

Short Communication

Synthesis and Characterisation of New Mesogenic 4-n-Alkoxy Benzaldehyde Semicarbazones

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Available online at: www.isca.in

(Received 1st August 2011, revised 13th August 2011, accepted 06th September 2011)

Abstract

Synthesis of homologous series of mesogenic benzaldehyde semicarbazones starting from *p*-hydroxy benzaldehyde via alkylation with *n*-alkyl bromide under phase transfer condition is described. The physical characterization was carried out along with spectroscopic techniques (FT-IR, ¹H NMR and mass spectroscopy). The liquid crystalline properties were investigated by differential scanning calorimetry (DSC) and polarizing optical microscope. It is observed that all the members of the series exhibit the general mesomorphic properties found in other analogous series. The thermal stabilities of the present series are compared with those of the other related homologous series.

Key words: Semicarbazones, alkylation, phase transfer catalyst and liquid crystals.

Introduction

Many organic compounds exhibiting liquid crystalline properties contain two phenyl rings with substituents in the para positions. On moving from two ring mesogens with one linking unit to three ring mesogens with two linking units, mesophase thermal stabilities are greatly enhanced. The synthesis and liquid crystalline properties of a new series of diacylhydrazine derivatives are reported. All compounds exhibit a smectic C (SmC) phase. The first homologues display a monotropic SmC mesophase, whereas the highest homologues exhibit an enantiotropic SmC phase¹. Thirteen compounds with ester and amide linkages were synthesized and their mesogenic properties evaluated. Methyl to *n*-propyl derivatives exhibit nematic phases, *n*-butyl to *n*-decyl derivatives exhibit smectic and nematic mesophases, whereas *n*-dodecyl to *n*-octadecyl derivatives exhibit only smectic phases. All the smectic homologues exhibit smectic C phases. Middle members of the homologous series exhibit polymorphism of smectic mesophase². The advent of bistable, fast-switching, electrooptic light – valve based on the properties of liquid crystals have gained considerable interest in the synthesis of new smectogenics suitable for the application of display device technology³. A number of structurally different liquid crystals have been synthesized which possess interesting properties⁴. Literature survey indicates that mesogenic compounds having semicarbazones have been neither studied nor synthesized extensively. In view of the rarity of the mesogenic semicarbazones, it is proposed to synthesize 4-*n*-alkoxy benzaldehyde semicarbazones via alkylation of *p*-hydroxy benzaldehyde using phase transfer catalyst to evaluate the effect of chemical constitution on mesomorphism.

Material and Methods

Reagents and Instruments: All the reagents in this investigation were of analytical grade and used as received. The prepared samples were characterized by spectral studies. IR spectra were recorded in nujol mull on a SHIMADZU FT-IR 8300 spectrophotometer. ¹H NMR spectra were recorded either on a Bruker 300 MHz or Jeol 60 MHz spectrophotometer in CDCl₃ or DMSO solution. Tetramethylsilane was used as an internal standard, chemical shifts are expressed in ppm (δ) and following abbreviation was used: s = singlet, d = doublet, t = triplet and m = multiplet. The ¹³C NMR spectra were measured at 75 MHz and the values are in parts per million down field from tetramethylsilane. Mass spectra were obtained on a Fennigen 4021 mass spectrophotometer and important fragments are given with the relative intensities (in the bracket). Thin layer chromatography (TLC) was done with pre-coated silica gel G plates using chloroform as eluent. Melting points were taken in open capillary tubes and are uncorrected. The optical textures exhibited by the liquid crystals are examined by the polarizing microscope. For the experimental investigation of optical texture, the specimen has taken in the form of thin film in the order of 25 to 30 microns thickness between slide and coverglass. The phase transition temperatures of the liquid crystalline compounds were determined using a polarizing microscope in conjunction with a conventional hot stage. The samples were sandwiched between a slide and cover slip. The temperature of the specimen was varied across the transition points at the rate of 0.2°C per minute. The DSC thermograms were undertaken for all the semicarbazones.

Experimental Section: The simple alkylation of p-hydroxy benzaldehyde (2) with alkyl bromides was not successful. In continuation to of our previous work⁵⁻⁶, we examined the reaction of p-hydroxy benzaldehyde (2) with alkyl bromide in the presence of solid KOH and a quaternary ammonium salt under anhydrous conditions (Scheme-1). In this manner we achieved the alkylation in good yield (83%). The structures of all the 4-n-alkoxy benzaldehyde semicarbazone are evident from IR and ¹H NMR (60MHz). 4-n-Alkoxy benzaldehyde serves as a precursor for mesogenic semicarbazones. The transformation of 3 to 4 (Scheme-2) was best achieved by condensation of 3 with semicarbazide hydrochloride in presence of sodium acetate using ethanol as solvent in good yield ranging from 77 to 93%.

General Procedure for the Preparation of Alkoxy Ethers:

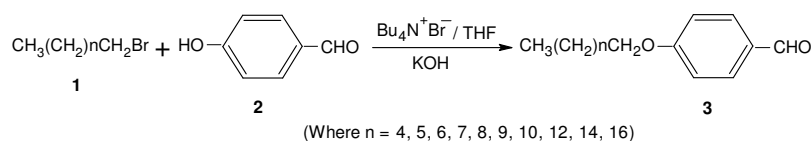
Typical procedure for the synthesis of 4-n-decyloxybenzaldehyde (3g): To a solution of 4-hydroxybenzaldehyde (2, 1.5g, 12.29mmol) in dry tetrahydrofuran (20ml), tetrabutylammonium bromide (0.3g, 0.93mmol), powdered potassium hydroxide (0.5g, 8.9mmol) and n-decylbromide (1g, 2.5g, 12.02mmol) was added and stirred at room temperature for 6h. The mixture was then filtered and washed with 10% cold sodium hydroxide (2 x 25ml) to remove traces of 4-hydroxybenzaldehyde. The solvent was dried over anhydrous sodium sulphate and evaporated under reduced pressure to give solid 4-n-decyloxybenzaldehyde (3g) in 75% yield (2.41g). It was further purified by recrystallisation using alcohol; m.p. 119-120°C; IR (nujol): 2990-3000, 1670, 1600, 1400, 1330 cm⁻¹; ¹H NMR (CDCl₃): δ 0.90 (t, 3H, CH₃), 1.2-1.4 (bm, 16H, CH₂), 4.00-4.10 (t, 2H, OCH₂), 6.80-6.90 (dd, 2H, ArH), 7.20-7.30 (dd, 2H, ArH), 8.20 (s, 1H, CH=O).

General Procedure for the Preparation of Semicarbazone: *Typical procedure for the preparation of 4-n-decyloxybenzaldehyde semicarbazone (4g):* Mixture of semicarbazide hydrochloride (1.0g, 8.9mmol) and crystallized sodium acetate (1.5g, 18.28mmol) in water

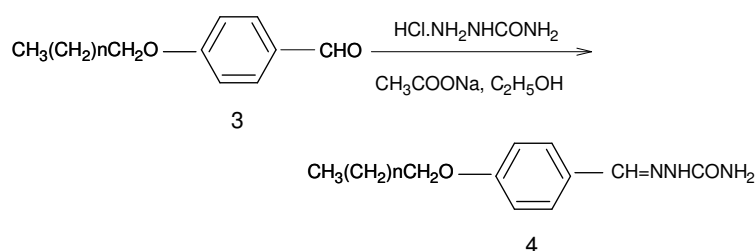
(10ml) was added slowly to a solution of 4-n-decyloxybenzaldehyde (3g, 0.3g, 1.14mmol) in alcohol was added until a clear solution was obtained; stirred the mixture for few minutes and allowed to stand. The reaction was accelerated by warming the mixture on a water bath for few minutes and then cooled in ice-water. Crystals were filtered off, washed with a little cold water and recrystallised from alcohol to give 4g as crystalline solid in 90% (0.328 g) yield, m.p. 148 - 150°C. ¹H NMR (CDCl₃): 0.89-0.90 (t, 3H, CH₃), 1.2-1.4 (BM, 16H, CH₂), 4.00-4.10 (t, 2H, OCH₂), 5.60 (bs, 2H, NH₂), 6.80-6.90 (dd, 2H, ArH), 7.20-7.30 (dd, 2H, ArH), 7.72 (s, 1H, CH=N), 9.7 (bs, 1H, NH); Mass spectrum m/e (relative intensity) 320 (MH⁺, 100), 321 (15), 293 (88), 270 (11), 153 (16); Anal. Calcd. for C₁₈H₂₉N₃O₂: C 67.66, H 9.16, N 13.16; found: C 67.60, H 9.08, N 13.19.

4-n-Hexyloxybenzaldehyde semicarbazone (4c): Obtained from (3c) (0.3g, 1.4mmol) and semicarbazide hydrochloride (1g, 8.9mmol) as a solid in 92% (0.34g) yield, m.p. 141 - 142°C; ¹H NMR(CDCl₃): δ 0.90 (t, 3H, CH₃), 1.20-1.60 (m, 8H, CH₂), 4.03 (t, 2H, OCH₂), 5.78 (bs, 2H, NH₂), 6.84 (d, 2H, ArH), 7.22 (d, 2H, ArH), 7.75 (s, 1H, CH=N), 9.72 (bs, 1H, NH); Mass spectrum m/e (relative intensity) 264 (MH⁺, 100), 268 (30), 236 (12), 221 (72), 168 (3); Anal. Calcd. for C₁₄H₂₁N₃O₂: C 63.84, H 8.04, N 15.96; found: C 63.80, H 8.00, N 15.90.

4-n-Heptyloxybenzaldehyde semicarbazone (4d): Obtained from (3d) (0.3g, 1.36 mmol) and semicarbazide hydrochloride (1g, 8.9mmol) as a solid in 92% (0.34g) yield, m.p. 138 - 139°C; ¹H NMR (DMSO): δ 0.85 (t, 3H, CH₃), 1.20-1.70 (m, 10H, CH₂), 3.95 (t, 2H, OCH₂), 5.81 (bs, 2H, NH₂), 6.89 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.73 (s, 1H, CH=N), 9.90 (bs, 1H, NH); Mass spectrum m/e (relative intensity) 278 (MH⁺, 27), 393 (52), 361 (100), 318 (35), 292 (31), 225 (27), 137 (36); Anal. Calcd. for C₁₅H₂₃N₃O₂: C 64.94, H 8.36, N 15.16; found: C 64.90, H 8.32, N 15.10.



Scheme - 1



Scheme-2

4-n-Octyloxybenzaldehyde semicarbazone (4e): Obtained from (3e) (0.3g, 1.28 mmol) and semicarbazide hydrochloride (1g, 8.9mmol) as a solid in 89% (0.33g) yield, m.p. 150 – 151°C; ¹H NMR (DMSO): δ 0.89 (t, 3H, CH₃), 1.30-1.60 (m, 12H, CH₂), 4.01 (t, 2H, OCH₂), 5.88 (bs, 1H, NH₂), 6.82 (d, 2H, ArH), 7.21 (d, 2H, ArH), 7.75 (s, 1H, CH=N), 10.02 (bs, 1H, NH); Mass spectrum m/e (relative intensity) 292 (MH⁺, 80), 281 (15), 264 (100), 248 (16), 186 (12), 93 (8); Anal. Calcd. for C₁₆H₂₅N₃O₂; C 65.94, H 8.65, N 14.43; found: C 65.90, H 8.63, N 14.49.

4-n-Nonoyloxybenzaldehyde semicarbazone (4f): Obtained from (3f) (0.3g, 1.2 mmol) and semicarbazide hydrochloride (1g, 8.9mmol) as a solid in 94% (0.34g) yield, m.p. 141–142°C; ¹H NMR (DMSO): δ 0.85 (t, 3H, CH₃), 1.20-1.61 (m, 14H, CH₂), 3.95 (t, 2H, OCH₂), 5.80 (bs, 2H, NH₂), 6.92 (d, 2H, ArH), 7.41 (d, 2H, ArH), 7.75 (s, 1H, CH=N), 9.02 (bs, 1H, NH); Mass spectrum m/e (relative intensity) 306 (MH⁺, 27), 393 (52), 361 (100), 318 (35), 292 (31), 225 (27), 137 (36); Anal. Calcd. for C₁₇H₂₇N₃O₂; C 66.84, H 8.92, N 13.76; found: C 66.80, H 8.90, N 13.80.

4-n-Dodecyloxybenzaldehyde semicarbazone (4h): Obtained from (3h) (0.3g, 1.03 mmol) and semicarbazide hydrochloride (1g, 8.9 mmol) as a solid in 91% (0.32g) yield, m.p. 141–142°C; ¹H NMR (CDCl₃): δ 0.86 (t, 3H, CH₃), 1.25-1.55 (m, 20H, CH₂), 4.01 (t, 2H, OCH₂), 5.78 (bs, 2H, NH₂), 6.82 (d, 2H, ArH), 7.24 (d, 2H, ArH), 7.76 (s, 1H, CH=N), 10.09 (bs, 1H, NH); Mass spectrum m/e (relative intensity) 348 (MH⁺, 100), 321 (15), 293 (88), 270 (11), 153 (16); Anal. Calcd. for C₂₀H₃₃N₃O₂; C 69.11, H 9.58, N 12.10; found: C 69.09, H 9.56, N 12.19.

4-n-Tetradecyloxybenzaldehyde semicarbazone (4i): Obtained from (3i) (0.3g, 0.94 mmol) and semicarbazide hydrochloride (1g, 8.9mmol) as a solid in 90% (0.31g) yield, m.p. 146–148°C; ¹H NMR (DMSO): δ 0.85 (t, 3H, CH₃), 1.25-1.65 (m, 24H, CH₂), 3.94 (t, 2H, OCH₂), 6.4 (bs, 2H, NH₂), 6.91 (d, 2H, ArH), 7.42 (d, 2H, ArH), 7.75 (s, 1H, CH=N), 10.12 (bs, 1H, NH); Mass spectrum m/e (relative intensity) 376 (MH⁺, 70), 363 (24), 346 (100), 318 (21), 290 (72), 210 (16), 150 (17); Anal. Calcd. for C₂₂H₃₇N₃O₂; C 70.35, H 9.94, N 11.19; found: C 70.37, H 9.90, N 11.21.

4-n-Hexadecyloxybenzaldehyde semicarbazone (4j): Obtained from (3j) (0.3g, 0.86 mmol) and semicarbazide hydrochloride (1g, 8.9mmol) as a solid in 92% (0.32g) yield, m.p. 151–152°C; ¹H NMR (DMSO): δ 0.85 (t, 3H, CH₃), 1.2-1.6 (m, 28H, CH₂), 3.95 (t, 2H, OCH₂), 6.52 (bs, 2H, NH₂), 6.96 (d, 2H, ArH), 7.42 (d, 2H, ArH), 7.75 (s, 1H, CH=N), 10.08 (bs, 1H, NH); Mass spectrum m/e (relative intensity) 404 (MH⁺, 27), 393 (52), 361 (100), 318 (35), 292 (31), 225 (27), 137 (36); Anal. Calcd. for C₂₄H₄₁N₃O₂; C 71.41, H 10.25, N 10.42; found: C 71.45, H 10.22, N 10.51.

Results and Discussion

When the specimen 4-n-Dodecyloxybenzaldehyde semicarbazone (4h) is cooled from isotropic phase, the genesis of nucleation starts with continuous domain formation with planar structure with deep violet colour and exhibits specular reflection. This texture is characteristic of a cholesteric phase. This phase appears to be unstable and changes over to smectic a phase. On further cooling radial fringes develop on the fans of the focal conic fan textures and this phase is associated with chiral smectic phase S_C^{*}. S_C^{*} phase is stable for large range of temperature. The other homologues of this series were also found to exhibit various liquid crystalline phases. These compounds exhibit cholesteric phase at higher temperatures.

Conclusion

The alkylation reaction using phase transfer catalyst yields good result. The semicarbazones prepared in second step found to show liquid crystal properties. The phase transition temperatures obtained from Leitz polarizing microscope are very well in agreement with the DSC thermograms.

Acknowledgement

The authors are very much grateful to the management of K. L. University, Vaddeswaram, for their continuous support, encouragement and for providing the necessary infrastructure facilities for executing this work.

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