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ScienceDirect
Karbala International Journal of Modern Science 1 (2015) 152–158
http://www.journals.elsevier.com/karbala-international-journal-of-modern-science/

Synthesis, characterization and mesomorphic properties of new symmetrical dimer liquid crystals derived from benzothiazole

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Received 26 October 2015; accepted 1 November 2015
Available online 10 December 2015

Abstract

Present works report the synthesis and characterization of a series of homologous symmetrical dimers α,ω-bis[4-(6′-methoxybenzothiazol-2′-yl)iminomethylphenoxy]alkane. Total of five members with different lengths of alkyl spacer groups of even parity varying from butyl (C_4H_8) to dodecyl ($C_{12}H_{24}$) were prepared and characterized. Infrared and nuclear magnetic resonance (^{1}H and ^{13}C NMR) together with electron-ionization mass spectrometric techniques were employed to confirm the molecular structures of the dimers. The phase phase transition and associated enthalpy changes were obtained using differential scanning calorimetry. Textures studies and mesophase identification were conducted using a polarizing optical microscope attached to hotstage. A diversity of phase-transition behavior was observed as the length of the alkyl spacer increased from C_4H_8 to $C_{12}H_{24}$. Almost all title compounds exhibited nematic phase except the dimers containing butyl and hexyl spacers in which the mesomorphic properties were absent.

Keywords: α,ω-bis[4-(6′-methoxybenzothiazol-2′-yl)iminomethylphenoxy]alkane; Schiff bases; Nematic; Symmetrical dimer

1. Introduction

Liquid crystals play a significant role in today's world of science and technology owing to their applications. Technological applications of liquid crystals include optical imaging, liquid crystal displays, organic light emitting diodes, anisotropic networks and semiconductor materials [1–3].

Liquid crystals incorporating a benzothiazole moiety have been used for displaying positive hole-transporting character due to its low ionization potential. As such, they could serve as hole-transporting materials in organic light-emitting devices [4–7]. Over the past few decades, liquid crystals containing heterocyclic core

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Peer review under responsibility of University of Kerbala.

http://dx.doi.org/10.1016/j.kijoms.2015.11.001

have received intense attention due to their unique properties [7–9]. Early results show that the introduction of heterocyclic ring influenced the mesomorphic properties of the calamitic molecules due to their unsaturation and/or polarizability [10]. The system involving heterocyclic liquid crystals has expanded from usual low-molar mass molecules to dimeric or oligomeric structures. Basically, the mesogenic units of dimers have at least two rings and are commonly found to be symmetric. Recently, Imrie and co-workers have reported a review on various dimers and oligomers in which a great attention has been focused on the structure-property relationship [11]. The dimers themselves have attracted attention as they display an unusual mesomorphism different to that of the corresponding monomers. Moreover, they have the ability to perform as model compounds for semi-flexible main-chain/side-chain liquid crystalline polymers [12].

In continuation of our research on heterocyclic benzothiazole-based liquid crystals [13–17], the present interest focuses on the synthesis and mesomorphic properties of a new series of symmetrical dimer molecules in which two mesogens (benzothiazole with Schiff base linkage) are connected by a flexible spacer. To the best of our knowledge, no reports are documented in the literature on symmetric liquid crystal dimer, α,ω-bis[4-(6′-methoxybenzothiazol-2′-yl)iminomethylphenoxy]-alkane. The phase behaviour and the effect of changing the spacer length of the dimers were discussed, wherein these dimers differ from one another in spacer length $(CH_2)_n$ in which n = 4, 6, 8, 10 and 12. Besides, the dimers containing $-(CH_2)_8-$, $-(CH_2)_{10}-$ and $-(CH_2)_{12}-$ as spacers are compared with the previously reported analogues, N-(4-(n-(4-(benzothiazol-2-yl)phenoxy)alkyloxy)benzylidene)-4-chloroanilines [18] in order to study the connectivity between the transitional behaviour and the length of the alkyl spacer bridging both benzothiazole and benzylideneimine moieties.

2. Experimental

2.1. Reagents

2-Amino-6-methoxybenzothiazole, 4-hydroxybenzaldehyde, 1,n-dibromoalkane ($C_nH_{2n}Br_2$ where $n = 4$, 6, 8, 10, 12), and potassium carbonate were purchased from Merck (Germany).

2.2. Physical measurements

Electron ionization mass spectrometry was carried out on a Finnigan MAT95XL-T mass spectrometer. The infrared (IR) spectra for all compounds were recorded in the frequency range 4000-400 cm^{-1} using a Perkin–Elmer 2000 FTIR spectrophotometer with the samples embedded in KBr discs. The ^1H and ^{13}C NMR spectra were obtained using a JEOL LA-400 MHz NMR spectrometer. The deuterated chloroform was used as solvent and tetramethylsilane as the internal standard. The liquid crystalline textures were observed under a Carl Zeiss Axioskop 40 polarising optical microscope (POM) equipped with a Linkam TMS94 temperature controller and a LTS350 hot stage. The transition temperatures and enthalpy changes were measured by a Mettler Toledo DSC823 differential scanning calorimeter at a rate of 10 °C min^{-1} for both heating and cooling cycles.

2.3. Synthesis

The syntheses of intermediates and corresponding dimers were carried out based on the procedures as shown in Fig. 1.

2.3.1. Synthesis of 6-methoxy-2-(4-hydroxybenzylidenamino)benzothiazole, *1*

A mixture of 2-amino-6-methoxybenzothiazole (40 mmol) and 4-hydroxybenzaldehyde (40 mmol) in 50 mL of ethyl alcohol, with three drops of acetic acid as catalyst was added, the mixture allowed to stir and heated under refluxed for 3 h. The reaction mixture was filtered and the ethanol was removed from the filtrate by evaporation. The dry yellowish solid thus obtained was recrystallized several times with ethanol.

2.3.2. Synthesis of α,ω-bis[4-(6′-methoxybenzothiazol-2′-yl)iminomethylphenoxy]alkane, *2–6*

6-Methoxy-2-(4-hydroxybenzylidenamino)benzothiazole (5 mmol), was dissolved in minimum amount of DMF, then 40 mL of acetone was added with potassium carbonate (5 mmol) and 6 mmol of appropriate 1,*n*-dibromoalkane (n = 4, 6, 8, 10, 12) were refluxed for 19 h. Then the reaction mixture was filtered and allowed it to cool to room temperature. The yellow precipitate formed was collected by filtration. The solid thus obtained was recrystallized several times with ethanol until transition temperatures are constant. The percentage of yields of the title compounds are given in Table 1. Spectroscopic data (IR, NMR) for the representative compound **4** are summarized as follows.

Compound **4**: EI-MS *m/z* (rel. int. %) (Fig. 2): 678.4 (12) [M^+], 514.3 (100); IR ν_{max} (KBr, cm^{-1}): 3067 (C–H aromatic), 2918, 2851 (C–H aliphatic), 1598 (C=N Schiff base), 1570 (C=N benzothiazole), 1247