SYNTHESIS AND CHARACTERIZATION OF HELICAL ARCHITECTURE DICARBOXYLIC ACID BASED BOLAAMPHIPHILIC CONTAINING DIESTER GROUP

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***ABSTRACT**: A new class of dicarboxylic bola-shaped compounds 1–2, possessing phthalyl head groups and diol spacers are synthesized and characterized. Keeping phthalyl head group common for all two diester-dicarboxylic acids, the spacer moiety is systematically altered by three and eight carbon atoms in 1 and 2, respectively. The flexible spacer moiety propane-1, 2-diol in compound 1 is replaced by1, 4- cyclohexane dimethanol in 2, respectively. The compounds were characterized using elemental analysis, and various spectroscopic techniques such as Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy, ESI-Mass Spectroscopy and Field Emission Scanning Electron Microscopy (FE-SEM). The FE-SEM structure obtained for compounds 1 and 2 indicates the formation of self-assembled single stranded helical architecture structure mediated through O–H. . .O; C–H. . .O interaction of the end carboxylic acids. The thermal behaviours of these compounds under nitrogen atmosphere in the range 150-400°C have been stidies.*

Keywords: bola-shaped, helical architecture, hydrogen bonded

I. INTRODUCTION

Dicarboxylic acids are organic compounds that are substituted with two carboxylic acid functional groups. In molecular formulae for dicarboxylic acids, these groups are often written as HOOC-R-COOH, where R may be an alkyl, alkenyl, akynyl, or aryl group [1]. Although the dicarboxylic acids do not occur in appreciable amounts as components of animal or vegetal lipids, they are in general important metabolic products of fatty acids since they originate from by oxidation [2, 3]. Dicarboxylic acids are suitable substrates for preparation of organic acids for the pharmaceutical and food industries. Furthermore, they are useful materials for the preparation of fragrances, polyamides, adhesives, lubricants, and polyesters [4-6].

Dicarboxylic acids can be used to prepare copolymers such as polyamides and polyesters. In general; dicarboxylic acids show the same chemical behavior and reactivity as monocarboxylic acids. Here we have synthesized some new class of dicarboxylic acid, structurally similar to bolaamphiphiles and their corresponding metal macrocyclic compounds. This form the basis for a number of areas of research in chemistry and biochemistry, notable that of lipid polymorphism, material chemistry etc. depending on length and flexibility of the linker, some bolaamphiphiles can be fold in half and micelles [7,8]. Bolaamphiphiles show abundant interfacial confirmation and the potential to form a nano structures in organized assemblies. It has been reported that bolaamphiphiles can form multilayer film or some exotic structure on sub phases containing various metal ions [9,10]. Diester-dicarboxylic compounds had gained significant importance, due to their potentiality for the formation of macrocyclic dilactones and tetralactones [11-15]. Understanding the importance of the diester-dicarboxylic compounds, by the researchers constant attempts have been made to synthesis these compound, adapting various synthetic methodologies [16-19]. Among the synthetic method, the synthetic strategy involving desymmetrization [20, 21] of cyclic anhydride using dihydroxy compounds is considered to be superior method because of its high yield. With an understanding on the COOH-COOH intermolecular association, we recently demonstrated that these diester-dicarboxylic compounds are potential compounds for the formation of hollow microtubes by introducing appropriate spacer moiety through its self assembly process [22-24] intermolecular interaction and the literature on morphology structures of varieties of fatty acids are rich. To best of our knowledge, the present paper in addition to reporting the compounds containing the lowest number of carbon atom in the spacer segment (i.e. three in compound 1 and eight in 2), illustrate the formation of the first amide-free dicarboxylic-based helical structure. All these compounds possessing almost similar helical structure, the FE-SEM micrograph recorded for compound **1** and **2** indicates the formation of ''helical architecture structure''.

II. MATERIALS AND METHOD

All the chemicals are purchased from Aldrich & Co. and are used without any further purification. Microanalysis of the compounds was done using an Elemental HITACHI CHNS/O analyzer, Germany. Mass analysis was performed using electron spray ionization (ESI$^+$) technique on water Q T of-micro mass spectrometer. IR spectra were recorded using KBr pellets on a Perkin-Elmer Spectrum DRS, FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded (200 and 50.3 MHz, respectively) on a BRUKER Advance DPX 200 NMR spectrometer using methanol-d4 or CDCl$_3$. 90^0 pulses for ^{1}H (8.9 μs) and ^{13}C (5.9 μs) nucleus was determined using Bruker XWIN-NMR software using standard ''paropt'' pulse program at CSIR, CSMCRI, Bhavnagar, Gujarat. All ^{1}H NMR spectra were calibrated with respect to TMS and TMS was used as an internal reference for solvents such as CDCl$_3$ and CD$_3$OD. Thermal decomposition experiments using Mettler Toledo TGA/DSC^1, STAR^e under a nitrogen atmosphere. The hating rate for the thermal decomposition employed was 10°C min^{-1}.

2.1 Synthesis of compounds

2.1.1 Phthalic acid 1-[2-(2-carboxy-benzoloxy)-propyl] ester

Phthalic anhydride (0.02 mmol) and propane-1,2-diol (0.01 mmol) in dichloromethane were mixed homogeneously under nitrogen atmosphere. The reaction mixture was thermostated at 0^0C and added 0.06 mol of triethylamine (TEA). The whole reaction mass was allowed to continue with same condition for three hours with constant stirring. The thermostat was removed and continued with constant stirring for overnight at room temperature. After all the anhydride was reacted, the solvent was evaporated. The residue was cooled again at 0^0C and added 200 mL of saturated NaHCO$_3$ solution in fractions and treated with ether. The aqueous layer was cooled and acidified with dilute HCl with constant stirring till the effervescence stops. A white precipitate obtained was filtered, washed by water thoroughly and dried. Anal data: yield (90%). **MS [ESI$^+$]** Calcd. for C$_{19}$H$_{16}$O$_8$Na (M+Na)$^+$, 372, found: 372.1. Anal. Calcd. for C$_{19}$H$_{16}$O$_8$: C, 60.33; H, 3.93%, found: C, 60.65; H, 4.1%. **^{1}H NMR** (methanol-d$_4$, 200 MHz, TMS) 7.85-7.60 (m, 8H, Ar-H), 1.42-1.38 (d, 3H, -CH$_3$), 4.69-4.41 (m, 2H, -CH$_2$), 5.49-5.37 (t, 1H, -CH). **^{13}C [methanol d$_4$, 50 MHz] NMR**: 173.8 (C=O), 167.2 (C=O), 131.5, 130.9 (quat –C), 129.9, 128.5, 128.3, 128.2 (=CH), 70.5-67.5 (–OCH$_2$), 15.4 (-CH$_3$). **IR spectra (v, cm^{-1})**. 3426 (-OH), 3071 (Ar.-CH), 2966, 2877 (Aliphatic -CH), 2675, 2542, 2110, 1721 (C =O ester), 1694 (C=O acid), 1601, 1420, 1311, 1126 (C-O).

2.1.2 Phthalic acid 1-[4-(2-carboxy-benzoloxyloxymethyl)-cyclohexylmethyl] ester

The above-mentioned procedure was repeated except the addition 1, 4-cyclohexane dimethanol (0.01 mmol) in place of propane 1, 2-diol for the synthesis of **2**. Suitable single crystals were obtained in 1:1 ethanol–water mixture in a week time. Yield (90%). Anal data: yield (90%). **MS [ESI$^+$]** Calcd. for C$_{24}$H$_{24}$O$_8$Na (M+Na)$^+$, 440, found: 440.4. Anal. Calcd. for C$_{24}$H$_{24}$O$_8$: C, 65.45; H, 5.49%, found: C, 65.21; H, 5.39%. **^{1}H NMR** (methanol-d$_4$, 200 MHz, TMS) 7.78-7.63 (m, 4H, Ar-H), 4.26-.12-4.09 (t, 4H, OCH$_2$), 2.26-1.87 (m, 2H, -CH), 1.61-1.29 (t, 8H, CH$_2$). **^{13}C [methanol d$_4$, 50 MHz] NMR**: 174.46 (C=O), 167.37 (C=O), 132.80, 132.62 (quat –C), 132.56, 131.19, 129.30, 128.58 (=CH), 70.50 (–OCH$_2$), 39.03 (-CH), 28.93, 24.55 (-CH$_2$). **IR spectra (v, cm^{-1})**. 3478 (-OH), 3030 (Ar.-CH), 2922, 2879 (Aliphatic -CH), 2558, 2363, 1743 (C =O ester), 1689 (C=O acid), 1598, 1492, 1283, 1249, 1125 (C-O).

III. RESULTS AND DISCUSSION

3.1 Synthesis

Following the synthetic strategy of compounds shown in scheme **(Fig 1)**, compound **1** and **2** were synthesized upon phthalic anhydride with appropriate diol such as propane-1, 2-diol and 1,4- cyclohexane dimethanol respectively. The bola-shaped diester-dicarboxylic compounds were characterized using various spectroscopic techniques such as NMR, IR, MS and TGA/DSC. All these compounds possess two terminal hydroxyl head groups and the anhydride in common. The two anhydride moieties possessing bollamphiphilc dicarboxylic acid at its terminal positions, they are bridged covalently through saturated and unsaturated diol, such as propane-1, 2-diol and 1, 4-cyclohexane dimethanol respectively.
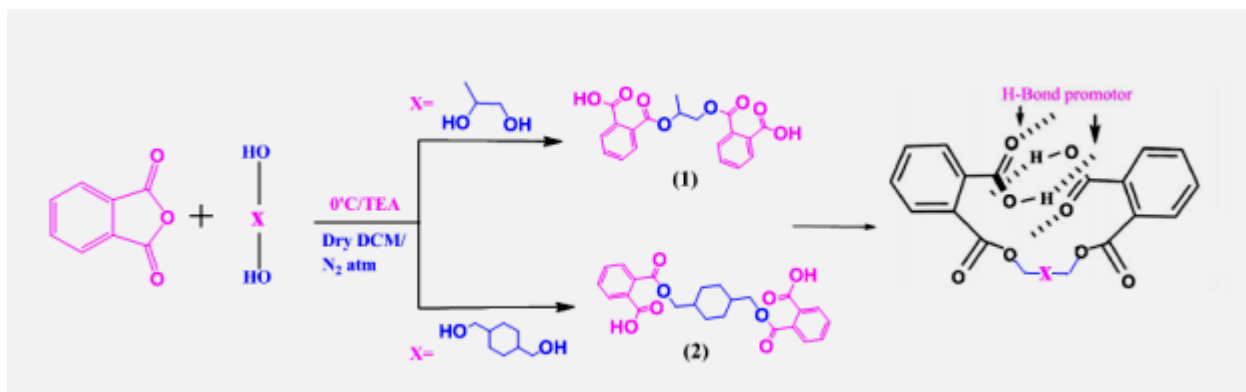
Fig 1. **(a)** Compound **1** and (b) compound **2** with their functional role [22].

The presence of carboxylic acid groups in the both terminal position of the compound **1** to the phenyl ring and the flexibility at the central spacer segment combinedly facilitates to interconnect the adjacent molecules and form single stranded helical superstructure through its strong intermolecular carboxylic O-H…O hydrogen bond shown in compound **1** (Fig. 3 a and b) [25-27]. The propagation of helical assembly mediated through O-H….O interaction of carboxylic acid being common for compound **1** and **2**, the C-H…O interaction mediated through C=O group of the ester unit, involves in strong inter helical interaction with the neighbouring helices and defines the dimensionality of the molecules packing as shown in the Fig. 3a and b respectively. The increase in the number of carbon and the flexibility on the spacer moiety, increase the pitch distance of the helical strand in the order **1< 2.**
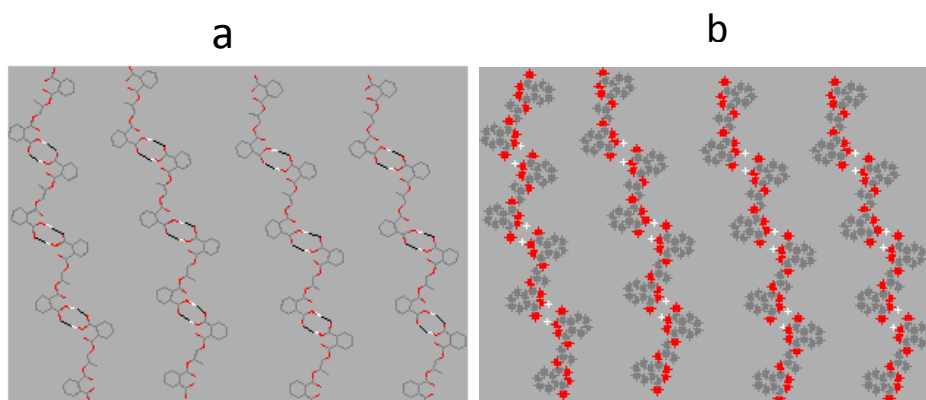

Fig 3. (a) and (b) one dimensional handed helical construction of compound **1** through strong O-H…O interaction between the terminal carbonyl groups (red balls represent oxygen atoms and black white line represent O-H….O Hydrogen bonding).

3.2 Morphological characterizations

The helical architecture obtained in the **Fig 4a and b** respectively, the crystal growth pattern inspired us to investigate their morphology using FE-SEM. All these attempts have resulted the compound **1** and **2** in solid state except ethanol:water mixture. A simple room temperature evaporation of compound **1** and **2** dissolved in 1:1 water :ethanol mixture of microcrystalline samples after one week. Interestingly the FE-SEM micrograph obtained with gold cotted for compound **1** and **2** shown the formation of helical architecture . Interestingly, the helical structure for **1** and **2** measured with an understanding from the crystal structure and its packing diagram influenced by the weak C–H. . .O and O–H. . .O interaction, an attempt has been made to derive a plausible growth mechanism to understand the morphological difference obtained by FE-SEM image. Thus the direction and strength of the C–H. . .O interaction observed from the crystal structure dictates, the nucleation process during crystallization, which ultimately defines the morphology as helical architecture for compound **1** and **2**.
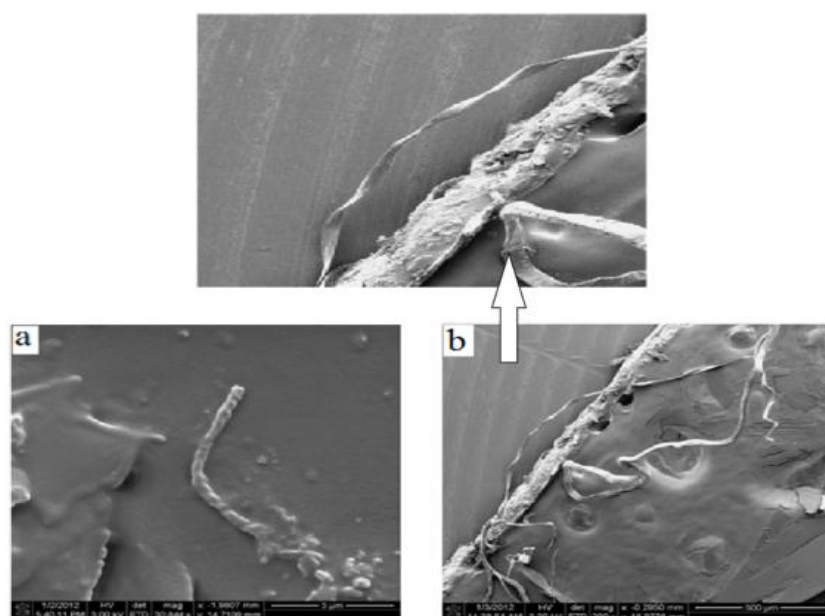
Fig 4. FE-SEM emages (a) and (b) of compound **1** and **2** in 1:1 ethanol: water mixture showing the halical architecture.

3.3 IR Investigation

All bolaamphiohilc compounds **1-2** possessing carboxyl unit as well as ester functional group in common. The peak at 1700-1730 cm^{-1} region for all compounds described to the C=O stretching mode of end COOH group characteristic of the formation of carboxylic dimmers [28]. The peak appeared around 3400 cm^{-1} indicates the presence of carboxylic OH group **Fig 5**.

The additional signal in the IR region at 1700-1740 cm-1 region indicates the spacer COO group. Thus, the two set of IR peak appeared at this region indicates the presence of terminal and spacer COO group in all these compounds **1** and **2**.
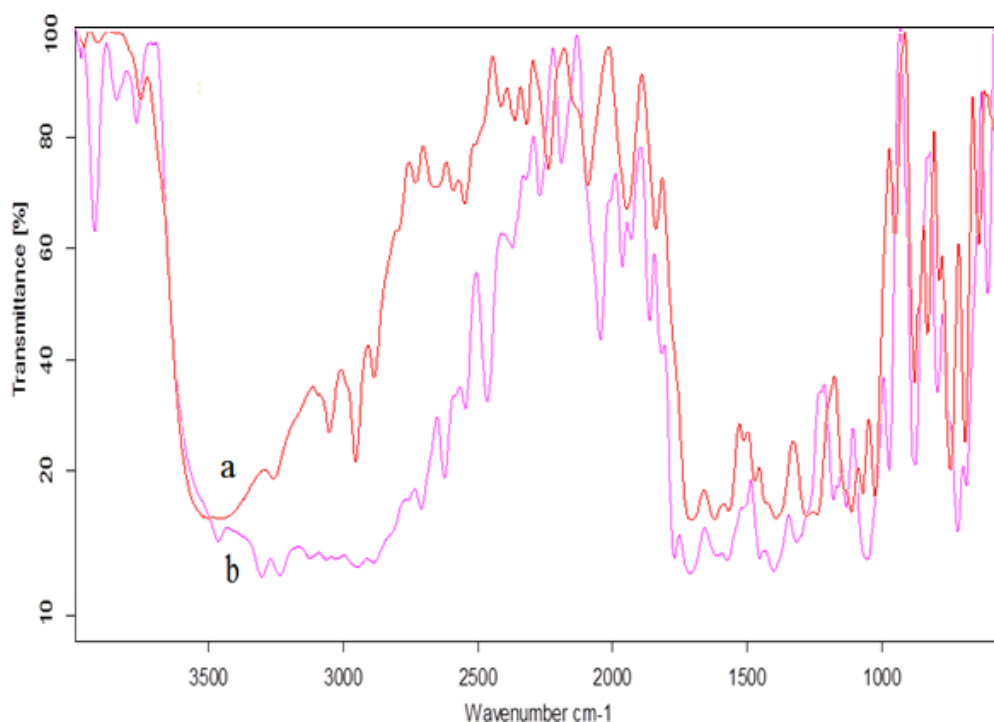

Fig 5. FT-IR Spectra of compound 1 and 2.

3.4 Thermal analysis

The TGA curves of the compounds **1** and **2** are shown in **Fig. 6a and b** respectively. The weight loss in the TGA curves of the compounds **1** and **2** appear at a tempreture below 165°C, and are related to the removal of the uncoordinated water molecule due to water:ethanol mixture of microcrystalline. Compounds **1** and **2** have the same decomposition tempreture with the DTA sharp endothermic peaks around onset 346.69 and 358.51°C, suggesting that they both have thermal stabilities and may have similar decomposition pathways on TGA curves[24]. The weight losses occurred in the tempreturer range 150-400°C for the compound **1** and **2** are mainly due to the breakage of intermolecular carboxylic O–H...O hydrogen bond. The first decomposition values are 7.46 and 1.40 mg of compound **1** and **2**, respectively. From Fig. 6a and b, it can also be that the continunig weight loss in the TGA corve of compound of compound **2** above 750°C are entirely cause by the gradual elimination of carbon decomposition resulting from compound decomposition under N_2 atmosphere.
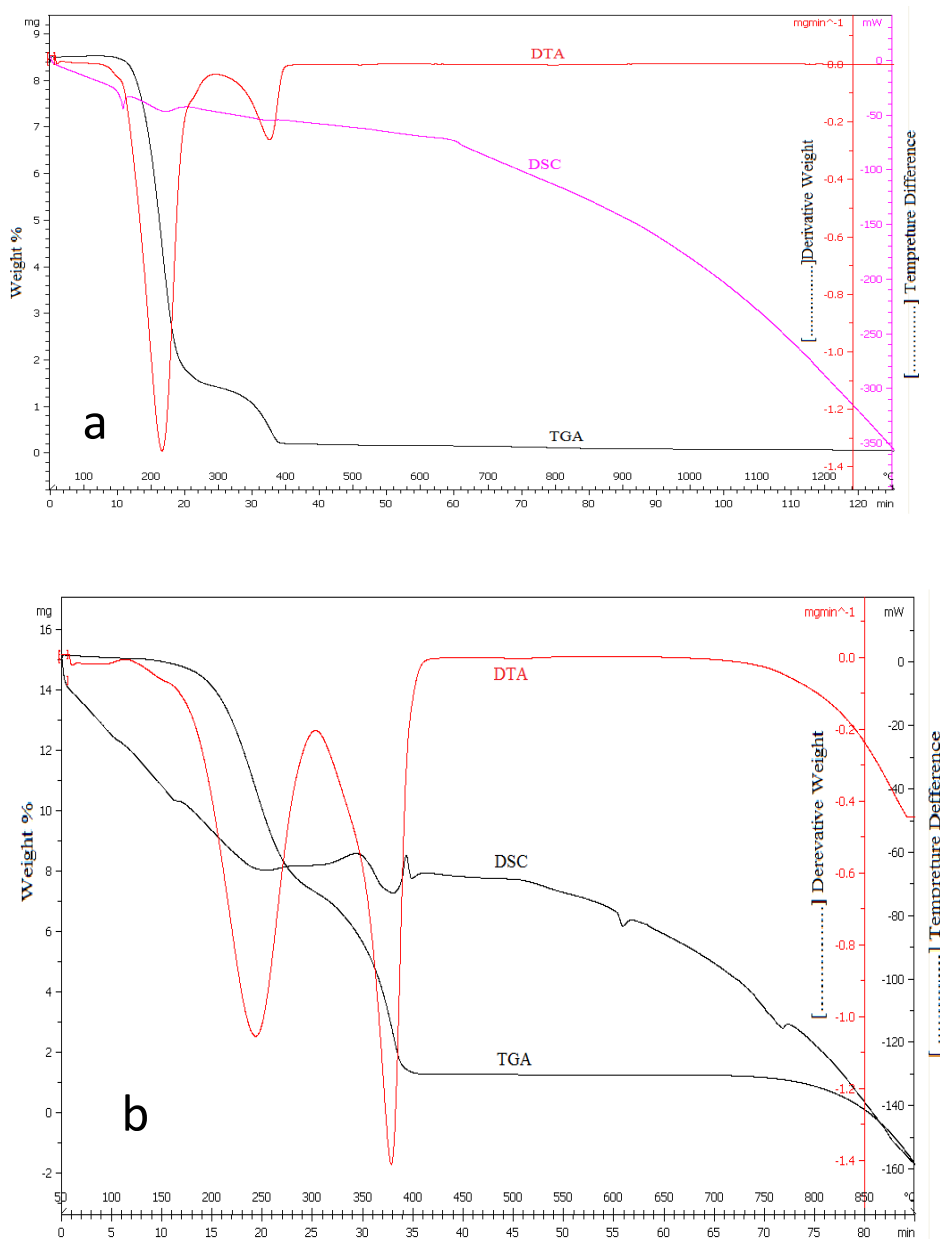

Fig 6. TGA-DTA/DSC curves of compounds **1** and **2.**

IV. CONCLUSIONS

In summary, the diester-dicarboxylic bola-shaped compounds were shown to form helical structure. The O–H. . . O interaction involves in constructing the supramolecular helices and the C–H . . . O interaction involves in bringing the helices into closer contact is illustrated in detail. The FE-SEM images establishes that the compound **1** and **2**, forming helical. Thus the supramolecular self-assembly process mediated through C–H. . .O and O–H. . .O interaction establishes the morphology. The helical strands in **1** and **2** with respect to their pitch distance in the order **1 < 2**, the flexible spacer moiety and weak H-bonding interactions are combinedly plays significant role in bringing the morphology. The thermal analysis also shows that compounds **1** and **2** possess high thermal stabilities and have similar decomposition pathway.

ACKNOWLEDGMENTS

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