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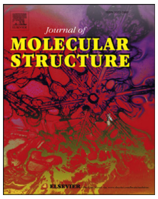

Design and characterization of novel *bis*-benzamide liquid crystalline materials

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ABSTRACT

A new homologous series of symmetric, bent-shaped *bis*-benzamide dimers have been prepared. Several 1,n-*bis*(*p*-aminophenoxy)alkanes (n = 3, 5, 9,10,11) were employed as spacers and *p*-hexyloxy tails have been synthesized and appended to the spacers by amide linking groups. Different important parameters were explored using computational analysis by semi empirical method. The experimental results were correlated with theoretical studies and relationship between molecular structure and mesogenic behavior has been established. The mesomorphic properties of the resultant dimers were characterized by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) equipped with a hot stage. Change in mesomorphic properties with change of methylene spacers was observed. Enantiotropic mesogenic behavior was exhibited by D_3A_6, $D_{10}A_6$ and $D_{11}A_6$ and the needle like and blurred schleiren textures were observed. It was observed that increased methylene spacers chain length decreased the melting temperatures. Thermogravimetric analysis revealed the thermal stability of dimers upto 360 °C.

1. Introduction

Liquid crystal materials are one of the extensively investigated dynamic research area playing an important technological role in new and emerging electro-optics [1]. Thermotropic liquid crystals are the type of liquid crystals which consist of either rod like or disc like organic molecules. Rod like thermotropic liquid crystals contain linearly linked ring systems and flexible chains having polarizable moieties [2,3]. As the functional groups influences the mesophase behaviour so functional groups having permanent dipole moment are commonly incorporated to maintain the linearity as well as the stability of mesogens. Azo [4–6], azomethine [7,8], esters [9] are among the commonly used linking groups and are known for mesomorphic properties.

Flexible spacers having similar groups on either side are termed as dimeric mesogens which possess the decisive fundamental components of many thermotropic main group polymers [10,11]. Additionally, liquid crystalline behaviour of dimeric compounds is mostly controlled by its molecular design and a minor change in the molecular architecture can significantly amend its properties [12]. Modification in spacer length and terminal chain length brings about variation in liquid crystalline phases. A variety of mesogenic compounds based on *p*-alkoxybenzoic acid tails and their derivatives with different flexible spacers have been widely explored for the design of diversity in liquid crystalline behaviour [13–18].

The compounds having amide linking groups with aromatic rings are thought to promote the formation of hydrogen bonding between different molecules. Such arrangement of molecules may support the formation of layered structures thus imparting mesomorphic behaviour. An extensive literature survey revealed that liquid crystals having an amide linkage along with a flexible methylene spacer may exhibit unique properties like supramolecular arrangement and stability [19]. Distinctive macroscopic polarization within layers of bent shape molecules are capable of special steric interactions causing liquid crystalline behaviour [20–22].

H-bonding between molecules both in calamitic and bent-shaped materials supports smectic mesomorphism [23]. Very recently, the amino group has been also utilized for the formation of an amide linking unit in bent-shaped materials which exhibited a smectic A phase whereas no liquid crystalline properties appeared in corresponding N-methyl derivatives owing to an altered molecular conformation and missing hydrogen bonding [24]. It is generally well acknowledged that the amide group

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exhibits higher rigidity due to the partial double bond character of the C—N bond, which results in higher clearing temperatures of mesogens in comparison to the analogous materials possessing different linking groups like esters, schiff bases etc. [25]. However, there are only a few examples of low molecular weight mesogens with an amide linking group to evaluate the role of the amide group on mesomorphic properties. In another work three series of novel bent-shaped liquid crystals based on a 3-aminophenol central core possessing five aromatic units have been reported [26]. In literature so far, no such symmetrical dimeric benzamide mesogens have been investigated, so keeping in mind the importance of this class of compounds [27] we have synthesized various *bis*-benzamides. Our newly prepared *bis*-benzamides have different methylene spacers with ether linkage (to induce flexibility in molecular chains), two amide groups as linking groups and four benzene rings to induce rigidity in structures.

2. Experimental

2.1. Materials

Alkyl di bromides (1,3- 1,5- 1,9- 1,10- 1,11-), hexylbromide, 4-hydroxybenzoic acid, hydrazine monohydrate, 4-nitrophenol, palladium on activated carbon (Pd/C, 10%), anhydrous ethanol (EtOH) were purchased from Aldrich Chemical Co. and used as received. All other solvents and reagents were purchased commercially and used without further purification.

2.1.1. General procedure for the p-aminophenoxy alkanes synthesis (D_n)

The synthesis of *p*-aminophenoxy alkanes was accomplished in two steps, as shown in Fig. 1. In the first step various *p*-nitrophenoxyalkanes were synthesized according to the given procedure [28]. Finely powdered anhydrous potassium carbonate (7.86 g, 57 mmol) was added to a solution of *p*-nitrophenol (8.0 g, 57 mmol) in DMF (50 mL) and toluene (30 mL). The reaction mixture was stirred at room temperature for 1 h under an inert atmosphere of nitrogen. Afterwards, dropwise addition of the corresponding dibromoalkane (28.5 mmol) was made over a period of 30 min and the mixture was maintained at 120 °C for 12 h. The conversion of reactants into the product was monitored by TLC (n-hexane: ethyl acetate 1:4). After the complete consumption of reactants, the reaction mixture was cooled to room temperature and then precipitated in distilled water, filtered and recrystallized from ethanol. In the second step, 10% Pd/C (0.03 g) was added in solution of *p*-nitrophenoxy alkanes (4 mmol) in 90 mL of ethanol followed by the dropwise addition of hydrazinium monohydrate (3.8 mL) to the reaction mixture over a period of 1 h. The reaction mixture was refluxed for 3 h after which the catalyst was filtered off. The *p*-aminophenoxy alkanes (D_3,D_5,D_9,D_{10} and D_{11}) were obtained by precipitation in distilled water, followed by drying and recrystallization in the smallest possible volume of ethanol [29].

2.1.2. Synthesis of 4-hexyloxybenzoic acid (A_6)

4-hexyloxy benzoic acid (A_6) was prepared by hexylation and hydrolysis of ethyl 4-hydroxybenzoate using standard procedure. To the solution of ethyl 4-hydroxybenzoate (120.4 mmol, 20 g) in acetone (80 mL) and 10% dry DMSO, 20 g of finely powdered anhydrous K_2CO_3 was added. Afterwards, dropwise addition of 1-bromohexane (120.4 mmol, 19.8 g) was made while subsequently purging with nitrogen gas and refluxing the reaction mixture for 48 h and monitored by TLC using (n-hexane:ethylacetate: methanol 9:4:1). After successful completion reaction mixture was cooled to room temperature poured into 200 mL of water, acidified with few drops of dil. HCl. Later product was separated by extracting with DCM and dried over $MgSO_4$ anhydrous, filtered and then solvent was evaporated. (Yield 78%). In next step, a mixture of hexyloxy ester (3 g, 0.012 mol), 0.5 M KOH in ethanol and 5% H_2O (150 mL) was heated under reflux for 12 h. The mixture was acidified with 10% HCl and precipitated in water. The solid was filtered and recrystallized in absolute ethanol. Product was dried under vacuum at room temperature. Yield 82%, m.p. 100–105 °C (lit.103–105 °C).

2.1.3. Synthesis of bis-benzamides (D_nA_6)

The synthetic route used in the preparation of *bis*-benzamides is illustrated in Fig. 1. p-hexyloxy benzoic acid was converted into *p*-hexyloxy benzoyl chloride and then coupled with 1,n-*bis*(*p*-aminophenoxy)alkanes to yield respective *bis*-benzamides. The synthetic details for *bis*-benzamide compounds are as follows, *p*-hexyloxy benzoic acid (**A_6**) was reacted with five diamines including D_3, D_5, D_9, D_{10} and D_{11} to synthesize five novel dimeric *bis*-benzamides (D_3A_6, D_5A_6, D_9A_6, $D_{10}A_6$ and $D_{11}A_6$). For this purpose, **A_6** was converted into respected acid chloride, under anhydrous condition. Afterwards an equimolar amount of diamine completely dissolved in dry THF and triethylamine, was added in one portion into the acid chloride, while stirring for 24 h under inert conditions. The precipitates formed when reaction mixture was poured into acidified water and filtered. Products thus obtained were found to be pure enough by TLC (EtOAc: n-hexane 2:1).

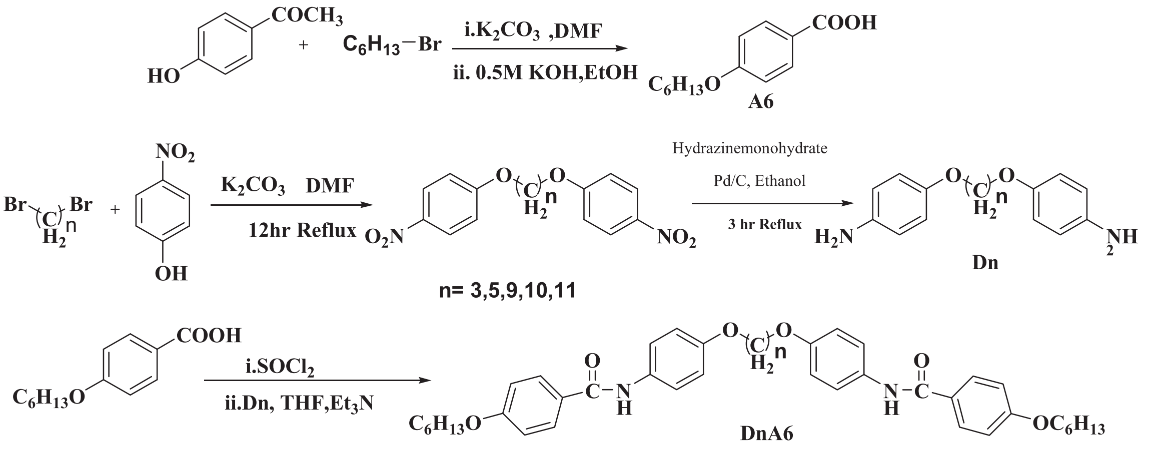

Fig. 1. Synthesis of *bis*-benzamides.