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Columnar Liquid-Crystalline Phase from a Series of Symmetrical Bent Diphenylamine Derivatives: Synthesis and Characterization

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Columnar Liquid-Crystalline Phase from a Series of Symmetrical Bent Diphenylamine Derivatives: Synthesis and Characterization

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A series of symmetrical bent-shaped materials with six alkoxy chains at the terminal position has been designed and synthesized. All except one exhibit columnar mesophase behavior. The mesomorphic properties of the compounds have been studied with the help of polaralizing optical microscopy (POM) and differential scanning colorimetry (DSC) experiments.

Keywords Bent shape; columnar phase; diphenylamine; Schiff's base

Introduction

Liquid crystals (LCs) formed by bent-shaped molecules represent an expanding topic in liquid crystal research [1,2]. These materials form new smectic and two-dimensional phases that are unlike those obtained from normal calamitic molecules [3]. Mesophases formed by discotic liquid crystals are now well recognized as suitable for many device applications [4,5]. Most of the discogens reported to date consist of a flat, or nearly flat, rigid core surrounded by a number of aliphatic side chains having binary, trigonal, tetragonal, or hexagonal symmetries [6–9].

General mesomorphic properties are a result of interplay between many competing and/or cooperative molecular interactions, though it can be argued that to a great extent the type of mesophase, lamellar, or columnar phases are predominantly formed by molecules having disc-like [10] or bow-like shapes [11]. In particular, columnar phases, characterized by indefinitely long molecular columns aggregating into two-dimensional (2D) lattices with different symmetries, are of great of significance. This is because they allow the possibility of combining several physical properties with the orientational control of the molecular order, self-healing of structural defects, and ease of processability when compared to the inorganic semiconductors or zone-refined single crystals currently used in electronic applications. The commonly observed columnar mesophases are hexagonal columnar

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(Col_h), rectangular columnar (Col_r), lamellar columnar (Col_L), or nematic columnar (Col_N) [12]. A transition between these phases, for example, $Col_h \rightarrow Col_r$ or $Col_h \rightarrow Col_N$, was occasionally observed, and these phase transitions were all related to the temperature dependency or/and side chain length dependency of compounds. Wang et al. [13] first synthesized a series of mesogenic derivatives based on triphenyl amine. They observed that mesophases were side-chain dependent. Compounds with one, two, and three side chains formed a lamellar columnar phase and compounds with four and six side chains exhibited a hexagonal columnar phase. In our earlier communication [14] on liquid-crystalline material based on a triphenylamine (TPA) core we reported that tri-substitution on TPA core with a Schiff's base linkage resulted in columnar mesophase behavior. Recently we have also reported [15] a homologous series of Schiff's bases consisting of *N*-methyl diphenylamine moiety at the central core with two alkoxy side-chains exhibiting temperature dependent $SmA_d \rightarrow SmA_2$ transition. Here we report the synthesis and characterization of bent-shaped materials based on an *N*-methyl diphenylamine core having six alkoxy chains. We have also attempted to investigate the effect of number of alkoxy chains on the mesophase behavior.

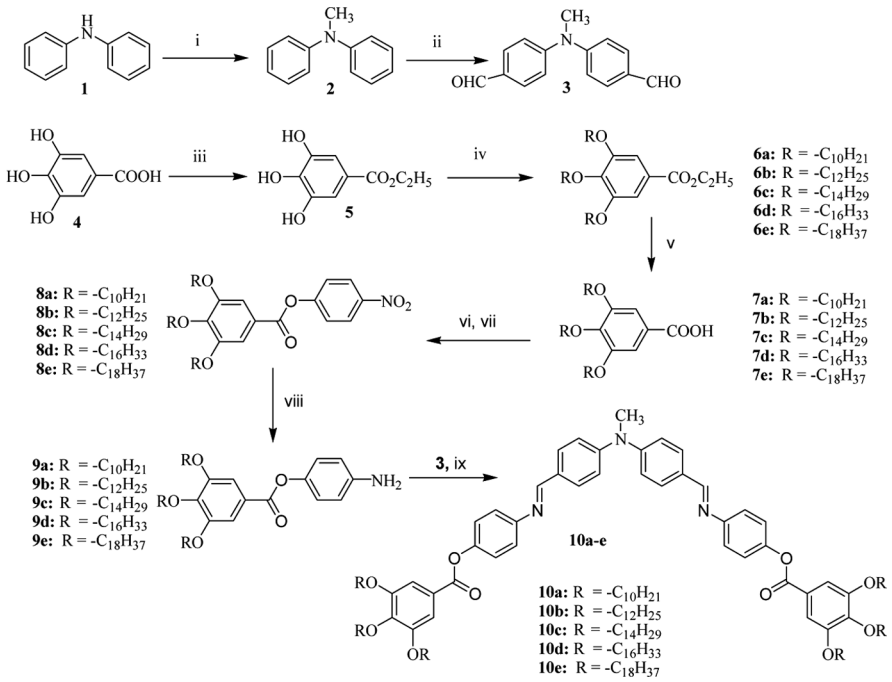
Experimental Details

Reagents and Technique

All chemicals were procured from either Sigma Aldrich Chemicals Pvt. Ltd. or Spectrochem Pvt. Ltd. Mumbai, India. Silica gel (60–120 mesh) was used for chromatographic separation. Silica gel G (E-Merck, India) was used for thin layer chromotography (TLC). Petroleum ether refers to the fraction boiling between 60°C and 80°C. Infrared (IR) spectra were recorded on a Perkin-Elmer (India) Pvt. Ltd. L 120-000A spectrometer (ν_{max} in cm^{-1}) on KBr disks. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker India Scientific Pvt. Ltd. DPX-400 and Bruker DPX-300 spectrometer, respectively, using $CDCl_3$ as a solvent and TMS as an internal standard ($\delta = 0.00$ ppm). The liquid-crystalline properties for compounds **10a-e** were established using a Nikon polarizing microscope (Nikon Corporation, Japan) LV100POL attached with Instec hot and cold stage HCS302, with STC200 temperature controller configured for HCS302 and the phase transitions were confirmed by differential scanning calorimetry (Perkin-Elmer Diamond DSC Pyris1 system). CHN was recorded on a 2400 series II CHN analyzer Perkin Elmer (India) Pvt. Ltd.

Synthesis

4-4′-Diformyl-*N*-methyldiphenylamine **3** was prepared starting from diphenylamine **1** by subsequent methylation with methyliodide, followed by Vilsmeier-Haack reaction. 3,4,5–Trialkoxy benzoicacids (**7a-e**) were prepared by the reaction of ester derivative of gallic acid **5** with long-chain alkyl bromides in the presence of anhydrous potassium carbonate and catalytic amount of sodium iodide in refluxing acetone for 7–9 days, followed by hydrolysis of the esters **6a-e** with potassium hydroxide in ethanol and subsequent acidification with concentrated hydrochloric acid. The acid derivatives **7a-e** were then converted into their nitro derivatives **8a-e** by reacting the acid chlorides with *p*-nitrophenol in dichloromethane (DCM) in the presence of triethylamine as a base and 4-dimethylamino pyridine (DMAP)



Scheme 1. (i) CH_3I, and anhydrous K_2CO_3, dry acctone, reflux, 24 h. (ii) $POCl_3$, DMF, 90°C, 4 h (iii) EtOH, conc. H_2SO_4, reflux, 6 h. (iv) RBr, anhydrous K_2CO_3, NaI, dry accetone, reflux, 5–7 days. (v) KOH, rectified spirit, reflux, 6 h, HCl. (vi) $SOCl_2$, reflux, 3 h. (vii) *p*-Nitrophenol, DMAP, NEt_3 dry CH_2Cl_2, r.t., overnight. (viii) H_2-Pd/C, EtOAc, r.t., overnight. (ix) Dry EtoH, AcOH, reflux, 3–6 h.

as a catalyst. The nitro derivatives **8a-e** on hydrogenation give the corresponding amine derivatives **9a-e**. The condensation between aldehyde **3** and amines **9a-e** give corresponding Schiff's base derivatives **10a-e** (Scheme 1).

*Substrate **3** and **9a-e** were Prepared According to the Published Procedure [14,15].*

*General Procedure for the Preparation of Compounds **10a-e** by Schiff's base Formation.* Compound **3** (0.209 m.mol) was dissolved in dry hot ethanol (3 mL) and a catalytic amount of glacial acetic acid was added. To this solution amine derivatives **9a-e** (0.418 m.mol) dissolved in dry hot ethanol (5 mL) were added drop-wise. After 4–6 h a yellowish-brown gummy material separated out, which was filtered in hot condition and washed thrice with hot ethanol (3×5 mL) to give a solid compound **10a-e** as a pure one.

*Compound **10a**.* Yield 90% (pale yellow solid); IR ν_{max} 2905, 1720, 1585, 1494 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ_H 0.86–1.86 (m, 114H), 3.47 (s, 3H), 4.05 (t, 12H, $J = 4.5$ Hz), 7.17–7.29 (m, 12H), 7.42 (s, 4H), 7.85 (d, 4H, $J = 8.7$ Hz), 8.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.14, 22.71, 26.10, 29.38, 29.60, 29.76, 30.37, 31.95, 40.13, 69.27, 73.59, 108.55, 120.41, 121.84, 122.38, 123.91, 130.28, 142.99, 148.94, 150.66, 152.98, 159.63, 165.19. Anal. Calcd. for $C_{101}H_{151}N_3O_{10}$: C, 77.40; H, 9.71; N, 2.68. Found: C, 77.60; H, 10.01; N, 2.78%.

Compound ***10b***. Yield 85% (pale yellow solid); IR ν_{max} 2910, 1720, 1580, 1488 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.85–2.15 (m, 138H), 3.43 (s, 3H), 4.02 (t, 12H, $J = 5.28$ Hz), 7.16–7.30 (m, 12H), 7.40 (s, 4H), 7.83 (d, 4H, $J = 8.56$ Hz), 8.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.13, 22.71, 26.10, 29.38, 29.41, 29.60, 29.66, 29.76, 30.36, 31.95, 40.13, 69.27, 73.59, 108.55, 120.41, 121.84, 122.38, 123.91, 130.27, 142.99, 148.93, 150.66, 152.97, 159.65, 165.19. Anal. Calcd. for $C_{113}H_{175}N_3O_{10}$: C, 78.20; H, 10.16; N, 2.42. Found: C, 78.43; H, 10.41; N, 2.73%.

Compound ***10c***. Yield 80% (pale yellow solid); IR ν_{max}: 2911, 1722, 1578, 1490 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.85–1.84 (m, 162H), 3.43 (s, 3H), 4.02 (t, 12H, $J = 5.12$ Hz), 7.16–7.30 (m, 12H), 7.40 (s, 4H), 7.83 (d, 4H, $J = 8.6$ Hz), 8.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.14, 22.71, 26.10, 29.32, 29.40, 29.60, 29.66, 29.69, 29.73, 29.76, 30.37, 31.95, 40.13, 69.27, 73.59, 108.55, 120.41, 121.83, 122.37, 123.90, 130.26, 142.99, 148.93, 150.65, 152.97, 159.65, 165.20. Anal. Calcd. for $C_{125}H_{199}N_3O_{10}$: C, 78.85; H, 10.54; N, 2.21. Found: C, 79.07; H, 11.01; N, 2.23%.

Compound ***10d***. Yield 95% (pale yellow solid); IR ν_{max}: 2900, 1720, 1581, 1495 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.85–1.84 (m, 186H), 3.46 (s, 3H), 4.02 (t, 12H, $J = 5.28$ Hz), 7.16–7.27 (m, 12H), 7.40 (s, 4H), 7.83 (d, 4H, $J = 8.44$ Hz), 8.41 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 14.06, 22.67, 26.09, 29.35, 29.39, 29.70, 30.36, 31.92, 40.07, 69.34, 73.58, 108.73, 120.40, 121.78, 122.32, 123.95, 129.94, 130.20, 143.18, 148.96, 149.98, 150.68, 152.99, 159.53, 165.12. Anal. Calcd. for $C_{137}H_{223}N_3O_{10}$: C, 79.40; H, 10.85; N, 2.03. Found: C, 78.92; H, 11.10; N, 2.49%.

Compound ***10e***. Yield 92% (pale yellow solid); IR ν_{max}: 2910, 1718, 1575, 1490 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.85–1.84 (m, 210H), 3.46 (s, 3H), 4.02 (t, 12H, $J = 5.0$ Hz), 7.16–7.30 (m, 12H), 7.40 (s, 4H), 7.83 (d, 4H, $J = 8.44$ Hz), 8.41 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.14, 22.71, 25.95, 26.10, 29.32, 29.38, 29.42, 29.60, 29.66, 29.72, 29.76, 30.37, 31.95, 40.14, 69.26, 73.59, 108.54, 120.41, 121.84, 122.39, 123.90, 130.29, 142.99, 148.94, 150.65, 152.97, 159.63, 165.19. Anal. Calcd. for $C_{149}H_{247}N_3O_{10}$: C, 79.87; H, 11.11; N, 1.88. Found: C, 79.56; H, 11.21; N, 2.11%.

Results and Discussion

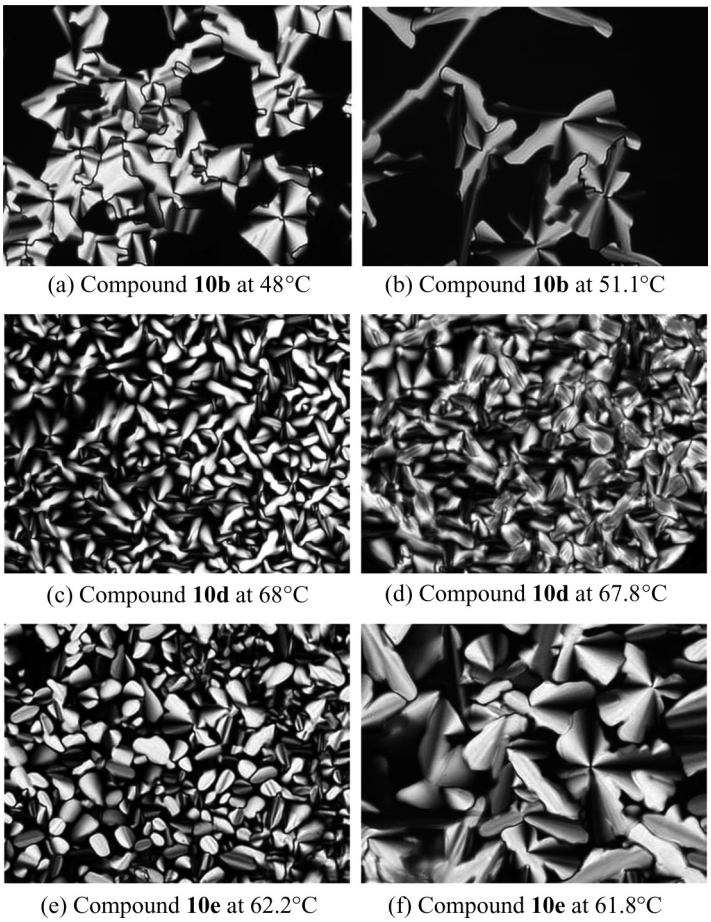
Mesogenic Properties

The liquid-crystalline phase transitions have been characterized by differential scanning calorimetry (DSC) and the characterization of textures was confirmed by viewing the birefringence of the samples between crossed polarizers in a polarizing microscope. The clearing transition peak in DSC (from liquid crystal to isotropic liquid phase) was somewhat broad in all samples. The phase transition temperatures and associated enthalpy recorded from DSC studies are summarized in Table 1. Phase types were assigned by comparison of the microscopic textures observed in polarized light with those published for reference compounds and established trends in thermodynamic stability [16–18]. Compound **10a** did not show mesomorphic property due to the shorter chain length at the terminal position but all the other compounds **10b-e** exhibited enantiotropic hexagonal columnar phase with decreasing clearing temperatures as terminal chain length increased. A typical pseudo-focal conics or fan-shaped texture was observed on both heating and cooling cycle of the compound **10b** when placed in a thin cell with a cell gap of $d = 5 \pm 0.2$ μm under

Table 1. Transition temperatures and associated enthalpy calculated from DSC Thermogram

10b	[i]Cr	$\xrightarrow[(0.48)^{n}]{43.50^{m}}$	Col_h	$\xrightarrow[(14.73)]{74.97}$	I	$\xrightarrow[(1.01)]{55.73}$	Col_h	$\xrightarrow[(0.21)]{39.50}$	Cr (0.60)[j]
10c	Cr	$\xrightarrow[(40.89)]{44.72}$	Col_h	$\xrightarrow[(8.73)]{68.40}$	I	$\xrightarrow[(0.58)]{50.62}$	Col_h	$\xrightarrow[(0.29)]{40.47}$	Cr (0.85)
10d	Cr	$\xrightarrow[(87.13)]{51.11}$	Col_h	$\xrightarrow[(2.04)]{66.82}$	I	$\xrightarrow[(1.92)]{65.80}$	Col_h	$\xrightarrow[(77.76)]{41.23}$	Cr (0.60)
10e	Cr	$\xrightarrow[(67.41)]{59.43}$	Col_h	$\xrightarrow[(30.65)]{62.58}$	I	$\xrightarrow[(1.92)]{58.85}$	Col_h	$\xrightarrow[(117.97)]{53.56}$	Cr (0.30)

Scan rate for all the samples is 5 degrees per minute.
m = corresponds to temperature in °C.
n = change in enthalpy $KJmol^{-1}$.
i = Cr, crystal; Col_h, hexagonal columnar; I, isotropic.
j = width at half height (in centimeter) on heating cycle.



(a) Compound **10b** at 48°C (b) Compound **10b** at 51.1°C

(c) Compound **10d** at 68°C (d) Compound **10d** at 67.8°C

(e) Compound **10e** at 62.2°C (f) Compound **10e** at 61.8°C

Figure 1. Polarizing micrograph of all compounds (a) and (b) were taken in indium tin oxide (ITO) coated cell with cell gap of $d = 5 \pm 0.2\,\mu m$. (c) to (f) taken in glass plate sandwiched by a coverslip.

homogeneous planar boundary conditions (Figs. 1a and b). This type of texture is characteristic or signature of hexagonal columnar (Col_h) phases [19–21]. On the DSC analysis, all compounds exhibited two enantiotropic transitions, crystal-to-columnar ($Cr \rightarrow Col_h$) and columnar-to-isotropic ($Col_h \rightarrow I$). Other compounds **10b,c** showed the same type of characteristic texture and shape of textures is somewhat dumbbell like in appearance (Figs. 1c–e), but compound **10d** having 16 carbon terminal trialkoxy chain showed the focal conic texture as well as dumbbell like texture, and compound **10e** showed the spherulitic texture (Fig. 1f), which is also a characteristic texture of columnar mesophase [22].

Computational Details

All computational calculations have been performed by the Chem3D version 10 [23] with Gaussian 03 Interface [24]. The geometry was optimized by the semi-empirical AM1 method to obtain the value of dipole moment and dipolar orientation of the molecules. The value of dipole moment was calculated for six terminal trialkoxy chains with C_6 units. The calculated dipole moment of the molecule was found to be 2.0656 D ($X = 1.277204$, $Y = -0.377771$, $Z = 1.579031$). If we suppose the Z-axis, as the molecular axis and the maxima of dipole is along the positive Z-axis, then the location of the dipole is along the central part of the molecule (Fig. 2). We assume that there must be axial dipole moment in the molecule as the dipolar orientation is along the molecular axis. The appearance of columnar phase in this bent shaped molecule may be due to the absence of transverse dipolar moment that can stabilize the B phases by orienting the molecules in near-neighbor antiparallel fashion. In the case of axial dipole the near neighbor correlation cannot be established, which disfavors the formation of banana phases.

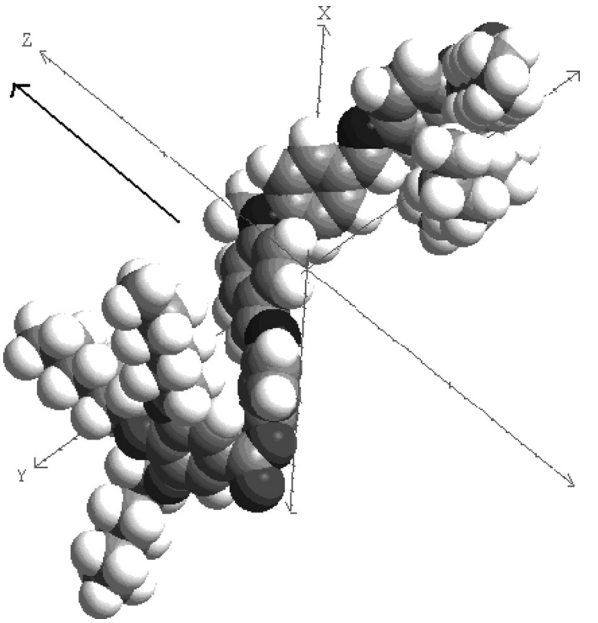


Figure 2. The optimized structure of compound **10** having six alkoxy chains with C_6 unit at the terminals. The arrow indicates the direction of net dipole moment.

Summary and Conclusions

In our earlier communications [14,15] we have confirmed that triphenylamine (TPA)- and diphenylamine (DPA)-based molecules exhibit columnar, SmA_d, and SmA_2 phases. *N*-Methyldiphenylamine shows a partial bilayer SmA_d to bilayer SmA_2 transition as temperature is lowered when the terminal chain is monoalkoxy. Here we report the substitution by a trialkoxy chain at the terminal of both the arms of the bent-shaped molecule. The mesophase observed was identified as hexagonal columnar phase except for compound **10a**. The molecules (**10b-e**) are bent in shape but the presence of trialkoxy terminal chains makes the difference in mesophase behavior because it is assumed that the chains are spread all over to form a disc-like shape.

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