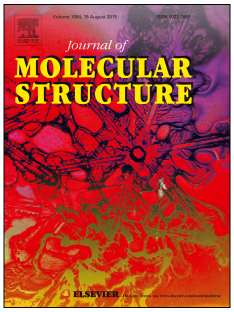

Design and characterization of novel *bis*-benzamide liquid crystalline materials

Asma Iqbal, Humaira Masood Siddiqi, Zareen Akhter, Muhammad Qaiser Fatmi

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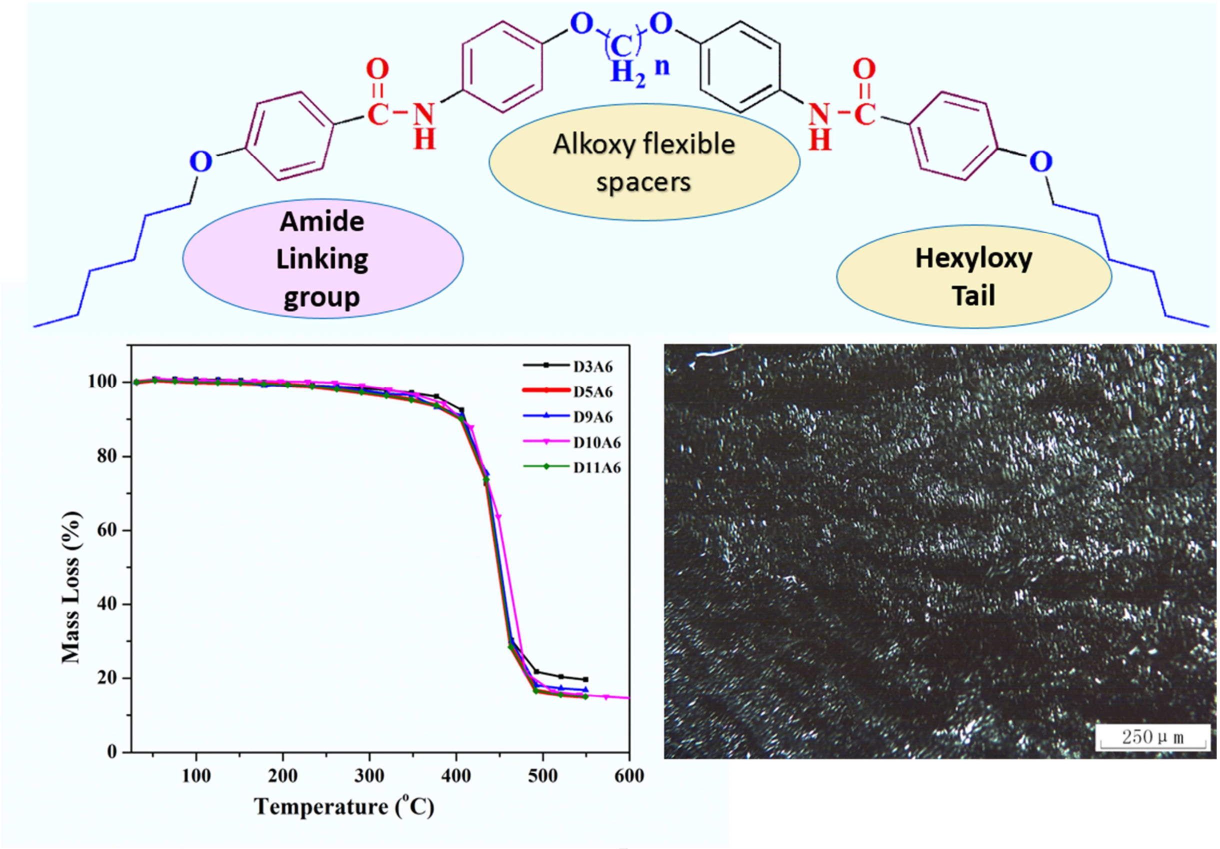
O
O
C
H2 n
O
C-N
H
N-C
H
O
O
O
Alkoxy flexible spacers
Amide Linking group
Hexyloxy Tail
D3A6
D5A6
D9A6
D10A6
D11A6
Mass Loss (%)
0
20
40
60
80
100
100
200
300
400
500
600
Temperature (°C)
250 μ m

Design and characterization of novel bis-benzamide liquid crystalline materials

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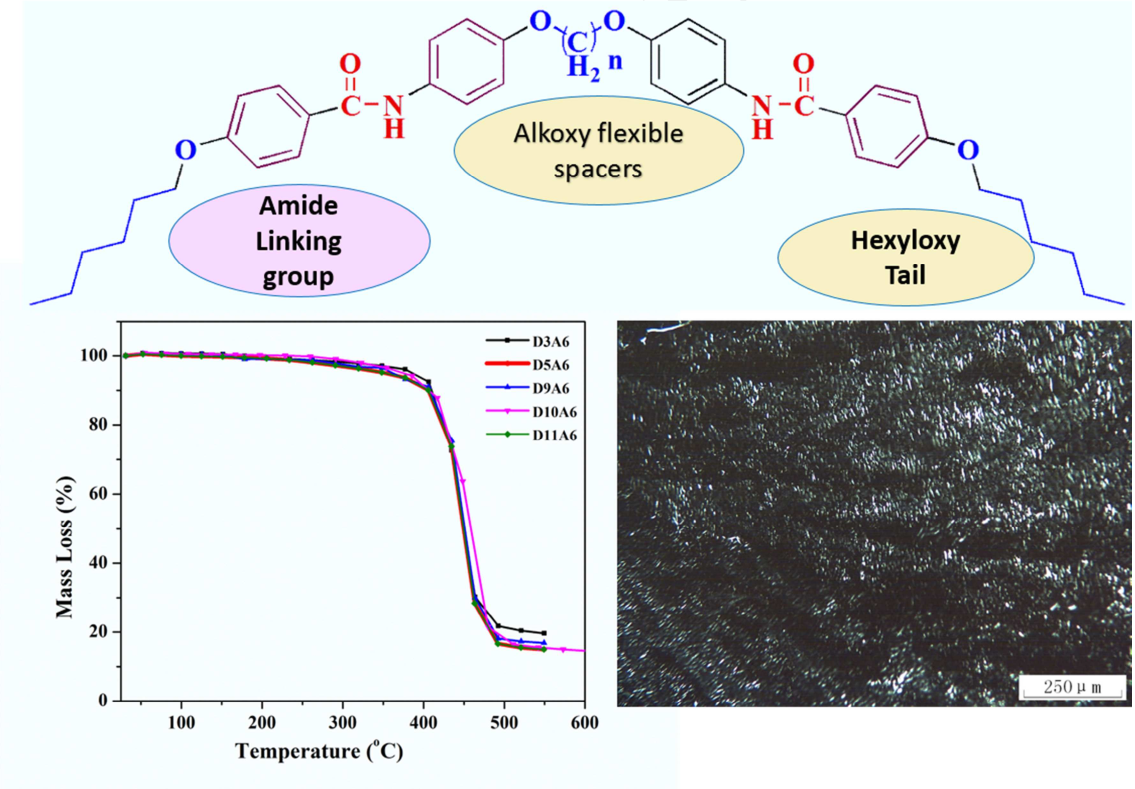
Graphical Abstract:



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.

Keywords: symmetric *bis*-benzamides; enantiotropic mesogens; blurred schleiren; thermally stable.

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 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 Figure. 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 one hour under an inert atmosphere of nitrogen. Afterwards, dropwise addition of the corresponding dibromoalkane (28.5 mmol) was made over a period of 30 minutes and the mixture was maintained at 120 ºC for 12 hours. 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 hour. The reaction mixture was refluxed for three hours 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].

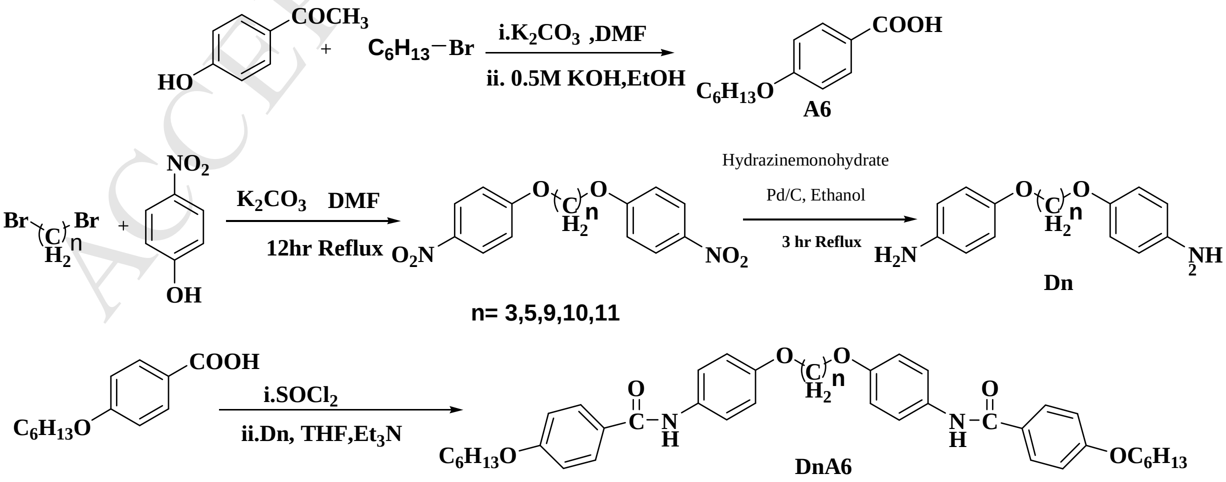


Figure 1. Synthesis of *bis*-benzamides

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 hours 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 (3g, 0.012 mol), 0.5M KOH in ethanol and 5 % H_2O (150 mL) was heated under reflux for 12 hours. 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^{0}C (lit.103- 105^{0}C)

2.1.3 *Synthesis of bis-benzamides (D_nA_6)*

The synthetic route used in the preparation of *bis*-benzamides is illustrated in Figure. 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 hours 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). The purity of products further confirmed by NMR, FTIR, and CHN analysis.

2.1.3.1 *Synthesis of 4,4’-bis[4-(dihexyl)oxy]benzamidediphenoxypropane (D_3A_6)*

Yield 75%, m.p.166-203 °C, $R_f = 0.6$. Anal. for ($C_{41}H_{50}N_2O_6$) in wt% Calc. C = 73.85, H = 7.56, N = 4.20 and found to be C = 74.01, H = 7.48, N = 3.99. FTIR:

($\bar{\upsilon}$/cm^{-1}) N-H (3343), C$_{sp3}$-H (2917, 2850), C=O (1639), C=C (1607, 1506), C-O (1251), para disubstitution (840). ^{1}H NMR (300MHz, DMSO) δ (ppm): 9.95 (s, 1H, H-N), 7.93(d, 4H, ortho to C=O) 7.63(d, 4H, ortho to NH-C=O), 6.93(d, 8H, ortho to O-Ph), 4.05(t, -OCH$_2$), 1.729 (quint. -CH$_2$ next to -OCH$_2$), 2.14 (pent, 1H, H$_{12}$), 1.24(m, 6H, methylene H's), 0.84(t, 3H, -CH$_3$).

2.1.3.2. Synthesis of 4,4'-bis[4-(dihexyl)oxy]benzamidediphenoxypentane (D$_5$A$_6$) Yield 78%, m.p.208°C, R$_f$ = 0.62. Anal. for ($C_{43}H_{54}N_2O_6$) in wt% Calc. C = 74.32, H = 7.83, N = 4.03 and found to be C = 74.01, H = 7.98, N = 3.99. FTIR: ($\bar{\upsilon}$/cm^{-1}) N-H (3276), C$_{sp3}$-H (2927, 2857), C=O, (1643), C=C (Ar) (1607, 1513), C-O (1240), p-disubstitution (838). ^{1}H NMR (300 MHz, DMSO) δ (ppm): 9.94(s, 2H, H-N), 7.91(d ,4H,ortho to C=O), 7.63(d, 4H, ortho to NH-C=O), 6.90 (d, 8H, ortho to O-Ph), 4.08 (t, -OCH$_2$), 3.96 (t, (b), 2H, H$_{11}$), 1.74 (quint.-CH$_2$ next to -OCH$_2$), 1.42(m, 7H, Methylenic H's), 0.82(t, 3H, CH$_3$).

2.1.3.3. Synthesis of 4,4'-bis[4-(Dihexyl)oxy]benzamidediphenoxynonane(D$_9$A$_6$). Yield 78%, m.p.148-199 °C, R$_f$ = 0.56. Anal. for ($C_{47}H_{62}N_2O_6$) in wt% Calc. C = 75.17, H = 8.32, N = 3.66 and found to be C = 74.97, H = 7.98, N = 3.59 , FTIR: ($\bar{\upsilon}$/cm^{-1}): N-H (3303), C$_{sp3}$-H (2920, 2850), C=O, (1637), C=C (Ar) (1604, 1508), C-O (1245), p-disubstitution (836).^{1}H NMR (300MHz, CDCl$_3$) δ (ppm): 7.83 (d, 4H, ortho to C=O), 7.52 (d, 4H, ortho to NH-C=O), 6.82 (d, 8H, ortho to O-Ph) 4.006 (t, -OCH$_2$), 1.77 (quint.-CH$_2$ next to -OCH$_2$), 1.37(m, 11H, Methylene H's), 0.90 (t, 3H, -CH$_3$).

2.1.3.4. Synthesis of 4,4'-bis[4-(dihexyl)oxy]benzamidediphenoxydecane (D$_{10}$A$_6$). Yield 75%, m.p.112-198 °C, R$_f$ = 0.68. Anal. for D$_{10}$A$_6$ ($C_{48}H_{64}N_2O_6$) in wt% Calc. C = 75.36, H = 8.43, N = 3.66 and found to be C = 75.60, H = 8.24 , N = 3.49 FTIR: ($\bar{\upsilon}$/cm^{-1}): N-H (3309), C$_{sp3}$-H (2918, 2849), C=O, (1637), C=C (Ar) (1609, 1512), C-O (1247), p-disubstitution (836). ^{1}H NMR (300MHz, DMSO) δ (ppm): 9.92 (s, 2H, H-N), 7.91(d, 4H, ortho to C=O),7.68 (d, 4H, ortho to NH-C=O), 6.95 (d, 8H, ortho to O-Ph),4.02 (t, -OCH$_2$), 1.80 (quint.-CH$_2$ next to -OCH$_2$), 1.33 (m, 13H, Methylene H's), 0.81 (t,3H,-CH$_3$).

2.1.3.5. Synthesis of 4,4'-bis[4-(dihexyl)oxy]benzamidediphenoxyundecane (D$_{11}$A$_6$) Yield 75%, m.p.112-198 °C, R$_f$ = 0.71. Anal. for D$_{11}$A$_6$, ($C_{49}H_{66}N_2O_6$) in wt% Calc. C = 75.54, H = 8.54, N = 3.60 and found to be C = 75.77, H = 8.68, N = 3.55, FTIR: ($\bar{\upsilon}$/cm^{-1}) N-H (3307), C$_{sp3}$-H (2917, 2849), C=O, (1638), C=C (Ar) (1608, 1513), C-O (1247), para-di substitution (836).^{1}H NMR (300MHz, DMSO) δ (ppm): 9.94 (s, 2H, H-N), 7.90(d,4H,ortho to C=O), 7.67 (d, 4H, ortho to NH-C=O), 6.97 (d, 8H, ortho to O-Ph), 4.03 (t, -OCH_2), 1.70 (quint., 4H,) 1.31(m, 13H, Methylene H's), 0.84(t, 3H, -CH_3).

2.2. Characterization

The structures of all intermediates and final compounds were verified using ^{1}H-NMR and ^{13}C-NMR on a Bruker AM (300 MHz) NMR spectrometer in DMSO-d^6 solution, using TMS as an internal standard reference. IR spectra were recorded on Thermo scientific Nicolet 6700 ATR spectrophotometer. Gallenkamp (Sanyo) model MPDBM 3.5 with digital thermometer was used to determine the melting points. The elemental analysis were performed on CHNS analyzer, Thermoscientific (Flash 2000series). Thermogravimetric analyses were carried out on Mettler Toledo thermal analysis system TGA-851. Phase transition temperatures of the *bis*-benzamides were determined by Mettler Toledo DSC-823 system in an inert nitrogen atmosphere. Heating and cooling rates were maintained at 5 ^{o}C/min. The thermal transition temperatures were taken from the position of peak maxima. The textures of the mesophases were examined on a Leica DM-2500p polarizing microscope fitted with a temperature controller and a hot stage. Computational studies were carried out as mentioned by Khushi *et. al.*[30] by using the same semi-empirical method available in molecular orbital package (MOPAC2009).

3 Results and Discussions

3.1 Synthesis and structural confirmation of bis-benzamides.

The synthesis of *bis*-benzamides was designed and prepared to investigate their LC properties. As the presence of hydrogen bonding in amides is a well-established fact [25] the synthesized compounds possess bent conformations due to the presence of flexible methylene spacers and formation of the intermolecular hydrogen bonding as shown in Figure.2. [31,32] The two hexyl groups were introduced at the two ends of these flexible spacers to test the effect of these segments on the LC behavior of the resulting dimers. Aliphatic chains, including n-propyl, n-pentyl, n-nonyl, n-decyl and n-undecyl, were appended to the backbones and linked to the aromatic rings via amide and ether linkage from the two sides of the spacers. These *bis*-benzamides were designed and studied for their concomitant influence on the LC property. The synthetic routes for the new dimesogens are provided in Figure 1. In the reported series, the terminal hexyloxy chain length was kept constant while varying the methylene unit spacers and explored their thermal and LC properties.

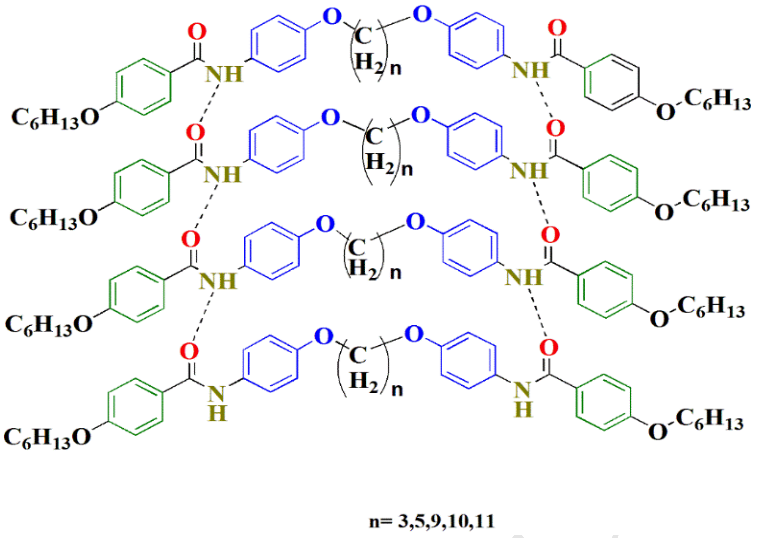


Figure2. Bent structure of *bis*-Benzamides

The synthesized *p*-hexyloxybenzoic acid (**A_6**) was reacted with various diamines like D_3, D_5, D_9, D_{10} and D_{11} (where 3,5,9,10,11 represents CH_2 spacer units) in a stoichiometric amount which led to the synthesis of several novel dimeric *bis*-benzamides. The structures of final compounds were established by the ^{1}H-NMR, ^{13}C-NMR, IR spectroscopy and elemental analysis. IR spectral data revealed strong IR absorption bands at about 3343 cm^{-1} for the –NH of amide pointing towards the formation of required *bis*-Benzamides. The other IR stretching vibrations of the prepared dimeric compounds were 2917, 2850cm^{-1} for the C_{sp3}-H stretching vibration and at 1639 cm^{-1} C=O, Aromatic C=C 1607, 1506, C-O 1251 cm^{-1}. The ^{1}H-NMR spectral data exhibited analogous splitting patterns in all the *bis*-benzamides showing a diagnostic NH-C=O- signal at around 9 ppm. The aromatic region was confirmed by the presence of signals in between 6.8-7.9 ppm. Alkoxy protons resonated at 4.0 ppm whereas the protons resonated at 0.9 and 4.1 ppm were attributed to aliphatic protons. *bis*-benzamides were only partially soluble in DMSO which resulted the signal broadening in ^{1}H-NMR. The NMR spectrum of a representative *bis*-benzamide is given in S1.

3.2 Mesomorphic properties

Differential scanning calorimetry was employed to investigate phase transitions in the synthetic dimeric compounds. DSC thermograms of D_3A_6 and $D_{11}A_6$ compounds are displayed in Figure 3, whereas, the phase transition temperatures and enthalpy changes are presented in table 1. From the second heating cycles of the DSC thermograms transition temperatures for melting (Table 1) were obtained. Better results were obtained for the compounds having spacer lengths of 3, 10 and 11 as compared to other members of series.

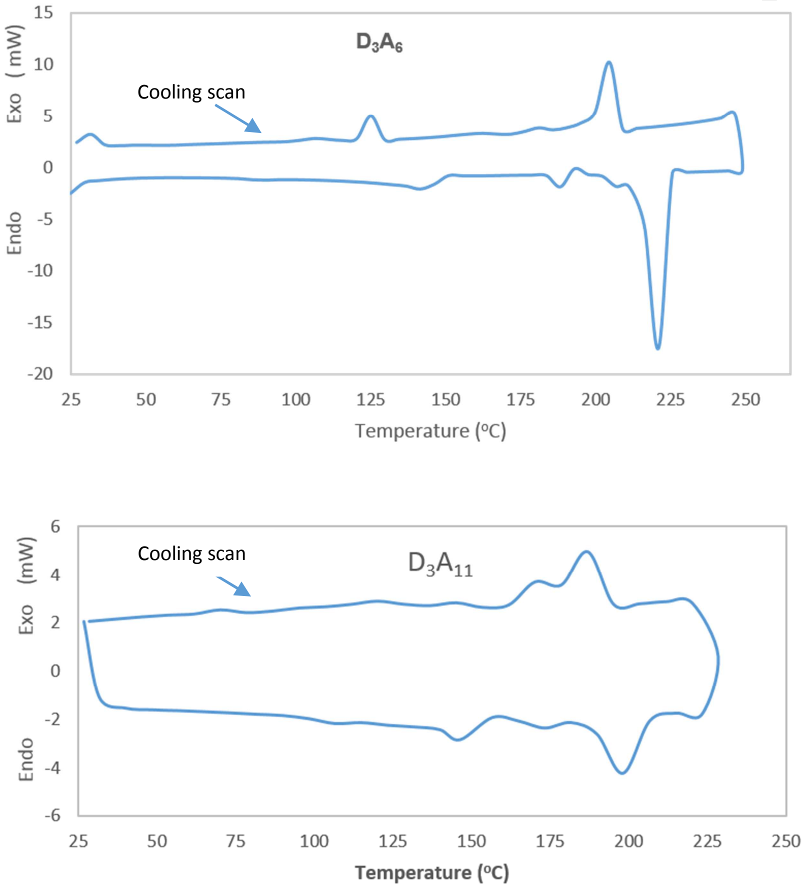


Figure 3. DSC scans of D_3A_6 and D_3A_{11} showing heating and cooling scans.

A large endothermic peak showing melting transition and another smaller peak which was thought to be the liquid crystalline transition were observed in the heating scan of D_3A_6. In the cooling scan of D_3A_6, a large exothermic peak and smaller exothermic peaks appeared displaying an enantiotropic mesogenic behavior. As shown in the Figure.3 in the cooling curve of D_3A_6, it displays an isotropic liquid phase to nematic phase transition at 206 ^{o}C, a nematic to smectic phase transition at 185 ^{o}C and smectic to crystal at 124 ^{o}C. D_3A_6 when observed under polarizing optical microscope with (1ºC/min) heating and cooling rate, the conical fan like and dendritic thread like texture characteristic of the smectic and nematic mesophases were observed which are presented in Figure.5 (a).

Table 1. Phase Transitions of *bis*-benzamides

Compound	Transitions	Transition Temperature °C/ ΔH (Jg^{-1})	$\Delta T=T_i-T_m$ °C
D_3A_6	Cr-Sm Sm-Nem Nem-Isotropic	143(10.13) 185(3.50) 219 (85.46)	76
D_5A_6	Cr-I	208 (27.85)	-
D_9A_6	Cr-I	192 (73.36)	-
$D_{10}A_6$	Cr-Sm Sm-I	128 (1.82) 204 (44.01)	76
$D_{11}A_6$	Cr-nem Nem-isotropic	146(1.46) 173 (9.70) 194 (24.07)	48

T_i= Isotropic liquid temperature, T_m =mesophase temperature, ΔT= mesophase range , Cr= Crsytal, Sm= Smectic, Nem= Nematic, I= Isotropic

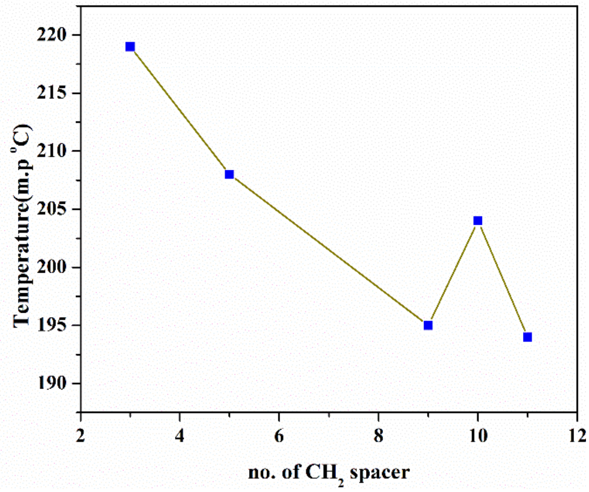
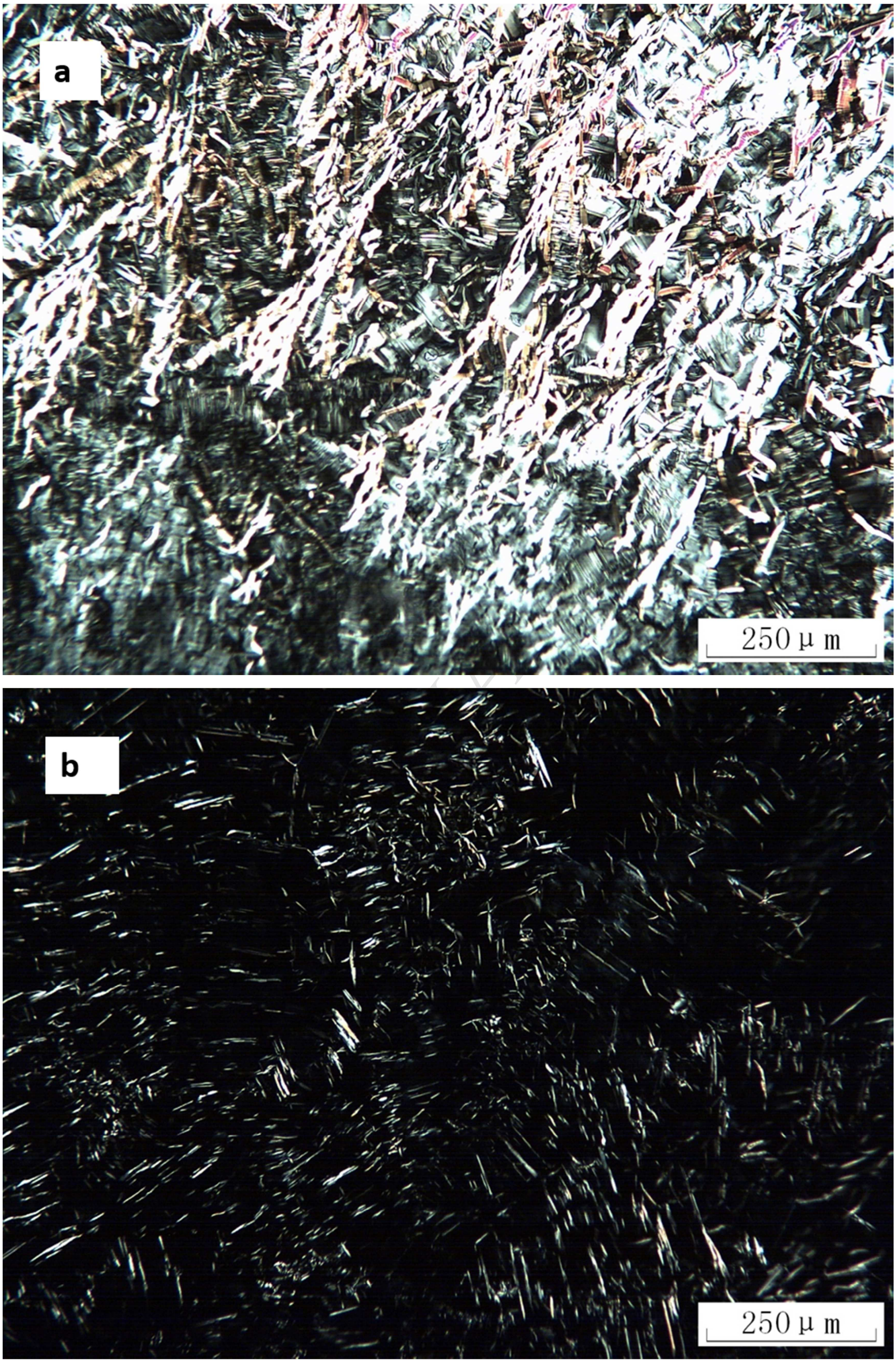


Figure 4. Dependence of melting points of *bis*-benzamides -CH_2 spacer length.

Since the molecules have different methylene spacers it was anticipated that increasing methylene spacer chain length will increase the length-to-breadth ratio significantly, which may result in liquid crystal phase changes. The results demonstrated that the increased methylene spacers decreased the melting range, as D_3A_6 has melting point at 219 ^{o}C whereas $D_{10}A_6$ and $D_{11}A_6$ has 204 ^{o}C and 194 ^{o}C respectively as shown in the Figure. 4.

As shown in the Figure 5a conical fan like texture was observed at 160 ^{o}C which showed another transition into dendritic thread like and mosaic texture at around 200 ^{o}C and converted into isotropic liquid at 219 ^{o}C. The compounds having spacer lengths of 5 and 9 exhibited only a single large peak which corresponds to the melting transition in their DSC thermographs. Whereas the heating and cooling scans of $D_{10}A_6$ and $D_{11}A_6$ also showed enantiotropic behavior and two peaks indicating the presence of mesophase were observed for these compounds. POM studies revealed clear finger print like (smectic) texture which on further cooling converted to the needle like texture for $D_{10}A_6$ as shown in (Figure. 5 b,c).The DSC thermograph of the highest homologue $D_{11}A_6$ first phase transition appeared from the 190 to 175 ^{o}C and the other phase transition originated from 175 to 140 ^{o}C, which was ascertained to be a liquid crystal to crystal transition. Blurred line texture at 145 ^{o}C was observed for $D_{11}A_6$ which converted into blurred schleiren nematic at around 180 ^{o}C when $D_{11}A_6$ was observed under POM. (Figure. 5d)[14].


a
250 μ m
b
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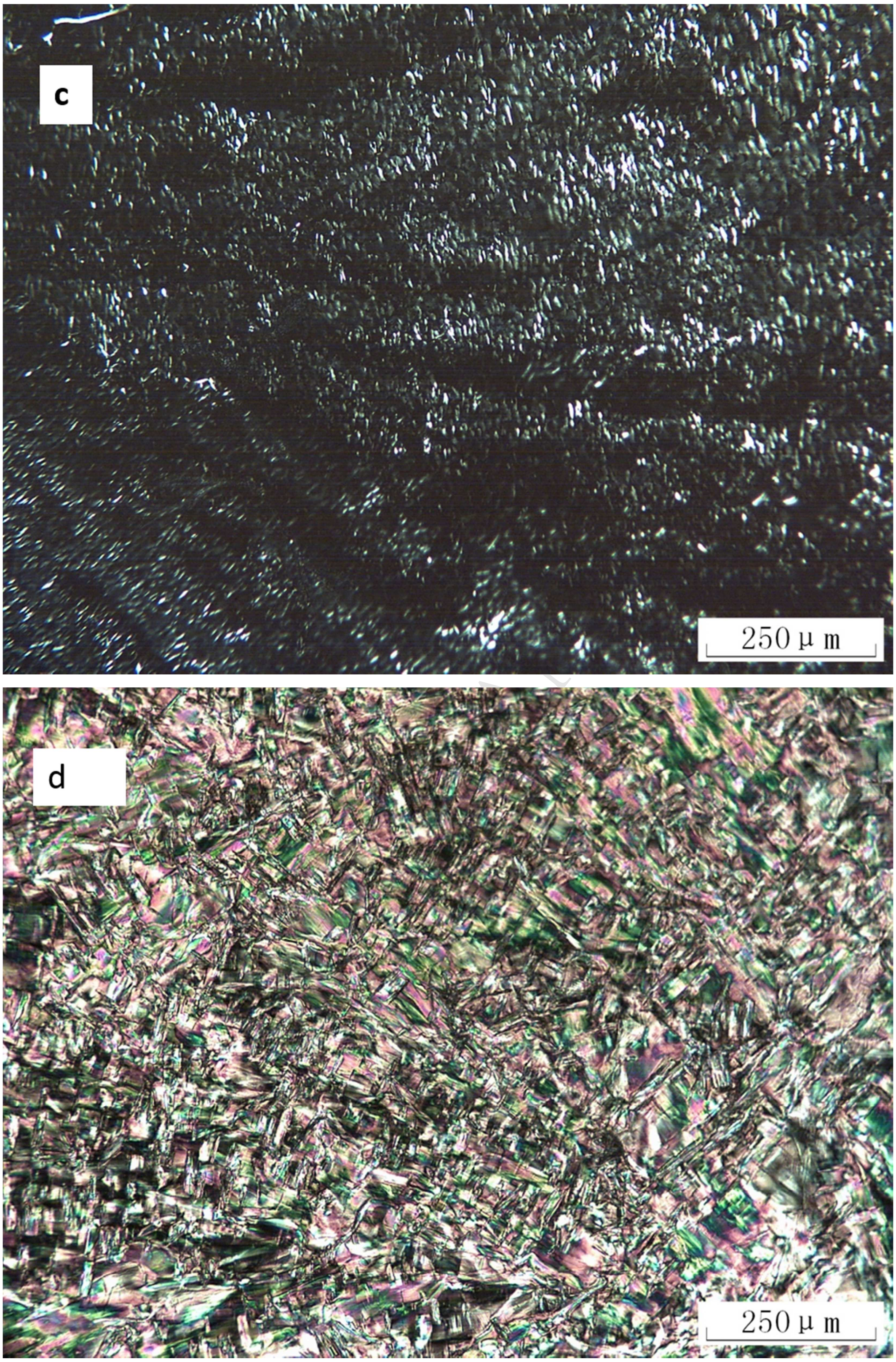


Figure 5. POM images 5a. showing nematic and smectic images D_3A_6, b,c. needle like structure of $D_{10}A_6$ are shown , and d showing nematic thread like structures of $D_{11}A_6$.

These results validate that the tendency towards the mesomorphic thermal stability of mesogenic phase decreased with increasing spacer chain length which may account for the increasing flexibility of spacers. The presence of terminal hexyloxy chains at an angle to the long molecular axis may bring about the molecular tilt between neighbouring molecules consequently decreasing the intermolecular hydrogen bonding[33].

3.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out to examine the thermal stability of the obtained *bis*-benzamides. The TGA thermograms of the examined compounds are presented in the (Figure 6). The mass loss associated with the processes of degradation up to 600 ^{o}C in nitrogen atmosphere were estimated in terms of in terms of 5%, 10% and 50% weight loss (T_d, $T_{10,}$ T_{50}) as summarized in Table 2. The TGA curves of *bis*-benzamides, indicated main one step degradation process with no noteworthy weight losses up to 360 ^{o}C pointed towards the thermal stability of these novel *bis*-benzamides up to this temperature. The T_d and T_{10} varied from 362-395 ^{o}C and 390-408 ^{o}C, respectively. The temperature at which the maximum decomposition occurred (T_{max}) ranged between 445-455 ^{o}C as shown in Table 2.

Out of all the *bis*-benzamides, D_3A_6 exhibited a higher thermal stability than other members of the series, which is owed to the inclusion of the only three methylene spacers units. However, the introduction of the longer methylene spacers units augmented the molecular flexibility consequently reducing the thermal stability of higher homologues of synthesized *bis*-benzamides.

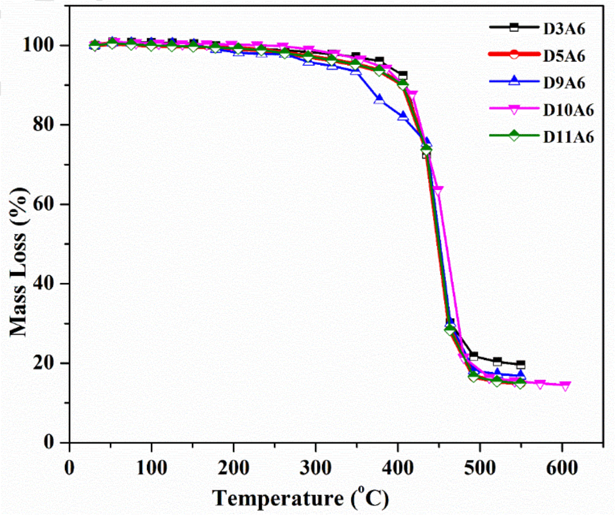


Figure 6. TGA graphs of *bis*-benzamides.

Table 2. TGA data of compounds (D_nA_6)

Sr.	T_d °C	T_{10} °C	T_{max}°C	Char yield at 490°C
D_3A_6	395	408	448	22
D_5A_6	374	400	445	18
D_9A_6	3682	379	451	17
$D_{10}A_6$	370	399	455	15
$D_{11}A_6$	362	404	449	16

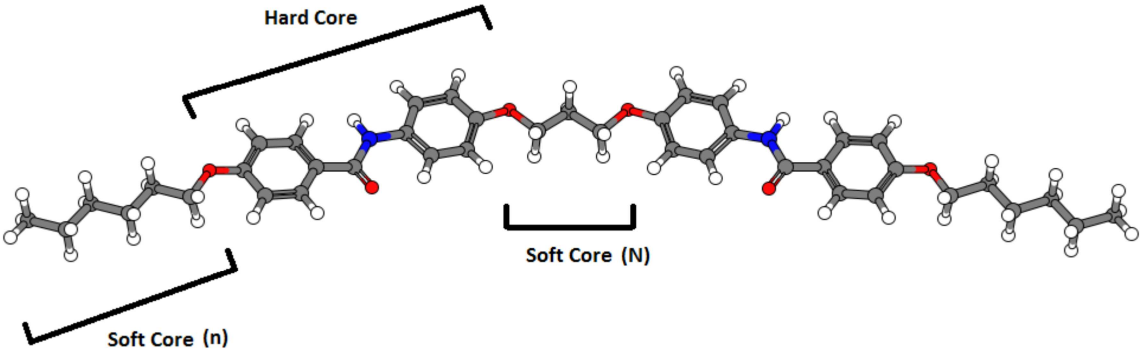
(T_d) (based on 5% weight loss), 10% weight loss temperatures (T_{10})

3.4 Semiempirical Calculations

Theoretical studies were carried out to optimize the geometry of prepared *bis*-benzamides by employing semi-empirical method (MOPAC2009). Different characteristics of synthesized *bis*-benzamides including the soft core length (F) and molecular core arm (R), soft to rigid parts ratio (F:R ratio), mean polarizability and enthalpies of formation were estimated and the results were very much alike as reported by Muhammad K. *et. al.*[30] as presented in Table 3.

The relative sizes of soft parts to hard core play an important role in imparting mesogenic properties. The total length of the flexible unit was achieved by adding up the lengths of terminal hexyloxy groups to the lengths of methylene spacers. The hard core length was determined from terminal hexyloxy's oxygen atom to the oxygen group of methylene spacers, which also includes the amide linkage, as displayed in the Figure 7.

The size of the flexible units were varied between 19.46 to 29.4A° whereas hard core was calculated to be 23.98 Å. The F/R ratio ranged between 0.81 for three methylene spacers **(D_3A_6)** and 1.23 for eleven methylene units substituted ligand **(D_3A_{11})**. It has also been reported that the compounds having F:R ratio ranging from 0.76 to 1.62 showed liquid crystalline properties, similarly our prepared *bis*-benzamides displayed the F/R ratio from 0.81 to 1.23. Among all the compounds D_3A_6, $D_{10}A_6$, and $D_{11}A_6$ displayed mesomorphic properties whereas rest of the members besides having reasonable soft to hard ratio revealed no mesomorphism indicating the involvement of some other factors. Polarizability of the molecule also influences the optical anisotropy of a macroscopic material, particularly, the phase transition temperature[34]. Maier–Saupe theory suggests that the nematic-isotropic phase transition is mainly stabilized and dependent on the anisotropy of the molecular polarizability of mesogens. It could be inferred that the increasing polarizability causes the lowering of melting temperature as mentioned in table 1. The increase in length of methylene spacer groups caused an average raise of 1.75 A^3 per methylene (CH_2) group thus increasing the polarizability. The polarizability values were ranged from 86.09 to 100.46.



N' and 'n' stand for number of carbon atoms

Figure 7. The hard and soft core is mentioned in the image. Grey, blue, red and white colours represent carbon, nitrogen, oxygen, and hydrogen atoms, respectively. N and 'n' stand for number of carbon atoms in spacer and terminal chain respectively.

Table 3. Calculated parameters of D_nA_6 using semi empirical method.

Sr.	Structure		Soft Core (F) (2n+N) Ang	Molecular Core Arm (R)	Ratio (F:R)	Polarizability Ang^3	H^o_F
	Flexible spacer (N)	Flexible chain (n)					Kcal/mol
D_3A_6	3	6	19.461	23.984	0.811	86.07912	-231.35057
D_5A_6	5	6	22.001	23.984	0.917	89.62968	-243.14108
D_9A_6	9	6	27.078	23.984	1.129	96.83429	-264.05429
$D_{11}A_6$	11	6	29.616	23.984	1.235	100.46970	-274.33424

Enthalpy of formation is also an important factor as it controls the viscosity of the material. The switching times of liquid crystal displays and their power consumption is also influenced by the viscosity of the material[35]. Consistent increase in the estimated enthalpy values were observed with increasing methylene spacer's chain length. The D_3A_6 has smaller H_f value than rest of the members of the series and hence expected to be less viscous than higher members of the series[35].

From these computational results and experimental observations, it is inferred that the polarizability, enthalpy of formation, and F:R ratio values are in good agreement with the liquid crystals reported in literature[30,36].

Conclusions

A series of new bent-core dimers having four benzene rings with ether and amide linking groups have been synthesized and their thermal and mesomorphic properties were investigated. The dimers were also thermally stable up to 360 °C which make their use as multifunctional materials. Significant effect on the thermal stabilities of the reported *bis*-benzamides is also attributable to the length of methylene spacers. D_3A_6 was found to be the most stable of all exhibiting the onset degradation at 395 °C. Among all the presented compounds only D_3A_6, $D_{10}A_6$ and $D_{11}A_6$ showed enantiotropic mesogenic behaviour was and longest liquid crystalline temperature range of 76 °C was exhibited by D_3A_6.It was also observed that clearing temperature was decreased as the spacer length was increased from three to eleven. The POM studies revealed the existence of smectic and nematic phase transitions which were confirmed by the observation of lined and thread like textures. It can be established that the amide group serve as an appropriate linking group owing to the development of hydrogen bonds in bent-core molecules there by imparting good thermal stability as well as mesogenic properties. These newly prepared *bis*-benzamides may act as models for the preparation of polymeric benzamide liquid crystals with potential mesomorphic properties. This facile and inexpensive synthetic route could be followed and tailored by employing heterocycles to prepare a number of non-linear optical materials with unique mesomorphic properties. Furthermore, the thermal stability as well as the unique liquid crystalline textures make these materials multifunctional for microelectronics, non-linear optical properties and ferroelectric applications.

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Design and characterization of novel bis-benzamide liquid crystalline materials

- Symmetrical dimeric benzamides with four benzene rings, different methylene spacers and hexyloxy tail have been proposed to be potential mesogens.
- The synthesized compounds possess bent conformations due to the presence of flexible methylene spacers and formation of the intermolecular hydrogen bonding between the amide groups of different molecules thus forming layered structures.
- The prepared *bis*-benzamides are thermally stable up to 360 ^{o}C which make their use as multifunctional materials.
- The prepared compounds displayed enantiotropic mesogenic behavior. It is observed that clearing temperature decreased as the spacer length increased from three to eleven methylene units.