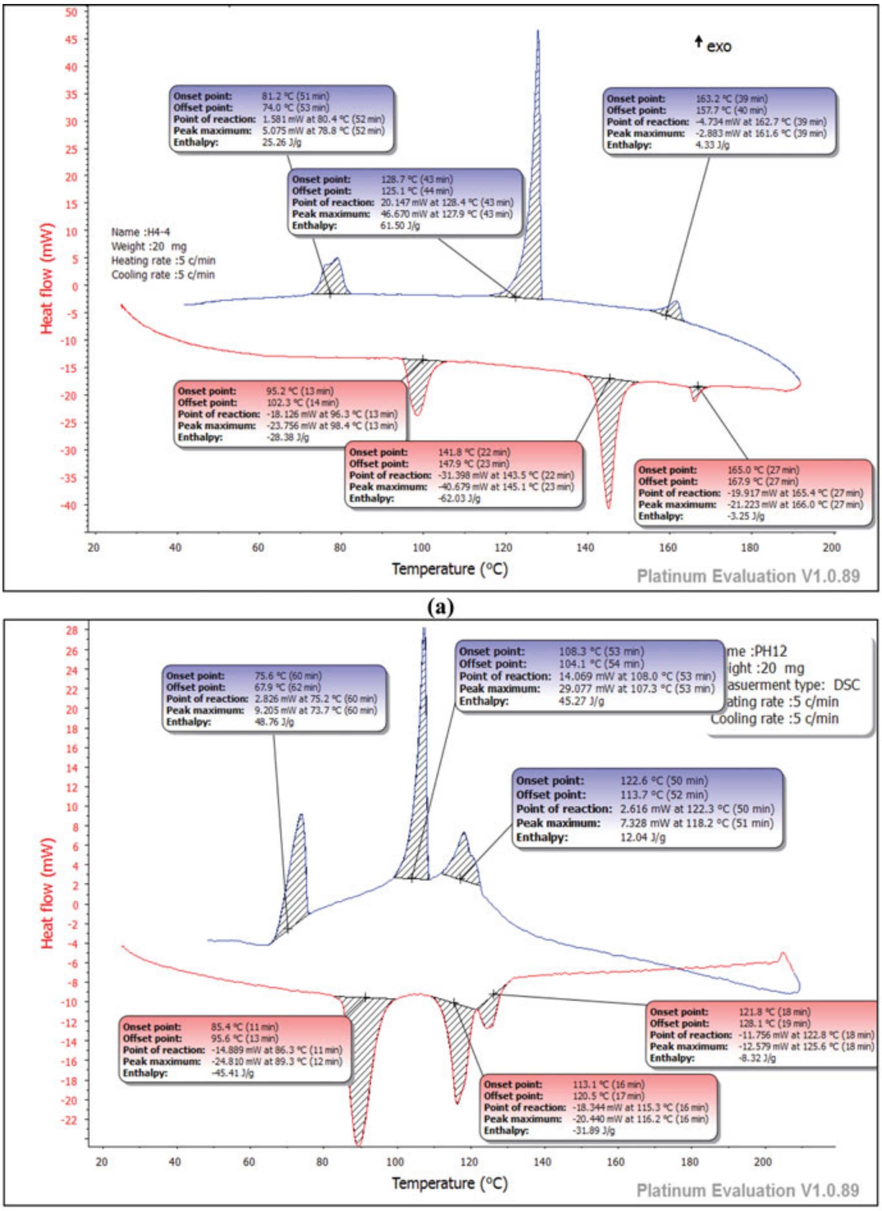
Cr: crystalline solid, SmA: smectic A mesophase, SmC: smectic C mesophase, N_D: nematic droplets-like texture, N_{Th}: nematic thread-like texture, I: isotropic liquid, n: alkyl chain length.

1,2-bis(4-dodecyloxybenzylidene)hydrazine (B_{11})

Yield = 66%. Elemental analysis (%) calc.: C 79.1, N 4.9, H 10.5; found: C 79.0, N 4.7, H 10.4. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2955 (w-m, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2916 (s, υ_{as}(C–H) of CH_2 group), 2849 (m, υ_s(C–H) of CH_2 group), 3069 (w, υ(C–H) aromatic), 1622 (m, υ(C=N)), 1605, 1574, and 1508 (m, m, m, υ(C=C) aromatic), 1250 (s, υ(C–O)), 1470 (m, δ(C–H)). UV-Vis (λ/nm): 228 (n–σ^*), 329 (π–π^*).^{1}HNMR (δ/ppm): 0.97 (6H, t, CH_3), 1.29–1.45 (36H, m, CH_2), 1.80 (4H, m, CH_2), 4.02 (4H, t, OCH_2), 6.94 (4H, d, J = 8.8 Hz, aromatic protons), 7.81 (4H, d, J = 8.8 Hz, aromatic protons), 8.62 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.05 (CH_3), 23.25 (CH_2), 26.69 (CH_2), 29.44 (CH_2), 30.11 (CH_2), 31.92 (CH_2), 68.07 (OCH_2), 114.41 (aromatic C–H), 126.89 (aromatic C), 129.79 (aromatic C–H), 161.22 (CH=N), 161.61 (aromatic C–O). Mass spect. (m/z): 576.

1,2-bis(4-hexadecyloxybenzylidene)hydrazine (B_{12})

Yield = 64%. Elemental analysis (%) calc.: C 80.2, N 4.1, H 11.1; found: C 80.0, N 4.0, H 11.1. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2955 (w-m, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2916 (s, υ_{as}(C–H) of CH_2 group), 2847 (s, υ_s(C–H) of CH_2 group), 3070 (w, υ(C–H) aromatic), 1624 (m, υ(C=N)), 1607, 1575, and 1510 (m, m, m, υ(C=C) aromatic), 1252 (s, υ(C–O)), 1462 (m, δ(C–H)). UV-Vis (λ/nm): 229 (n–σ^*), 329 (π–π^*). ^{1}HNMR (δ/ppm): 0.96 (6H, t, CH_3), 1.29–1.42 (52H, m, CH_2), 1.81 (4H, m,



(a)

(b)

Figure 3. DSC curves for (a) B_4 and (b) B_{11} at a rate of 5.0°C/min, red line is the heating cycle, while blue line is the cooling cycle.

CH_2), 4.01 (4H, t, OCH_2), 6.92 (4H, d, $J = 8.8$ Hz, aromatic protons), 7.80 (4H, d, $J = 8.8$ Hz, aromatic protons), 8.60 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.0 (CH_3), 23.12 (CH_2), 26.65 (CH_2), 29.23 (CH_2), 30.01 (CH_2), 31.88 (CH_2), 68.06 (OCH_2), 114.35 (aromatic C–H), 126.84 (aromatic C), 129.73 (aromatic C–H), 161.12 (CH=N), 161.55 (aromatic C–O). Mass spect. (m/z): 688.

1,2-bis(4-octadecyloxybenzylidene)hydrazine (B_{13})

Yield = 66%. Elemental analysis (%) calc.: C 80.6, N 3.8, H 11.4; found: C 80.5, N 3.7, H 11.3. Characteristic spectroscopic data: FTIR (U/cm^{-1}): 2955 (w-m, υ_{as}(C–H) of CH_3 group),

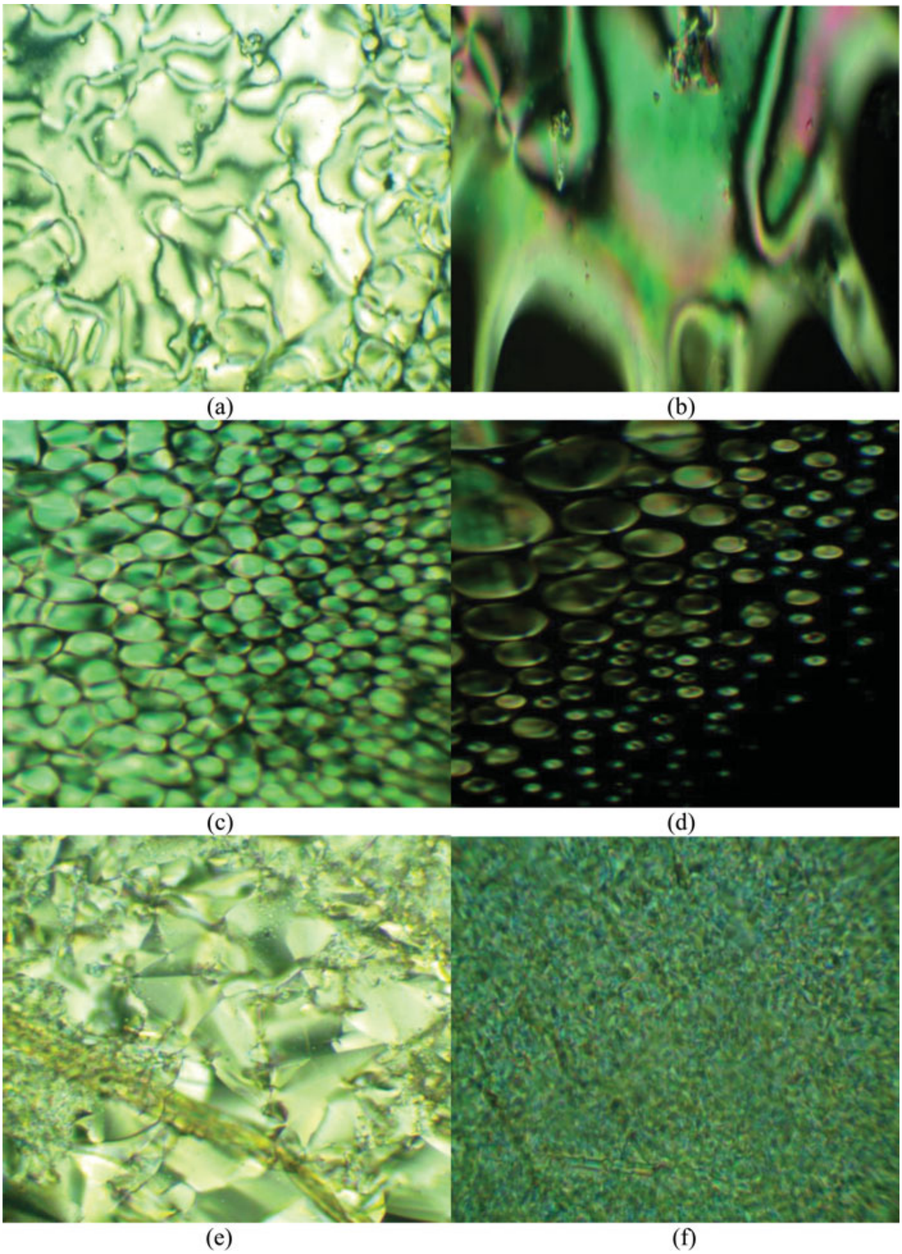


Figure 4. (a) Nematic thread-like texture of B_{10} at 113°C upon cooling. (b) Nematic thread-like texture of B_4 at 164°C upon heating. (c) Nematic droplets-like texture of B_9 at 127°C upon cooling. (d) Nematic droplets-like texture of B_5 at 147°C upon cooling. (e) SmA mesophase of B_{11} at 111°C upon cooling. (f) SmC mesophase of B_{10} at 101°C upon cooling.

2872 (w, υ_s(C–H) of CH_3 group), 2916 (s, υ_{as}(C–H) of CH_2 group), 2847 (s, υ_s(C–H) of CH_2 group), 3069 (w, υ(C–H) aromatic), 1624 (m, υ(C=N), 1607, 1576, and 1510 (m, m, m, υ(C=C) aromatic), 1252 (s, υ(C–O)), 1462 (m, δ(C–H)). UV-Vis (λ/nm): 230 (n–σ^*), 330 (π–π^*).^{1}HNMR (δ/ppm): 0.96 (6H, t, CH_3), 1.28–1.40 (60H, m, CH_2), 1.80 (4H, m, CH_2), 4.0 (4H, t, OCH_2), 6.90 (4H, d, $J = 9.0$ Hz, aromatic protons), 7.75 (4H, d, $J = 9.0$ Hz, aromatic protons), 8.58 (2H, s, CH=N). ^{13}CNMR (δ/ppm): 14.0 (CH_3), 23.10 (CH_2), 26.60 (CH_2), 29.17

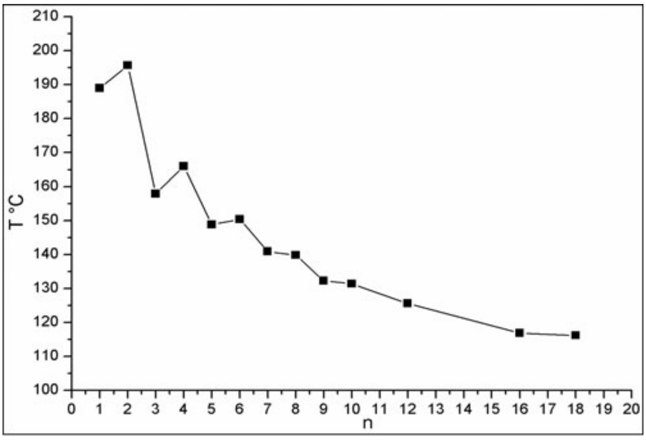


Figure 5. Transition temperatures as a function of alkyl chain length for 1,2-bis[4-(*n*-alkoxy)benzylidene] hydrazine compounds.

(CH_2), 29.80 (CH_2), 31.77 (CH_2), 68.02 (OCH_2), 114.30 (aromatic C–H), 126.73 (aromatic C), 129.60 (aromatic C–H), 161.01 (CH=N), 161.43 (aromatic C–O). Mass spect. (*m*/*z*): 744.

Result and discussion

Synthesis and characterization of the compounds

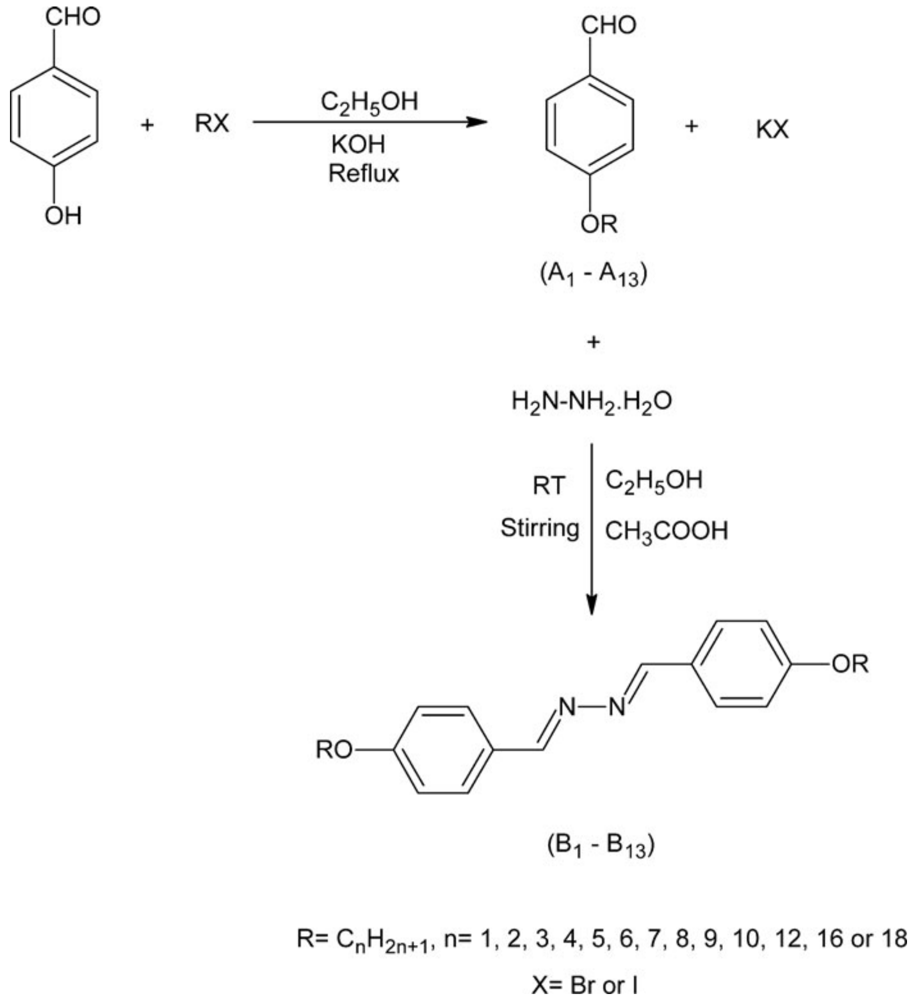
The present study reports a convenient and high-yielding protocol for the synthesis of 1,2-bis[4-(*n*-alkoxy)benzylidene]hydrazine compounds (where, *n*-alkoxy: $O(CH_2)_nH$, $n = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 16$, or 18). The synthesis was made in two stages (Scheme 1):

(i) Alkylation of the OH group of 4-hydroxybenzaldehyde using the Williamson method to obtain 4-(*n*-alkoxy) benzaldehydes.
(ii) Condensation reaction of hydrazine hydrate and appropriately 4-(*n*-alkoxy) benzaldehyde compounds (mole ratio (1:2) respectively) in acidic medium under ambient conditions.

The prepared organic compounds have been characterized and their structures were elucidated depending upon micro-elemental analysis and spectral data (IR, UV-Vis, ^{1}HNMR, ^{13}C{^{1}H}NMR, 2D ^{1}H-^{1}H-cozy, 2D ^{1}H-^{13}C- HSQC, and mass spectra).

Fourier transform infrared spectroscopy (FTIR) spectra of 1,2-bis[4-(*n*-alkoxy)benzylidene]hydrazine compounds (B_1–B_{13}) showed characteristic bands due to C–H, C=C, C=N, and C–O functional groups [25]; for details, see Experimental part. Furthermore, the FTIR spectra of these compounds were compared with that of the corresponding 4-(*n*-alkoxy) benzaldehyde compounds (A_1–A_{13}). Because of this comparison, the following aspects have been observed (for the comparison, see Figure 1):

(i) Appearance of a new band in all spectra of 1,2-bis[4-(*n*-alkoxy)benzylidene]hydrazine compounds (B_1–B_{13}) in the range: (1616–1624 cm^{-1}), which can be assigned to the stretching vibration of (C=N) group.
(ii) The bands related to the υ(C–H) aldehydic and υ(C=O) groups that observed in the spectra of 4-(*n*-alkoxy) benzaldehyde compounds (A_1–A_{13}) in the ranges (2729–2740 cm^{-1}) and (1680–1694 cm^{-1}), respectively, were disappeared in the spectra of 1,2-bis[4-(*n*-alkoxy)benzylidene]hydrazine compounds (B_1–B_{13}).



Scheme 1. Synthetic diagram for the preparation of 1,2-bis[4-(*n*-alkoxy)benzylidene]hydrazine compounds.

These facts might indicate the formation of azine compounds.

The ^{1}HNMR and ^{13}C{^{1}H}NMR spectra of the prepared compounds, displayed signals corresponding to the various proton and carbon nuclei (for further details, see Experimental section and for instant example, see Figure 2). The assignments of the chemical shifts in both ^{1}HNMR and ^{13}C{^{1}H}NMR spectra of these compounds are supported by the 2D spectra (^{1}H-^{1}H-cozy and ^{1}H-^{13}C- HSQC NMR spectra).

Liquid crystalline behavior of the compounds

Liquid crystalline behavior of the prepared organic compounds: 1,2-bis[4-(*n*-alkoxy)benzylidene]hydrazine was studied using polarized light optical microscopy (POM) and differential scanning calorimetry (DSC) techniques. The phase transition temperatures and thermodynamic data are summarized in Table 3 (the temperatures determined are peak temperatures). All of these compounds displayed enantiotropic LC properties. Smectic and nematic mesophases could be observed for the compounds: B_9–B_{13}, while only nematic mesophase is detected for B_1–B_8.

The DSC thermograms of B_2, B_4, B_5, B_9, B_{10}, and B_{11} show intense melting peaks (mainly due to transitions from crystal solid phases into nematic mesophase) followed by a weak clearing peak at higher temperatures (transition from nematic mesophase to the isotropic), examples are shown in Figure 3. No separated weak clearing peak could be noticed in the thermograms of B_{12} and B_{13} compounds, and instead an intense peak appeared. This could be attributed to phase transition from the more ordered mesophase (crystalline solid) to the isotropic, passing through smectic and nematic mesophases. Successive heat–cool cycles reproduce the same behavior. In the compounds of long length chain (B_{11}, B_{12}, and B_{13}), the phase transitions in both heating and cooling were found to be very close to each other. This is not true for rest of the compounds. Observation of the textures under microscope confirmed the liquid crystalline behavior (examples are shown in Figure 4). Upon cooling of all of the prepared compounds from the isotropic phase, nematic droplets-like texture were formed. These droplets joined together to give nematic thread-like texture [26]. Another element that confirms the identity of nematic mesophase is the transition enthalpy of the clearing point of compounds B_2, B_3, B_4, B_5, B_9, and B_{10}. The enthalpy being 0.59–2.04 KJ mol^{-1}. This is typical for nematic to isotropic transition [27–28]. Typical fan-shaped texture of a SmA mesophase has been shown by the compounds B_{11}, B_{12}, and B_{13}, while a texture of SmC was exhibited by B_9 and B_{10} compounds. As could be seen in Table 3, all compounds showed crystalline polymorphism. These solid-state transitions were observed by POM and confirmed by DSC. The phase behavior of our compounds is consistent with literature data on similar compounds [16, 17].

Increasing alkyl chain length may have different effects on the melting point. In general, increasing the chain length can increase the van der Waals interactions and therefore may increase the melting point. On the other hand, the flexibility of the alkyl chain tends to disrupt the lateral core–core interactions and therefore reduces the melting point. The effect of chain length on the melting point may thus vary from compound to compound of different core systems. Because the melting temperatures of these azine compounds decrease with increasing chain length, the melting process appears to be governed by the random motion of chains but is less affected by the van der Waals interactions between chains [29–31]. A plot of transition temperature values as a function of the length of terminal alkoxy chain for these compounds is shown in Figure 5, which shows odd-even effect. The effect being more pronounced for shorter terminal chains.

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