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Synthesis and Characterization of new Mesogenic 4-(n-Alkoxy)-3-methoxy-benzaldehyde Semicarbazones[+]

K. RAJASEKHARPRASAD [a] , NAGAPPA [b] & K. M. LOKANATHARAI [a]

[a] Department of Studies in Chemistry , University of Mysore , Manasagangothri, Mysore, 570006, India

[b] Department of Studies in Physics , University of Mysore , Manasagangothri, Mysore, 570006, India

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SYNTHESIS AND CHARACTERIZATION OF NEW MESOGENIC 4-(n-ALKOXY)-3-METHOXY-BENZALDEHYDE SEMICARBAZONES+

K. RAJASEKHAR PRASAD[a], NAGAPPA[b] AND K. M. LOKANATHA RAI[a]*

[a]Department of Studies in Chemistry,
bDepartment of Studies in Physics,
University of Mysore, Manasagangothri, Mysore 570 006, India.

Abstract: Synthesis of a homologous series of mesogenic 4-(n-alkoxy)-3-methoxy benzaldehyde semicarbazones starting from vanillin via alkylation with n-alkyl bromide under phase transfer condition is described.

The advent of a bistable, fast-switching, electrooptic light-valve based on the properties of ferroelectric smectic liquid crystals[1] have gained considerable interest in the synthesis of new smectogens suitable for the application of display device technology. A number of structurally different ferroelectric liquid crystals have been defined which possess interesting properties.[2] Consideration of the geometrical aspects of a molecule helps a great deal to understand the structure-property relationship. For instance chirality in liquid crystals have been shown increasing importance with respect to fundamental scientific significance and their applicability to electrooptic devices.[3] In order to increase the range of the ferroelectric phase with high spontaneous polarization, we have synthesized a homologous series of new ferroelectric liquid crystalline compounds.[4] Brown and Shaw[5] have reported various homologous series of p-n-alkoxy benzal phenyl hydrazones exhibit mesomorphism of very low thermal stability and a few of them also display phototropism

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* To whom correspondence should be addressed.

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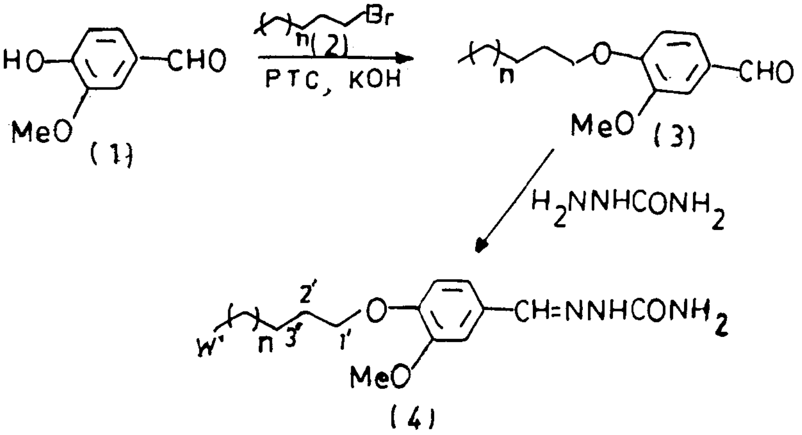
which is a characteristic of both organic and inorganic compounds. In light of the above facts and the rarity of the mesogenic semicarbazones, it is proposed to synthesize a homologous series of 4-(n-alkoxy)-3-methoxy-banzaldehyde semicarbazones to evaluate the effect of chemical constitution of mesomorphism.

In this paper we would like to report the synthesis of 4-(n-alkoxy)-3-methoxy-benzaldehyde semicarbazone (**4**) via alkylation of vanillin (**1**) using phase transfer catalyst.



a) n=2; b) n=4; c) n=6; d) n=8; e) n=10; f) n=12.

The simple alkylation of vanillin with alkyl bromides (**2**) was not successful. In continuation of our previous work, we examined the reaction of vanillin with alkyl bromide in the presence of solid KOH and a quarternary ammonium salt under anhydrous conditions. In this manner we achieved the alkylation in good yield (85%). The structure of all the 4-n-alkoxy-vanillins are evident from IR, ^{1}H NMR (60 MHz). Alkylated vanillins (**3**) serves as a precursor for mesogenic semicarbazones (**4**). The transformation of **3** to **4** was best achieved by condensation of **3** with semicarbazide hydrochloride in presence of sodium acetate using ethanol as solvent in good yield ranging 75 to 95%. Structure proof for semicarbazones were provided by ^{1}H NMR, ^{13}C NMR and mass

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spectral studies. Optical texture studies have been carried out using Leitz polarizing microscope. The phase transition temperatures are recorded by DSC and polarizing microscope.

EXPERIMENTAL SECTION

Melting points were taken on open capillary and are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured on a Bruker AM 300 MHz FT spectrometer using $CDCl_3$ *and DMSO using tetramethylsilane as internal standard.* The chemical shifts are expressed in δ and following abbreviation were used: s = singlet, d = doublet, t = triplet and m = multiplet. Mass spectra were obtained on a Finnigan 4021 mass spectrometer at an ionizing energy of 35 eV. Thin layer chromatography (TLC) was done with pre-coated silica gel G plates using chloroform as eluent.

General Procedure for the Preparation of Alkoxy Ethers:

Typical procedure for the generation of 4-n-decyloxy vanillin (**3c**): To a solution of vanillin (**1**, 1.5 g) in dry tetrahydrofuran (20 ml), tetrabutyl ammonium bromide (0.5 g), powdered potassium hydroxide (1.5 g) and n-decylbromide (**2c**, 1 mL) was added and stirred at room temperature for 6-8 h. The mixture was then filtered and washed with 10% cold sodium hydroxide (2X25 ml) to remove traces of vanillin. The solvent was dried over anhydrous sodium sulphate and evaporated under reduced pressure to give solid 4-n-decyloxy vanillin. After purification by recrystallisation using alcohol, (3c) obtained as pale yellow in 90 % (2.58 g) yield. **^{1}H NMR ($CDCl_3$)**: Ù 0.95-0.99 (bt, 3H, CH_3), 1.2-1.4 (bm, 16H, CH_2), 3.95 (s, 3H, OMe), 4.00-4.10 (q, 2H, CH_2), 6.90-7.3 (bm, 3H, ArH), 8.2 (s, 1H, CHO).

General Procedure for the Preparation of Semicarbazone:

*Typical procedure for the preparation of 4-n-decyloxy Vanillin Semicarbazone **4c***: Mixture of semicarbazide hydrochloride (1.0 g) and crystalized sodium acetate (1.5 g) in

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water (10 ml) was added slowly to a solution of 4-n-decyloxy vanillin (0.5 g) in alcohol. Alcohol was added until a clear solution is obtained; shaked the mixture for a few minutes and allowed to stand. The reaction was accelerated by warming the mixture on a water bath for a few minutes and then cooled in ice-water. Crystals were filtered off. washed with a little cold water and recrystallised from alcohol to give **4c** as crystalline solid in 92 % (0.54 gm) yield, m.p. 148-150°C. **^{1}H NMR ($CDCl_3$)**: δ 0.88 (t. 2H, CH_3), 1.3-1.4 (m. 4H, CH_2), 1.45 (m, 2H. CH_2), 1.85 (p, 4H. CH_2), 4.03 (t, 2H, CH_2), 7.07 (dd, 1H, CH), 6.84 (d, 1H, CH), 7.22(d, 1H, 1H), 7.72(s, CH=N). **^{13}C NMR ($CDCl_3$)**: δ 14.09 (q, w-C), 22.66 (t, {w-1}-C), 31.87 (t, {w-2}-C), 29.04, 29.29, 29.36, 29.52 X 2 (p, {3 to w-3}-C), 25.91 (p, 2-C), 69.02 (t, 1-C), 121.42 (d, 6-C), 108.56 (d, 5-C), 149.62 (d, 4-C), 150.46 (d, 3-C), 112.16 (2-C), 126.55 (p. 1-C), 142.30 (CH=N), 157.80 (C=O): Mass spectrum m/e (relative intensity) for $C_{19}H_{31}N_3O_3$ 350 (MH^+, 100), 321 (15), 293 (88), 270 (11), 153 (16). Anal. calcd. C 65.30, H 8.94, N 12.02; found C 65.22, H 8.82, N 11.94.

4a: Obtained from **3a** (0.5 g) and semicarbazide hydrochloride (1 g) as a solid in 91 % (0.455 g) yield, m.p. 141-142°C. **^{1}H NMR ($CDCl_3$)** : δ 0.90 (t, 2H, CH_3), 1.3-1.35 (m, 4H, CH_2), 1.45 (m, 4H, CH_2), 1.85 (p, 4H, CH_2), 4.03 (t, 2H, CH_2), 7.07 (dd, 1H, CH), 6.84 (d, 1H, CH), 7.22 (d, 1H, CH), 7.75 (s, CH=N). **^{13}C NMR ($CDCl_3$)**: δ 13.99 (q, w-C), 22.55 (t, {w-1}-C), 31.55 (t, {w-2}-C), 29.00 (p, {3 to w-3}-C), 25.59 (p, 2-C), 69.01 (t, 1-C), 121.41 (d, 6-C), 108.57 (d, 5-C), 149.60 (d, 4-C), 150.43 (d, 3-C), 112.15 (2-C), 126.58 (p, 1-C), 142.46 (CH=N), 158.09 (C=O); Mass spectrum m/e (relative intensity) for $C_{15}H_{23}N_3O_3$ 293 (M^+, 100), 268 (30), 236 (12), 221 (72), 168 (3). Anal. calcd. C 61.40, H 7.91, N 14.33; found C 61.25, H 7.75, N 14.20.

4b: Obtained from **3b** (0.5 g) and semicarbazide hydrochloride (1 g) as a solid in 87 % (0.46 g) yield, m.p. 150-151°C. **^{1}H NMR ($CDCl_3$)**: δ 0.89 (t, 2H, CH_3), 1.3 (m, 4H, CH_2), 1.45 (m, 4H, CH_2), 1.85 (p, 4H, CH_2), 4.01 (t, 2H, CH_2), 7.05 (dd, 1H, CH), 6.82 (d, 1H, CH), 7.21 (d, 1H, CH), 7.75 (s, CH=N). **^{13}C NMR ($CDCl_3$)**: δ 14.05 (q, w-C),

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22.60 (t, {w-1}-C), 31.75 (t, {w-2}-C), 29.02, 29.16, 29.30 (p, {3 to w-3}-C), 25.89 (p, 2-C), 68.97 (t, 1-C), 121.34 (d, 6-C), 108.54 (d, 5-C), 149.54 (d, 4-C), 150.35 (d, 3-C), 112.11 (2-C), 126.65 (p, 1-C), 142.44 (CH=N), 158.33 (C=O); Mass spectrum m/e (relative intensity) for $C_{17}H_{27}N_3O_3$ 322 (MH^+, 80), 281 (15), 264 (100), 248 (16), 186 (12), 93 (8). Anal. calcd. C 63.53, H 8.47, N 13.07; found C 63.42, H 8.34, N 12.91.

4d: Obtained from **3d** (0.5 g) and semicarbazide hydrochloride (1 g) as a solid in 89 % (0.56 g) yield, m.p. 141-142°C. **^{1}H NMR (CDCl$_3$)**: δ 0.88 (t, 2H, CH_3), 1.25-1.35 (m, 4H, CH_2), 1.45 (m, 4H, CH_2), 1.84 (p, 4H, CH_2), 4.01 (t, 2H, CH_2), 7.05 (dd, 1H, CH), 6.82 (d, 1H, CH), 7.21 (d, 1H, CH), 7.75 (s, CH=N). **^{13}C NMR (CDCl$_3$)**: δ 14.06 (q, w-C), 22.64 (t, {w-1}-C), 31.87 (t, {w-2}-C), 29.30, 29.59 (p, {3 to w-3}-C), 25.89 (p, 2-C), 68.96 (t, 1-C), 121.31 (d, 6-C), 108.53 (d, 5-C), 149.53 (d, 4-C), 150.33 (d, 3-C), 112.09 (2-C), 126.67 (p, 1-C), 142.37 (CH=N), 158.36 (C=O); Mass spectrum m/e (relative intensity) for $C_{21}H_{35}N_3O_3$ 378 (MH^+, 52), 355 (100), 354 (57), 337 (12), 321 (70), 169 (52). Anal. calcd. C 66.81, H 9.34, N 11.13; found C 66.72, H 9.22, N 10.94.

4e: Obtained from **3e** (0.5 g) and semicarbazide hydrochloride (1 g) as a solid in 89 % (0.61 g) yield, m.p. 146-148°C. **^{1}H NMR (DMSO)**: δ 0.85 (t, 2H, CH_3), 1.25-1.35 (m, 4H, CH_2), 1.40 (m, 4H, CH_2), 1.70 (p, 4H, CH_2), 3.94 (t, 2H, CH_2), 7.05 (dd, 1H, CH), 6.91 (d, 1H, CH), 7.42 (d, 1H, CH), 7.75 (s, CH=N). **^{13}C NMR (DMSO)**: δ 13.92 (q, w-C), 22.09 (t, {w-1}-C), 31.30 (t, {w-2}-C), 28.72, 28.76(2), 29.03(3), 29.06(3) (p, {3 to w-3}-C), 25.51 (p, 2-C), 68.11 (t, 1-C), 120.81 (d, 6-C), 108.44 (d, 5-C), 149.24 (d, 4-C), 149.28 (d, 3-C), 112.31 (2-C), 127.58 (p, 1-C), 139.42 (CH=N), 156.86 (C=O); Mass spectrum m/e (relative intensity) for $C_{23}H_{39}N_3O_3$ 406 (MH^+, 70), 363 (24), 346 (100), 318 (21), 290 (72), 210 (16), 150 (17). Anal. calcd. C 68.11, H 9.69, N 10.36; found C 67.97, H 9.55, N 10.22.

4f: Obtained from **3f** (0.5 g) and semicarbazide hydrochloride (1 g) as a solid in 94 % (0.69 g) yield, m.p. 116-118°C. **^{1}H NMR (DMSO)**: δ 0.85 (t, 2H, CH_3), 1.2-1.3 (m, 4H,

CH_2), 1.38 (m, 4H, CH_2), 1.70 (p, 4H, CH_2), 3.95 (t, 2H, CH_2), 7.04 (dd, 1H, CH), 6.92 (d, 1H, CH), 7.41 (d, 1H, CH), 7.75 (s, CH=N). **^{13}C NMR (DMSO)**: δ 13.85 (q, w-C), 22.00 (t, {w-1}-C), 31.20 (t, {w-2}-C), 28.61(2), 28.93(9) (p, {3 to w-3}-C), 25.41 (p, 2-C), 68.03 (t, 1-C), 120.74 (d, 6-C), 108.35 (d, 5-C), 149.15 (d, 4-C), 149.18 (d, 3-C), 112.23 (2-C), 127.49 (p, 1-C), 139.33 (CH=N), 156.76 (C=O); Mass spectrum m/e (relative intensity) for $C_{25}H_{43}N_3O_3$ 434 (MH^+, 27), 393 (52), 361 (100), 318 (35), 292 (31), 225 (27), 137 (36). Anal. calcd. C 69.25, H 9.99, N 9.69; found C 69.13, H 9.74, N 9.51.

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