Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

MOLECULAR STRUCTURE

Hydrogen bonded helices: Synthesis, crystal structure and self-assembled microtubes

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ARTICLE INFO

Article history: Received 20 June 2008 Received in revised form 11 August 2008 Accepted 16 August 2008 Available online 28 August 2008

Keywords: Hydrogen bond Self-assembly Helix Microtubes Supramolecular chemistry

ABSTRACT

Dicarboxylic bola-shaped compounds **1–3**, possessing phthalyl head groups and diol spacers are synthesized and characterized. Keeping phthalyl head group common for all three diester-dicarboxylic acids, the spacer moiety is systematically altered by two and four carbon atoms in **1** and **2**, **3**, respectively. The flexible spacer moiety ethane-1,2-diol in compound **1** is replaced by *cis*-but-2-ene-1,4-diol and 1,4-butane diol in **2** and **3**, respectively, to study the effect on the morphology of the microcrystal grown on them. Thus compound **2** and **3** though posses four carbon atoms in their respective spacer moiety, they differ by their rigidity. The single crystal X-ray structure obtained for **1**, **2** and **3** indicates the formation of self-assembled single stranded helical structure mediated through O–H…O interaction of the end carboxylic acids. Interestingly compound **1** self-assembled into microtubes in ethanol:water solvent mixture. The solvent and the O–H…O; C–H…O interaction combinedly play crucial role in molecular selfassembly process and defines the morphology for **1** into "microtube" whereas **2** and **3** forming "bar" fails to produce such tubular texture though their respective crystal structure shows single stranded helices. The role of weak C–H…O interaction, incorporation of rigid spacer and various other factors such as polarity of the solvents are discussed in detail to explore the difference in the morphology.

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1. Introduction

Carboxylic amphiphiles form variety of self-assemblies such as micelles, fibers and crystals [1-6]. Molecules with hollow tubular structures [1–7], and pores as synthetic ion channels [8–9] offer wide variety of applications in chemistry, biology, material science, molecular transporters [10], molecular containers [11], drug delivery system in pharma/medicine [12-15], host-guest inclusion and molecular separation, etc. Weak interaction [16-17], such as inter, intra molecular H-bonding, Van der waals and π -stacking are known to generate superstructure covering nano to micro level fibres, rods, ribbons, wires, sheets and tubular materials with attractive molecular architectures, such as helix, grids and knots, etc. Among the different supramolecular architecture, self-assembled helical structures are ubiquitous in nature and can be found in many biologically important macromolecules like DNA which possess two intertwined helices, and many proteins have helical substructures. Hence, chemists have made significant efforts to introduce and control the helicity in many artificial systems [18-19]. Extensive investigation on carboxamide-based bolaamphiphiles, with varying head groups such as nucleotides [20-22], peptides [23-27] and sugars [28-31] are reported to form tubes. Carboxylic bolaamphiphiles, upon treating with aliphatic amines, or their Na, K salt [32,33] with controlled pH, were also demonstrated to form microtubes. All these compounds possessing NH group in general, results into gel materials [20-33], caused by the complex inter and intra molecular interaction. Up-to-date report explores the formation of microtubes, mainly using carboxamide-based bolaamphiphiles, none of the above report, deals amide-free dicarboxylic acid bolaamphiphiles. Further, Shimizu's odd-even effect [24,29,31] correlating the number of the CH₂ group in the alkyl linker and microtube formation, gains significant importance. Carboxamide-based bolaamphiphiles with even number CH₂ group in the spacer from 6 to 20 though already reported, spacer moiety with less than six CH₂ group, were not attempted till today. With an interest to understand the nature of the supramolecular network, we aimed to synthesis an amide-free dicarboxylic system. Accordingly the compound 1-3 with phthalyl-based dicarboxylic head group, composed exclusively by terminal carboxylic acids and spacer ester moieties are synthesized. The compound **1**, possess $(CH_2)_n$ spacer where n = 2, while the compound **2** and **3** consists four carbon atom with rigid (–C=C–) spacer and flexible CH₂ groups, respectively. Surprisingly no report has been found exclusively on acid-based microtubes, though the understanding on acid-acid [25] intermolecular interaction and the literature on crystal structures of varieties of fatty acids are rich. To best of our knowledge, the present paper in addition to reporting the com-



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^{0022-2860/\$ -} see front matter @ 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2008.08.016

pounds containing the lowest number of carbon atom in the spacer segment (i.e. two in compound **1** and four in **2** and **3**), illustrate the formation of the first amide-free dicarboxylic-based microtube. All these compounds possessing almost similar helical structure, the SEM micrograph recorded for compound **1** indicates the formation of "microtube", while compound **2** and **3** does not form tube in the chosen solvent medium is explored based on the supramolecular self-assembly through vectorial propagation of the O–H...O and C–H...O

2. Experimental

All the chemicals are purchased from Aldrich & Co. and are used without any further purification. Microanalysis of the compounds was done using a Perkin-Elmer PE 2400 series II CHNS/O elemental analyzer. Mass analysis was performed using electron spray ionization (ESI⁺) technique on a waters Q Tof-micro mass spectrometer. IR spectra were recorded using KBr pellets on a Perkin-Elmer Spectrum GX FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded (200 and 50.3 MHz, respectively) on a BRUKER Avance DPX 200 NMR spectrometer using methanol- d_4 or CDCl₃. 90° pulses for ¹H (8.9 µs) and ¹³C (5.9 µs) nucleus was determined using Bruker XWIN-NMR software using standard "paropt" pulse program. All ¹H NMR spectra were calibrated with respect to TMS and TMS was used as an internal reference for solvents such as CDCl₃ and CD₃OD. SEM was performed on a LEO 1430VP. All solvents were freshly purified by general distillation process [34] and used as and when required.

2.1. Single crystal X-ray determination

In each case of compound **1**, **2** and **3**, a crystal of suitable size was selected and mounted on the tip of a glass fiber and cemented using epoxy resin. Summary of the crystallographic data for compound **1**, **2** and **3** are given in Table 1. Intensity data for both crystals were collected using Mo-K_{α} (λ = 0.71073 Å) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 100 K. The data integration and reduction were processed

Table 1

Summary	of	crystallographic	data f	for	compound	1, 3	2	and	3
						-,	_		-

Identification Code	1	2	3
Chemical formula	C ₁₈ H ₁₄ O ₈	C ₂₀ H ₁₆ O ₈	C ₂₀ H ₁₈ O ₈
Formula weight	358.29	384.33	386.34
Crystal color	Colorless	Colorless	Colorless
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P21/c	P21/c	P21/c
a (Å)	16.919(3)	15.634(6)	7.4200(13)
b (Å)	4.9581(9)	7.292(2)	10.2089(17)
c (Å)	20.580(4)	21.730(6)	11.947(2)
α(°)	90	90	90
β (°)	108.764(3)	133.220(17)	93.371(3)
γ(°)	90	90	90
Ζ	4	4	2
V (³)	1634.6(5)	1805.3(10)	903.4(3)
Density (mg/m ³)	1.456	1.414	1.420
Absorption coeff. (mm ⁻¹)	0.116	0.111	0.111
F(000)	744	800	404
Reflections collected	7112	8741	4373
Independent reflections	3230	3184	1576
R(int)	0.0480	0.0695	0.0528
Number of parameters	284	309	309
(Goodness of fit) on F^2	0.814	0.917	1.181
Final R ₁	0.0575	0.0539	0.0661
$wR_2(I > 2\sigma(I))$	0.1174	0.1030	0.1316
Weighted R_1 , wR_2 (all data)	0.1182/0.1383	0.1311/0.1337	0.0897/0.1398

with SAINT [35] software. An empirical absorption correction was applied to the collected reflections with SADABS [36]. The structures were solved by direct methods using SHELXTL [37] and were refined on F^2 by the full-matrix least-squares method using the SHELXL-97 [38] package. Graphics are generated using PLATON [39] and MERCURY 1.3. [Mercury 1.3 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2003-2004]. In both the compounds all non-hydrogen atoms were refined anisotropically till convergence is reached. Most hydrogen atoms in both the ligands were located from the difference Fourier map and refined isotropically and the rest are stereochemically fixed at idealized positions. CCDC number 640778, 640779 and 686003 contain the supplementary crystallographic data in CIF format for all three compounds reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2. Syntheses of compounds

2.2.1. 2-({2-[(2-Carboxybenzoyl)oxy]-ethoxy}carbonyl)benzoic acid (1)

Phthalic anhydride (0.04 mmol) and ethane-1.2-diol (0.02 mmol) in dry dichloromethane were mixed homogeneously under nitrogen atmosphere. The reaction mixture was thermostated at 0 °C and added 0.06 mmol 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 °C and added 200 mL of saturated NaHCO₃ 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. Suitable single crystals were obtained in ethanol-water mixture in a week time. Anal data: yield (85%). MS[ESI⁺] Calcd. for C₁₈H₁₄O₈Na (M+Na)⁺, 381.06, found: 381.12. Anal. Calcd. for C₁₈H₁₄O₈: C, 60.33; H, 3.93%, found: C, 60.65; H, 4.1%. ¹H NMR (methanol- d_4) 7.66 (m, Ar, 2H), 7.62 (m, 2H), 7.58 (m, 4H) 4.60 (-CH₂, 4H). ¹³C [methanold₄] NMR: 169.58 (C=O), 168.86 (C=O), 132.36, 132.01 (quat -C), 131.37, 131.05, 129.04, 128.53 (=CH), 63 (-CH₂). IR spectra (v, cm⁻¹). 3468, 2970, 1723, 1694, 1419, 1315, 1290, 1127.

2.2.2. cis-2-[({4-[(2-Carboxybenzoyl)oxy]but-2-en-1-yl}oxy) (hydroxy)methyl] benzoic acid (**2**)

The above-mentioned procedure was repeated except the addition *cis*-but-2-ene-1,4-diol (0.02 mol, 1.645 ml) in place of ethane-1,2-diol for the synthesis of **1**. Suitable single crystals were obtained in ethanol-water mixture in a week time. Yield (68%). MS[E-SI⁺] Calcd. for $C_{20}H_{16}O_8Na$ (M+Na)⁺ 407, found: 407.02; Anal. Calcd. for $C_{20}H_{16}O_8$: C, 62.50; H, 4.19%, found: C, 62.80; H, 4.30%. ¹H NMR (methanol-*d*₄): 7.65–7.64 (m, ArH, 2H), 7.60–7.56 (m, ArH, 6H) 5.94, 5.92, 5.90 (t, =CH, 2H, *J* = 4 Hz) 4.98, 4.96, 4.94 (d, -CH₂). ¹³C NMR (methanol-*d*₄): 170.35 (C=O), 169.68 (C=O), 134.03, 133.28 (quat -C), 132.48, 132.08, 130.26, 129.15 (=CH), 129.58 (quat -C), 62.31 (-OCH₂). IR spectra (ν , cm⁻¹). 3480, 2954, 1735, 1687, 1416, 1343, 1281, 1254, 1126.

2.2.3. 2-({4-[(2-Carboxybenzoyl)oxy]butoxy}carbonyl)benzoic acid (3)

The above-mentioned procedure for the synthesis of **1**, was repeated except the addition 1,4-butane-diol in place of ethane-1,2diol. Suitable single crystals were obtained in ethanol–water mixture in a week time. Yield (69%). Anal. data. MS[ESI⁺]: Calcd. for $C_{20}H_{18}O_8Na$ (M+Na⁺): 409, found: 409.28. Anal. Calcd. for $C_{20}H_{18}O_8$: C, 62.17; H, 4.70%, found: C, 62.21; H, 4.62%. ¹H NMR (CDCl₃) δ : 7.5 (b, 2H, OH), 7.536–7.822 (m, 8H, Ar-H), 1.879– 1.896 (m, 4H, $-CH_2$), 4.347–4.370 (m, 4H, $-CH_2$); ¹³C NMR. (CDCl₃) δ : 174.49 (C=O), 168.40 (C=O), 128.77 (quat -C), 129.33 (quat -C), 129.70 (=CH), 130.94 (=CH), 131.37 (=CH), 131.83 (=CH), 132.76 (=CH), 65.56 ($-OCH_2$), 24.91 ($-CH_2$). IR spectra (ν , cm⁻¹). 3438, 3236, 2644, 1957, 1757, 1732, 1598, 1489, 1451, 1392, 1247, 1130, 1074, 1039.

3. Results and discussion

Following the synthetic strategy shown in Scheme 1, compound **1–3** were synthesized upon desymmetrizing phthalic anhydride with appropriate diols such as ethane-1,2-diol, *cis*-but-2-ene-1,4-diol and 1,4-butane diol. The bola-shaped diester-dicarboxylic compounds were characterized using various spectroscopic techniques such as NMR, IR and MS. The single crystal X-ray structures for **1**, **2** and **3** were determined. All these compounds possess two terminal phthalyl head groups and the diol spacers in common. The two phthalyl moieties possessing dicarboxylic acid at its terminal positions, they are bridged covalently through saturated and unsaturated diol spacers, such as ethane-1,2-diol, *cis*-but-2-ene-1,4-diol and 1,4-butane diol in compound **1–3**, respectively.

ORTEP diagram with atom numbering scheme for compound 1 is depicted in Fig. 1. The presence of carboxylic acid group in the ortho position to the phenyl ring and the flexibility at the central glycolic chain, combinedly play significant role on the construction of the hydrogen bonded helical chain. The terminal phenyl rings (C2–C7 and C12–C17) show a slight twist by 8.64° from planarity. While the carboxyl group (C1–O1–O2) with respective phenyl ring (C2-C7), remains almost in the same plane (angle between the phenyl ring and carboxyl plane is 4.83°), the other carboxyl group (C18-07-08) is twisted by 23.11° with respect to the phenyl ring C12-C17. The glycolic spacer moiety (O4-C9-C10-O5) in 1. bridging the ester carboxylic groups, also shows a similar twist with torsion angle 65.28°. The opposite orientation of the end carboxylic acid and the twist in the flexible aliphatic spacer segment, combinedly facilitates to interconnect the adjacent molecules and form single stranded helical superstructure with pitch distance 4.958 Å through its strong intermolecular carboxylic O-H...O hydrogen bond (Fig. 2b). By virtue of the length and flexibility of the central aliphatic spacer moiety, the terminal carboxylic acid constructs an one-dimensional helical strand running along b-axis through its O-H...O hydrogen bond and generates both left (M) and right handed (P) helices as shown in Fig. 2a. [The pertinent O-H...O H-bond involved in the helical assembly is O2-H2...O7: H2...O7 = 1.67 Å;

02...07 = 2.624(3) Å; $(02-H2...07 = 168.11^{\circ} \text{ and } 08-H8...01;$ H8...01 = 1.83 Å; 08...01 = 2.639(3) Å; $(08-H8...01 = 167^{\circ}.]$

The packing structure as shown in Fig. 2c, further indicates that the alternate (P) and (M) helices are packed with their adjacent helical strands in *c*-axis through a strong C–H...O interaction [C15–H15...O3: H15...O3 = 2.48(3) Å, C15...O3 = 3.328(5) Å and (C15–H15...O3 = 168(3)°] between the phenyl hydrogen H15 and the ester carbonyl oxygen O3. Thus, the vectorial representation of the C–H...O interaction shown in the packing diagram, and the O–H...O mediated helices running down in *b*-axis combinedly creates a two-dimensional H-bonding network in *ac*-plane.

ORTEP diagram of the compound **2** with atom numbering scheme is depicted in Fig. 3. Unlike compound **1**, the double bond introduced at the central carbon atom C10-C11, restricts the flexibility at the spacer moiety in 2. The terminal phenyl rings are tilted by 42.39° with respect to each other. The terminal carboxylic groups C1-O1-O2 and C20-O7-O8 attached to the phenyl rings C2–C7 and C14–C19 are twisted by 24.71° and 43.16°, respectively. Similar to compound 1, the spacer segment O4-C9-C10-C11 and O5-C12-C11-C10 with its respective torsion angles 120.94° and -144.46° also indicates a twist. The H1 and H8 of the end carboxylic acid is involved in O-H...O H-bond, with O7 and O2 of the neighboring molecules and generates right and left handed helical strands (Fig. 4a). [Details of this H-bonding interactions is O1-H1...07: H1...07 = 1.80 Å; O1...07 = 2.615(3) Å; and (O1-H1... 07 = 170°; and 08–H8...02: H8...02 = 1.84 Å, 02...08 = 2.636(4) Å and $\langle 08-H8...02 = 165^{\circ}$.] Thus the orientation and flexibility of the spacer segment combinedly generates a helical strands with pitch distance 7.29 Å extending down in b-axis via intermolecular O-H...O hydrogen bond.

Packing diagram for compound **2** is depicted in Fig. 4c. The phenyl hydrogen H6 and the middle carbonyl oxygen O3 of the adjacent helix (Fig. 4c) involves in H-bonding network along *a*-axis. [Details of the C–H...O interaction: C6-H6...O3; H6...O3 = 2.52(4) Å; C6...O3 = 3.288(6) Å and (C6–H6...O3 = $138(4)^{\circ}$.] Similarly, the weak short contact between the phenyl hydrogen H3 and O7 of the spacer C=O is running through C3–H3...O7; H3...O7 = 2.71 Å; (C3–H3...O7 = $147.86(4)^{\circ}$, generates an another H-bonded network, which connects the helices in *c*-axis. Thus the O–H...O interaction promoting the formation of helical strand in *b*-axis, the weak C–H...O contact, propagates a two-dimensional supramolecular packing both in *a*-and *c*-axis (Fig. 4c), while helices running down in *b*-axis as shown in Fig. 4b. The C–H...O bond angle and distance are in the range reported by Desiraju [40] and Tay-



Scheme 1. Compound 1-3 with their functional role.



Fig. 1. ORTEP diagram of 1 with atom numbering scheme.



Fig. 2. (a) Right (P) and left (M) handed helical motifs present in the unit cell of **1** via strong O–H...O interaction between the carboxyl groups (side view). (b) Single helical strand of 1 running down *b*-axis through O–H...O interaction (red balls represents oxygen atoms and blue lines represents O–H...O H-bonding). (c) Packing diagram showing the C–H...O interaction along *c*-axis, which bridge the (P) and (M) helices. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)



Fig. 3. ORTEP diagram of 2 with atom numbering scheme.

lor and Kennard [41]. Similar to compound **1**, the (M) and (P) helices in **2** are packed alternatively as shown in Fig. 4c. The propagation of helical assembly mediated through O–H...O interaction of carboxylic acids 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 neighboring helices and defines the dimensionality of the molecular packing as shown in the Figs. 2c and 4c, respectively.

ORTEP diagram with atom numbering scheme for compound **3** is given in Fig 5. Compound **2** and **3** possessing four carbons, they differ by their rigid alkenyl and flexible alkyl spacer. Both the ter-

minal phenyl rings in the present compound projecting parallel, they are oriented opposite to each other. The phenyl ring and the ester spacer moiety possess a twist about -55.90° . The spacer moiety C804C9C10 exists with torsion angle -157.55° . Similar to previous compounds, the terminal carboxylate oxygen O1 and O2 mediates a strong O–H...O H-bond, with O2 and O1 of the next neighboring molecule from either end and forms COOH–COOH mediated single stranded helices with pitch distance 11.947 Å. [Details of this H-bonding interactions is O2–H2...O1 = 1.701 Å; O2–H2...O1 = 2.629(3) Å; and $(O2–H2...O1 = 172^{\circ})$.] The increase in the number of carbon and the flexibility on the spacer



Fig. 4. (a) Right (P) and left handed (M) helical motifs present in the unit cell of **2** via strong O–H...O interaction between the carboxyl groups (side view). (b) Top view of helical strand via carboxylic O–H...O hydrogen bond viewed down *b*-axis (red balls represents oxygen atoms and Hydrogen bonding interactions by blue dotted lines). (c) Packing diagram of the compound **2** showing the (P) and (M) helical strands bridged via C–H...O interactions both in *c*- and *a*-axis are indicated by dotted lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)



Fig. 5. ORTEP diagram of 3 with atom numbering scheme.

moiety, increases the pitch distance of the helical strands in the order 1 < 2 < 3.

The helical architecture obtained from single crystal X-ray structure and the flower like crystal growth pattern (Supplementary Fig. S1) inspired us to investigate their morphology using SEM. Accordingly an attempt to grow crystal in various solvents was carried out. All these attempts have resulted the compound 1-3 in semisolid state except ethanol:water mixture. A simple room temperature evaporation of compound 1 dissolved in 1:1 water ethanol mixture of volume ranging from 50 to 70 mL with respective concentration 5-3.6 mM provided us microcrystalline samples after 60 h. The SEM micrograph recorded for these samples collected from 50 to 70 mL batches are depicted in Fig. 6a and b, respectively. Interestingly the SEM micrograph obtained for compound **1**, shown in Fig. 6a and b indicates the formation of tubular texture. Thus while the SEM images of compound 1 showing tubular texture, a similar condition adopted to compound 2 and 3 failed to produce tube but forms bar type microcrystals (Supplementary Fig. S2).

Interestingly, the diameter of the hollow tube for **1** measured through SEM being nanometer range (200–700 nm), the corresponding helices show the hollowness in the molecular structure

in few Angstrom. Keeping this huge difference of the hollowness from molecule to material level, it is considered as essential to understand the mechanism through which the supramolecular self-assembly takes place.

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 SEM image. Accordingly, we have proposed two different mechanism for the formation of tube (Scheme 2a) and bar (Scheme 2b). Both compound 1 and 2 possess (P) and (M) helices in adjacent position and constructs an almost similar packing pattern, as shown in Fig. 2c and Fig. 4c. However they vary in their vectorial propagation of the C-H...O interaction as indicated in the dotted line. Thus the alternate (P) and (M) helices assembles as laver in PMPM. etc. manner through their inter-helical C-H...O interaction running through *c*-axis. The compound **1** giving hollow tubes in nanometer range suggest that the alternative layers PMPM, etc. rolls, one inside the other as indicated in the Scheme 2a, by making use of the C-H...O interaction.

A similar C–H...O interaction in compound **2** spreading both in *c*- and *a*-axis ties all the adjacent helices. Consequently, every (P)

Fig. 6. SEM images of compound 1 in 1:1 ethanol:water mixture showing the tubes at (a) 50 mL. (b) 70 mL.

Scheme 2. Possible mechanism for the formation of tube and bar through H–bond. The blue line represents the H-bonds and (P) and (M) indicates the right and left handed helical strands. Growth mechanism for the formation of (a) tube and (b) bar. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

helix is tied with four (M) helix and vice versa through their C-H...O interaction and forms two-dimensional packing network spreading both in *a*- and *c*-axis as shown in Scheme 2b. Accordingly this packing arrangement in **2**, following the Scheme 2b, restrict the molecules from folding and results into bars. 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 microtube for compound **1**. The increase in wall thickness from 400 nm to 1 μ m, while moving from 50 to 70 mL solution in compound **1** observed by the SEM micrograph, further supports that the tubular formation may tentatively follow the growth mechanism as represented in Scheme 2a.

4. Conclusions

In summary, the diester-dicarboxylic bola-shaped compounds were shown to form helical structure. The supramolecular H-bonding interaction C-H...O and O-H...O plays significant role in polar solvent medium such as water:ethanol mixture. 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 SEM images establishes that the compound **1** yields tube, while compound **2**, **3** are not forming tube. The two different mechanism proposed for their self-assembly process following tube and bar is explored based on the vectorial propagation of the C-H...O interaction. Thus the supramolecular self-assembly process mediated through C-H...O and O-H...O interaction establishes the morphology. The helical strands in **1**, **2** and **3** with respect to their pitch distance in the order **1** < **2** < **3**, the flexible spacer moiety and weak H-bonding interactions are combinedly plays significant role in bringing the morphology.

Acknowledgement

We are grateful to Department of Science and Technology New Delhi (India), who supports this work, vide Project Number.SR/S1/ IC-19/2005. We acknowledge Mr. C.K. Chandrakanth for recording the SEM.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2008.08.016.

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