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ABSTRACT

New five ring bent core mesogens derived from substituted 1,3-phenylenediamine (4-nitro-1,3-phenylenediamine) were synthesized. Their molecular structures, photophysical properties and mesogenic behaviors were investigated. The molecular structures and the purity of the bent core molecule have been characterized by spectroscopic studies and elemental analysis respectively. Photophysical properties of bent core compounds were investigated in chloroform by using UV–visible and fluorescence spectroscopic studies. The phase transition temperatures were detected by differential scanning calorimetry analysis and the phases are confirmed by polarizing optical microscopy. The polar substituents on bent core unit of bent shaped molecule influence the mesomorphic behaviors of the bent core mesogens. The polar nitro group at 4-position of the bent core unit displays tilted smectic C phase and unknown smectic X phase whereas chloro group at 4-position exhibits orthogonal senectic A phase. The bent core mesogens are fluorescent in nature. The density functional theory calculation was carried out to obtain the stable molecular conformation and chemical reactivity of the bent core molecules. Orbitals involved in the electronic transitions and their corresponding energies together with oscillator strengths have been reported.

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1. Introduction

Since more than last two decades, achiral bent core mesogens (BCMs) paid a special attention in the area of soft materials due to their interesting functional properties such as macroscopic polar order due to restricted rotation along molecular long axis (viz., ferro- and anti-ferroelectricity) [1], macroscopic chiral structure due to spontaneous achiral symmetry breaking [2] and exhibited fascinating optical textures. The manifestation of such interesting properties and exotic optical textures in BCMs depend on the molecular structural arrangement and their intermolecular interactions. The molecular structure and the intermolecular interactions are further governed by the factors such as bent core unit, number of the phenyl rings, length of the terminal chain, direction and the conjugation of the linking group between the two phenyl rings units and nature of substituents on the bending unit or outer phenyl ring of the bent core molecule. Moreover, in general, small changes in these factors led to drastic change in the

* Corresponding author. E-mail address: paulmanojaus@gmail.com (M.K. Paul). mesophase behavior and their transition temperatures. Generally, the substitutions viz., fluoro, chloro, bromo, nitro, cyano, methyl etc. attached to the central bending unit change the bending angle of the molecule which in turn leads to the formation of different types of mesophase [3]. The structure-property relationship of the bent core molecules are well documented in excellent reviews [4–7]. The most of the rigid bent core unit used in mesogenic bent core molecule consists of resorcinol molecule whereas mesogenic bent core molecules obtained from 1,3-phenylene diamine rigid bent core are rare and limited [8–10]. Further, lateral substituents on the central resorcinol bending unit or the outer phenyl ring significantly influence the mesogenic behavior [11–21]. Moreover, it is established that mesophase behavior of the BCMs are much more strongly influenced by the substituent at the central bent core unit than by these at the outer phenyl ring [22-25]. The dipolar effects are more significant than the steric effects due to the presence of the polar substituent on the central or outer phenyl ring of the molecule. The first symmetrical achiral bent core molecule derived from 1,3-phenylene diamine viz., N, N'-bis[4-(4'-n-alkoxybenzoyloxy)benzylidene]-phenylene 1,3-diamine exhibited B₆ and or B₁ phase depending on the 4-*n*-alkoxy chain length [26]. To



the best of our knowledge, influence of substitutions on bent core unit of a bent molecule N, N'-bis[4-(4'-*n*-tetradecyloxybenzoyloxy) benzylidene]-phenylene 1,3-diamine have not been studied. This may be due to the complexity in the synthesis and purification of the compounds. Moreover, in recent years, light emitting mesogens drags attention as new functional materials due to their potential application in organic light emitting diodes. The photophysical studies of the bent core mesogenic functional materials are less studied [27–30].

In this article, we report the influence of the strong (nitro) and weak (chloro) electron withdrawing lateral substituents on the bending unit of the bent core molecule. The dipolar properties of the nitro group are significantly differs from the chloro group. Therefore, the nature of the mesophase is greatly influenced by the substitution of nitro and chloro group at the bending unit of the bent core molecule. As mentioned, the two new bent core compounds **3-NO**₂ and **3-CI** have been synthesized and study their photophysical properties, mesophase behavior and to explore the structural and electronic properties of the BCMs by computational studies.

2. Experimental

2.1. Chemical and instruments

The chemicals used for the synthesis of BCMs were procured from M/s Alfa Aesar. Sigma Aldrich and Tokvo Kasei Kogvo Co. Ltd. The solvents and reagents are of AR grade and were distilled and dried before use. Micro analysis of C, H and N elements were determined on Perkin Elmer 2400elemental analyzer. IR spectra were recorded on a Shimadzu IR Prestige-21 on KBr disk. The ¹H nuclear magnetic resonance spectra were recorded either on JEOL AL300 FTNMR multinuclear spectrometer in CDCl₃ (chemical shift δ in parts per million) solution with TMS as internal standard. UV-visible absorption spectra of the compounds in chloroform were recorded on a Perkin Elmer lambda 35 UV-visible spectrophotometer (λ_{max} in nm). Fluorescence emission spectra of the compounds in chloroform were recorded with a Perkin Elmer LS45 spectro-fluorophotometer. The phase transition temperatures, associated enthalpies and entropies were recorded at a heating/ cooling rate of 5 °C min⁻¹ on differential scanning calorimetry (DSC) (Perkin-Elmer Pyris-1 system). The DSC was calibrated with indium (156.6 °C, 28.4 Jg⁻¹) and tin (232.1 °C, 60.5 Jg⁻¹). The liquid crystalline properties of the compounds were characterized by using polarized optical microscope (Nikon optiphot-2-pol attached with hot and cold stage HCS402, with STC200 temperature controller configured for HCS402 from INSTEC Inc. USA).

2.2. Computational details

The density functional theory (DFT) has been used to explore the structural and electronic properties of the BCMs. We have used Becke's three-parameterized exchange functional and Lee-Yang-Parr correlation functional (B3LYP) [31,32] and 6-31G (d) basis set [33–35]. All DFT calculations are performed with Gaussian 09 program package [36]. To see the effects of solvent, calculations are also presented in the presence of chloroform as solvents.

2.3. Synthesis of 4-n-tetradecyloxybenzoic acid (1)

4-*n*-tetradecyloxybenzoic acid was prepared following the earlier reported procedures [37].

2.4. Synthesis of 4-n-tetradecyloxybenzoyloxybenzaldehyde (2)

The synthesis of 4-*n*-tetradecyloxybenzoyloxybenzaldehyde was prepared by following earlier reported procedure [38].

2.5. General procedure for synthesis of bent core compounds (3-X)

4-*n*-tetradecyloxybenzoyloxybenzaldehyde (219 mg, 5×10^{-4} mol) was dissolved in absolute ethanol with few drops of glacial acetic acid and reflux for 30 min. To this refluxing solution, an absolute ethanolic solution of substituted 1,3-phenylenediamine [*viz.*, 4-nitro-1,3-phenylenediamine (39 mg, 2.5×10^{-4} mol), 4-chloro-1,3-phenylenediamine (36 mg, 2.5×10^{-4} mol)] was added drop by drop with constant stirring. The reaction mixture was refluxed for 4 h with constant stirring. The excess of ethanol was evaporated to obtain the yellow solid which was washed several times with ice cold dry hexane to get the compound.

2.5.1. N, N'-bis[4-(4'-n-tetradecyloxybenzoyloxy)benzylidene]-4nitrophenylene-1,3-diamine (**3-NO**₂)

Yield: 119 mg (46%); IR (ν_{max} in cm⁻¹): 1687 ($\nu_{C=0}$), 1606 ($\nu_{C=N}$ imine), 1564 ($\nu_{(C=C)}$ aromatic), 1487, 1447, 1387 (ν_{NO} nitro). ¹HNMR (CDCl₃, 300 MHz): $\delta = 8.60$ (s, 1H, CH=N), 8.20 (s, 1H, CH=N), 8.06-6.94 (19H, Ar-H), 4.04 (t, 4H, J = 6.4 Hz, -OCH₂-), 1.83-1.28 (m, 48H,-(CH₂)₁₂-), 0.90 (t, 6H, J = 6.8 Hz, -CH₃). Elemental analysis calculated for C₆₂H₇₉N₃O₈: C, 74.89; H, 8.11; N, 4.63; Found: C, 75.01; H, 8.24; N, 4.51%.

2.5.2. N, N'-bis[4-(4'-n-tetradecyloxybenzoyloxy)benzylidene]-4chlorophenylene-1,3-diamine(3-Cl)

Yield: 90 mg (37%); IR (υ_{max} in cm⁻¹):2981, 2850 (ν_{CH}), 1731 ($\nu_{C=0}$), 1606 ($\nu_{C=N}$ imine), 1564 ($\nu_{(C=C)}$ aromatic), 1487, 1447. ¹HNMR (CDCl₃, 300 MHz): $\delta = 8.45$ (s, 1H, CH=N), 8.19 (s, 1H, CH=N), 8.08-6.98 (19H, Ar-H), 4.03 (t, 4H, J = 6.8 Hz, -OCH₂-), 1.86-1.26 (m, 48H,-(CH₂)₁₂-), 0.89 (t, 6H, J = 6.6 Hz, -CH₃). Elemental analysis calculated for C₆₂H₇₉N₂O₆Cl: C, 75.92; H, 8.04; N, 2.93; Found: C, 75.70; H, 8.09; N, 2.85%.

3. Results and discussion

3.1. Synthesis and molecular characterization

Achiral five ring bent core molecules derived from 4-substituted 1,3-phenylenediamine possessing ester and imine linkage had been designed with 4-*n*-tetradecyloxy chain at both ends. The ester and imine linking groups are more commonly used linking group in liquid crystalline molecule due to fact that these linking moieties enhances conjugation of the molecule and in turn more conductive to liquid crystal formation. The detail synthesis of the compounds as shown in Scheme 1 was carried out by the following procedure described in experimental section. The alkylation of 4hydroxyethylbenzoate with 4-n-tetradecylbromide followed by acid hydrolysis to gives 4-n-tetradecyloxybenzoic acid (1). The 4-ntetradecyloxybenzoic acid was further esterified with 4hydroxybenzaldehyde by phase transfer method using tetrabutylammonium bromide (TBAB) as catalyst to gives4-n-tetradecyloxybenzoyloxybenzaldehyde (2). The condensation of 4-ntetradecyloxybenzoyloxybenzaldehyde (2) with substituted 1,3phenylene diamine (4-nitro-1,3-phenylediamine and 4-chloro-1,3-phenylenediamine) in absolute ethanol with a few drops of glacial acetic acid to yield final target achiral five ring bent core compounds (3-X, $X = NO_2$ and Cl). The introduction nitro and chloro substituents on the bending unit of bent core molecule is due to their strong and weak electron withdrawing nature which in turn influences the dipolar nature of the bent core molecule. The



Scheme 1. Synthetic route for the preparation of the bent core compounds. Reagents and conditions: (i) Absolute EtOH, KOH, KI (catalytic amount), reflux 40 h; (ii) HCl, H₂O, reflux, 6 h; (iii) SOCl₂, reflux, 3 h; (iv) Dry DCM, K₂CO₃, TBAB, Stir 24 h at room temperature; (v) Absolute EtOH, glacial AcOH, 4-nitro-1,3-phenylenediamine or 4-chloro-1,3-phenylenediamine.

compounds (**3-X**, **X** = **NO**₂and**CI**) were purified by washing precipitate several times with cold dry hexane till the appearance of single spot in neutral alumina thin layer chromatographic plate. The molecular structure and the chemical purity of the newly synthesized bent core compounds (**3-X**, **X** = **NO**₂and **CI**) were confirmed by spectral and elemental analysis. The formation of the compounds were confirmed by Fourier transform infrared (FTIR) with the appearance of characteristic imine (C=N) stretching peak in the range of 1606–1600 cm⁻¹, ester (C=O) stretching in the range of 1687–1649 cm⁻¹and ether C–O stretching at 1257 cm⁻¹respectively. ¹H NMR spectra of the bent core molecule (**3-X**, **X** = **NO**₂ and **CI**) show two signal appeared in the range of 8.20–8.60 ppm due to imine proton and confirmed the formation of the Schiff base. All the aromatic protons appeared in the range of 8.23–6.42 ppm.

3.2. Photophysical studies

The emission properties of organic bent core mesogens are currently an active area of research due to their potential applications in opto-electronics. Emissive mesogens are fascinating systems for soft materials research because they couple molecular self-assembly with intrinsic light generation capability. The substituent on the central core plays an important role in the modification of the electronic characteristics of the molecules. Hence, the absorption and emission properties of the compounds were studied, and the results are presented. The UV–visible absorption spectra of the bent core compounds (**3-X**, **X** = **NO**₂ and **CI**) in chloroform were studied at concentration of 1×10^{-4} M as presented in Table 1. The 4-nitro substituted bent core compound (**3-NO**₂) exhibited

Table 1	
A summary of the photophysical properties of the compounds in chloroform.	

absorption peak at 260 nm (ϵ_{max} = 21970 $Lmol^{-1}\ cm^{-1}$). These absorption band with large molar extinction coefficient reflects the π - π^* transition of polar C=O and C=N groups of the molecule. The absorption band ranging from 300 to 437 with small molar extinction coefficient ($\epsilon_{max} = 2310 \text{ Lmol}^{-1} \text{ cm}^{-1}$) indicates $n - \pi^*$ transition of the molecule as presented in Fig. 1. The chloro substituted bent core compound (**3-Cl**) exhibited absorption peaks at 290 nm ($\varepsilon_{max} = 53600$ Lmol⁻¹ cm⁻¹) and broad band ranging from 309 to 409 nm ($\epsilon_{max} = 1920 \text{ Lmol}^{-1} \text{ cm}^{-1}$) indicated *n*- π^* transition as presented in Fig. 2. The fluorescence emission spectra of the bent core compounds (**3-X**, **X** = **NO**₂ and **CI**) were examined in chloroform solution (1×10^{-5} M), and it was found that compound (3-NO₂) exhibited strong fluorescence in ultraviolet region $(\lambda_{em} = 305 \text{ nm})$ on excitation at 260 nm (see Fig. 3) whereas **3-Cl** emitted in the visible region ($\lambda_{em} = 420 \text{ nm}$) with a shoulder at 509 nm on excitation at 310 nm which is tailing over 600 nm as presented in Fig. 4. The photophysical properties of the ligands (3-**X**, $\mathbf{X} = \mathbf{NO}_2$ and **Cl**) in chloroform are presented in Table 1. The emission peak for compound (3-NO2) observed at 305 nm with a stoke shift (v_{ss}) of 222222 cm⁻¹ and **3-Cl** observed at 420 nm and 509 nm with a stoke shift of 90909 and 50251 cm^{-1} respectively. The stoke shift value of the **3-Cl** is larger as compared to the compound 3-NO₂. The larger stoke shift value for the chloro substituted compound can be due to the significant structural changes that occur between the ground and excited state. Despite similar skeletal structure of the molecule, a large red-shift in fluorescence ~115 nm for 3-Cl in contrast to 3-NO2 is intriguing. This may be due to the replacement of nitro group by the chloro group, which further led to change in the electronic structure of the molecule. Interestingly, 3-Cl showed characteristic dual emission peaks. The emission peak at the lower wavelength ~420 nm corresponds to the radiative transition from local excited state or Frank Condon state while the second emission peak observed at the longer wavelength ~509 nm due to intramolecular charge transfer transition state [39].



Fig. 1. UV–visible absorption spectra of **3-NO**₂ in chloroform ($c = 1 \times 10^{-4}$ M).

Compounds	Abs, λ_{max} (nm)	Molar extinction coefficient, ϵ (Lmol ⁻¹ cm ⁻¹)	Excited wavelength λ_{ex} (nm)	Fl. λ_{em} (nm)	Stoke shift, v_{ss} (cm ⁻¹)
3-NO ₂	260 300–437	21970 2310	260	305	222222
3-Cl	290 309–409	53600 1920	310	420 508	90909 50251



Fig. 2. UV–visible absorption spectra of **3-Cl** in chloroform (c = 1×10^{-4} M).



Fig. 3. Emission spectrum of compound (3-NO_2) recorded in chloroform (1 \times 10 $^{-5}$ M) at excited 260 nm.



Fig. 4. Emission spectrum of compound (3-Cl) recorded in chloroform (1 \times 10 $^{-5}$ M) at excited 310 nm.

3.3. Mesomorphic behavior: polarized optical microscopy and differential scanning calorimetric studies

To confirm the observed phase transition temperatures obtained by differential scanning calorimetry (DSC), the polarized optical microscopy (POM) were performed and examined liquid crystalline phases. The transition temperatures, enthalpies and entropies associated with the phase transitions of the BCMs (3-NO₂) and 3-Cl) which were obtained from DSC at a scan rate of 5 °C min⁻¹ in the first heating and cooling scans are presented in Table 2. The DSC thermogram of compound **3-NO**₂ is presented in Fig. 5. The phase transition temperature of compound **3-Cl** could not be recorded in DSC due to either viscous nature of the sample that leads to slow crystallization or vitrification of the mesophase. The compound **3-NO**₂ exhibited SmC and unidentified SmX phase whereas 3-Cl exhibited only SmA phase as observed by POM. On slow cooling the compound **3-NO₂** from isotropic liquid, branched like texture grow from black field (isotropic liquid) of the crossed polarizers at 127.1 °C as presented in Fig. 6a. The branched texture transform to two and four brushes defects schlieren texture at 126.5 °C as presented in Fig. 6b, a typical texture of smectic C phase. On further cooling, the smectic C phase undergoes a transition to an unidentified SmX phase at 123 °C as presented in Fig. 6c. The birefringent unidentified SmX phase completely grows as presented in Fig. 6d. Finally, crystallization occurs at 86 °C. The phase transition temperatures obtained from the DSC thermogram of the compound (3-NO₂) are matches with the transition temperature obtained from polarized optical microscopy. The DSC could not detect the SmC-SmX transition. This indicates that enthalpy change during SmC–SmX phase transition is very small (<0.01 kJ mol⁻¹) and is second order transition. The large enthalpy change (~6 kJ mol⁻¹) during isotropic to SmC transition indicate strong first order character of transition [40]. On slow cooling the sample (3-Cl) from isotropic liquid, batonnets texture appears which further coalesces to form typical focal conic texture with a dark (homeotropic) region at 116.8 °C indicates SmA phase as presented in Fig. 7a. The homeotropic region increases either by application of the mechanical stress or by shearing the glass slides, confirmed SmA phase. On further cooling, the homeotropic regions lowly disappeared to a focal conic texture. The focal conic SmA texture persist to room temperature as presented in Fig. 7b.

3.4. DFT studies

Geometry optimization was performed without imposing molecular symmetry constraints to determine the stable configuration. The optimized structures have no imaginary frequency which confirms that they correspond to minimum in the potential energy surface. Our calculation [see in supporting information Table S1 (a-b)] shows that some dihedral angles get changed in solvent phase compare to gas phase. The dihedral angles changed significantly near the rigid aromatic core region than the flexible long aliphatic region of the **3-X** (**X** = **Cl**, **NO**₂) molecule. Since nitro group is a strong electron withdrawing group than chloro group, the change in dihedral angles is more intensive near the nitro group than chloro group. It is observed that, in case of **3-NO**₂ substituted system, there is large change in bending angle when the system undergoes transition from gas phase to solvent phase and this change is much greater than **3-Cl** substituted system [see Fig. 8]. Therefore, a noticeable change in dihedral angle in solvent phase has been found near the core region for **3-NO₂** substituted system. The bending angle of core compounds $(3-X, X = NO_2 \text{ and } CI)$, reduced in solvent phase compare to gas phase.

The UV—visible absorption spectra of the compounds have been studied using time dependent density functional theory (TD-DFT). The calculated electronic excitations of maximum intensity as well as highest oscillator strength are listed in Table 3. For **3-NO**₂ substituted system, the UV—visible spectra in both gas phase and solvent phase shows that the maximum peak corresponds to highest oscillator strength. But for **3-CI** substituted system, in both gas phase and solvent phase the UV—visible spectra shows that the

Table 2

Phase transition temperatures (°C) of the bent core compounds recorded for first heating (first row) and first cooling (second row) cycles at 5 °C min⁻¹ from DSC and confirmed by polarized optical microscopy. The enthalpies (Δ H in kJ mol⁻¹) and entropies (Δ S in Jmol⁻¹ K⁻¹) respectively are presented in parentheses.

Compounds	Phase transition temperature in °C (enthalpy, entropy)				
3-NO ₂	Cr 85.4 (11.53, 32.17) SmX 88.8 (6.88, 19.01) SmC 128.5 (6.60, 16.43) Iso				
	Cr 78.1 (13.16, 37.27) SmX 86.0 (18.36, 51.14) SmC 127.3 (6.39, 15.96) Iso				
3-Cl^a	Cr 106.0 SmA 169.6 Iso				
	Iso 167.0 SmA 87.0 Cr				

^a Indicates the polarizing optical microscopic temperature.



Fig. 5. DSC thermogram of compound **3-NO₂** in the heating and cooling cycle at 5 °C/min.



Fig. 6. Polarizing optical photograph of **3-NO**₂ during cooling: (a) branched like schlieren growth from isotropic liquid at 127.1 °C; (b) Typical two and four brushes schlieren texture of the smectic C phase at 126.5 °C; (c) transition of smectic C phase to SmX phase at 123 °C. (d) unidentified SmX phase at 122.5 °C.



Fig. 7. Polarizing optical photograph of 3-Cl during cooling: (a) focal conic texture of smectic A at 116.8 °C; (b) focal conic texture of SmA phase at 30 °C.



Fig. 8. Optimized geometries of 3-Cl and 3-NO₂ with bending angle in both gas and solvent phase (a) 3-Cl in gas phase; (b) 3-Cl in chloroform; (c) 3-NO₂ in gas phase; (d) 3-NO₂ in chloroform.

Table 3

Calculated electronic transitions for maximum peak in UV–Visible absorption spectra of bent core compounds (**3-NO₂** and **3-Cl**) in gas medium and chloroform.

Compounds	Medium	Abs, λ _{max} (nm)	Oscillator strength, f	Excitation transitions
3-Cl	Gas	289.755 (maximum peak)	0.422	HOMO-3 → LUMO (15%) HOMO-2 → LUMO (16%) HOMO → LUMO+2 (19%) HOMO → LUMO+3 (33%)
		359.299 (highest Osc. strength)	0.5004	HOMO \rightarrow LUMO (29%) HOMO \rightarrow LUMO+1 (59%)
	Chloroform	294.981 (maximum peak)	0.5218	HOMO-2 \rightarrow LUMO+1 (39%) HOMO-1 \rightarrow LUMO+1 (30%)
		356.039 (highest Osc. strength)	0.626	HOMO \rightarrow LUMO (51%) HOMO \rightarrow LUMO+1 (37%)
3-NO ₂	Gas	354.542 (maximum peak)	0.754	HOMO-1 \rightarrow LUMO (34%) HOMO \rightarrow LUMO (41%)
		290.053 (2nd highest peaks)	0.364	HOMO-2 \rightarrow LUMO+1 (20%) HOMO-1 \rightarrow LUMO+1 (24%) HOMO-1 \rightarrow LUMO+2 (10%) HOMO \rightarrow LUMO+2 (19%)
	Chloroform	362.906 (maximum peak)	0.543	HOMO-3 \rightarrow LUMO (42%) HOMO-1 \rightarrow LUMO (40%)
		296.519 (2nd highest peaks)	0.408	$HOMO-1 \rightarrow LUMO+1 (64\%)$

peak that corresponds to highest oscillator strength is not the maximum one. The second highest peak corresponds to highest oscillator strength. The calculated UV-visible absorption spectra of the two compounds 3-NO2 and 3-Cl in different medium are shown in Figs. 9 and 10 respectively. For 3-Cl substituted system, the UV-visible spectra show two strong peaks. Interestingly, the inclusion of solvent lowers the intensity of maximum peak and increase the intensity of second highest peak compared to gas phase. Thus the difference in intensity between two strong peaks is less in solvent phase compare to gas phase. The compound 3-Cl in gas phase exhibit highest peak at 289.755 nm corresponds to oscillator strength f = 0.422 which agrees well with the experimental peak at 290 nm. This peak originates from the excitation transitions $(HOMO-3) \rightarrow LUMO, (HOMO-2) \rightarrow LUMO, HOMO \rightarrow (LUMO+2)$ and HOMO \rightarrow (LUMO+3). The orbital analysis shows that the transition is $n-\pi^*$. p_z orbital of Cl; p_z , p_y and p_x orbital of C; p_y and p_x orbital of N and p_z , p_x and s orbital of O is basically responsible for this transition. Moreover, the UV-visible absorption spectrum of the compound (3-Cl) in gas phase shows some possible transition at 359.299, 346.119, 318.134, 296.667, 292.241and 286.077 nm respectively. The second highest peak at 359.299 nm corresponds to highest oscillator strength f = 0.50. The compound **3-Cl** in solvent phase has highest peak at 294.981 nm with oscillator strength, f = 0.522. This peak is mainly characterized bν $(HOMO-2) \rightarrow (LUMO+1)$ and $(HOMO-1) \rightarrow (LUMO+1)$ transitions and indicate $n-\pi^*$ transition. This transition in originating mainly from p_z orbital of Cl; p_z , p_y and p_x orbital of C; p_y and of N and p_{y} orbital of O. Excluding maximum peak, there are some other transitions found at 355.131, 350.512, 319.725, 281.275, 266.315, and 263.895 nm respectively. The gas-phase calculated λ_{max} (maximum peak) value for compound 3-Cl is blue shifted compared to the experimental data but red shifted for solvent phase calculated value. Additionally, the gas-phase calculated λ_{max} (maximum peak) value for compound 3-Cl is closer with experimental data. A broad absorption band observed in the experiment from 309 to 409 nm and is also observed in our calculation. Similar to 3-Cl substituted system, the UV-visible spectra of 3-NO₂ substituted system also shows two peaks, but now the increase in intensity of second highest peak is comparatively less than that observed in 3-Cl substituted system. The calculated absorption spectrum of 3-NO2 in gas phase shows that the maximum peak is located at 354.542 nm with highest oscillator strength f = 0.754 and second highest peak at 290.036 nm with f = 0.364. In solvent phase, the maximum peak is observed at 362.906 nm with highest oscillator strength f = 0.543. In solvent phase another strong peak has been found at 296.519 nm with oscillator strength f = 0.408. The gas

phase calculation underestimate λ_{max} compares to experimental one, but the another peak (at $\lambda = 290.053$ nm) is relatively closer to experimental value (260 nm). Surprisingly, the solvent phase calculated λ_{max} (highest peak) leads to further underestimation. The broad absorption band extending up to 437 nm as seen in experiment is also found in the calculation. On comparing the absorption spectra in gas and solvent phases, it is seen from Table 3 that the maximum absorption peak of both compounds **3-Cl** and 3-NO₂ are red shifted in the solvent phase. Actually in solvent phase, the solvents interact with solute molecules and may lower the energy of the excited state or increase the ground state energy. Therefore, decreases the energy of transition and absorption maximum appears red shifted in going from gaseous medium to solvent medium. This red shift is comparatively smaller for **3-Cl** substituted system which indicates that, the interaction of solute molecule with solvent is less for 3-Cl substituted system compare to 3-NO₂ substituted system. That is why both the gas phase and solvent phase calculated λ_{max} of **3-Cl** substituted system is nearly equal to experimental value. Additionally, the comparison of UV-visible spectra of 3-Cl and 3-NO2 substituted system shows that, the substitution of the chloro group by the nitro group leads to a red shift of maximum peak towards lower energy both in gas phase and solvent phase.

3.5. Chemical reactivity

Frontier molecular orbitals i.e., the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are important quantum chemical parameters which determine the reactivity and light absorption ability of molecules. HOMO plays the role of electron donor and LUMO plays the role of electron acceptor. In accordance with the frontier molecular orbital theory, the transition state is arises due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants. Calculated values of HOMO and LUMO energies along with HOMO-LUMO energy gap are listed in Table 4. The HOMO and LUMO energies of the compound 3-Cl are lower than that of 3-NO2. Also, the HOMO and LUMO energies in solvent phase are higher than that of gas phase. HOMO-LUMO energy gap can reflect the chemical stability and can be used as stability index of the molecules. The HOMO-LOMO energy gaps for the compounds3-Cl and 3-NO2 are 4.035 and 3.911 eV respectively in gas phase. The corresponding HOMO-LUMO gaps in solvent phase are 4.099 and 3.805 eV respectively. The calculated gap indicates that **3-Cl** is more stable than **3-NO**₂. Moreover, the energy gap increases in the presence of chloroform solvent for 3-Cl compounds but decreases for 3-NO2 compounds. Fig. 11 depicts the



Fig. 9. UV-Visible absorption spectra of 3-NO2 (a) in gas and (b) solvent phases.



Fig. 10. UV-visible absorption spectra for 3-Cl. (a) in gas and (b) solvent phases.

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alculated HOMO, LUMO, HOMO-LUMO gap, IP EA, dipole moment and polarizability of bent core compounds (3-NO₂ and 3-CI) in gas medium and chlorofor	m.

Compounds	Medium	Energy (eV)		Energy gap (eV)	IP (eV)	EA (eV)	Dipole moment (Debye)	Polarizability (Bohr ³)
		НОМО	LUMO					
3-NO ₂	Gas	-6.106	-2.195	3.911	7.022	1.031	10.366	833.40
	Chloroform	-6.267	-2.462	3.805	6.373	2.232	13.661	952.20
3-Cl	Gas	-5.656	-1.620	4.035	6.762	0.654	7.391	820.60
	Chloroform	-5.904	-1.805	4.099	6.083	1.655	8.986	930.69

frontier HOMO-LUMO orbital pictures. The ionization potential can be correlated with the energy of the HOMO and the energy of the LUMO is directly associated with the electron affinity. Thus, the HOMO value indicates a tendency of the molecule to donate electrons to appropriate acceptor while the values of LUMO energy indicate the possibility to accept electrons. From Fig. 11, it is clearly observed that the charge density is different from one part of the molecule to the other. Both for 3-Cl and 3-NO2, the HOMO-LUMO plot in gas phase and solvent phase indicates that the charge is mainly accumulated in the central core and substituted functional group not in the outer phenyl rings. In case of 3-Cl substituted system, HOMO is mainly located on chloro group and LUMO has very small contribution on it, both in gas and solvent phase. Another observation is that, in HOMO, more charge is accumulated near chloro group in gas phase compare to solvent phase. In case of 3-NO₂ substituted system, in LUMO, the charge is mainly accumulated from the nitro group. Moreover, from the HOMO-LUMO orbital picture, it is found that the filled π -orbital (HOMO) is more extended in solvent phase than gas phase. In addition, the change in LUMO and HOMO picture due to inclusion of solvent indicates a substantial redistribution of π -electron densities in solvent phase and the redistribution of π -electron densities is more intensive in 3-NO₂ substituted system than 3-Cl substituted system. The dipole moment and polarizability provide information about the charge distribution in the molecule. Using the x,y,z cartesian component, the magnitude of total dipole moment and polarizability, can be written as,

$$\mu_{tot} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}}$$
(1)

$$\alpha_{tot} = \frac{1}{3} \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right) \tag{2}$$

There is a considerable increase in dipole moment and

polarizability in the solvent phase compare to gas phase for this core compounds (**3-X**, $\mathbf{X} = \mathbf{NO}_2$ and **Cl**), indicating a substantial redistribution of π -electron densities in solvent phase. In addition, the ground state dipole moment and polarizability is higher for 3-NO₂ substituted system than 3-Cl substituted system [see Table 4]. The presence of the lateral polar NO₂ group with large dipole moment at an angle to the long axis of the bent core molecule favors tilted and biaxial smectic C phase whereas lateral Cl group favors orthogonal smectic A phase as observed in the optical texture studies. Therefore, the suitable interplay of the molecular structural anisotropy and the shape factor with the required polarizability anisotropy can be important factor which lead to the biaxial smectic phase. Ionization potential (IP) has been calculated as the energy difference between neutral system and the positive ion *i.e.*, IP = E(N-1)-E(N). The electron affinity (EA) has been calculated as the energy difference between neutral system and the negative *i.e.*, EA = E(N) - E(N + 1). The calculated values of *IP* and *EA* are given in Table 4. In both gas and solvent phases, 3-Cl has lower *IP* as well as *EA* values than **3-NO**₂. In the solvent phase, both the compounds have lower values of *IP* than in the gas phase. On the other hand, the compounds have higher values of EA in the solvent phase than in the gas phase. Thus, it can be inferred that it is easier to remove or add electrons when the compounds are in solvent phase.

Global reactivity parameters help to study the reaction pathway [41]. Chemical reactivity descriptors such as chemical potential (μ), chemical hardness (η) and electrophilicity index (ω) can be successfully used to predict reactivity trends in different systems [42,43]. These quantities are calculated as

$$\mu = -\frac{IP + EA}{2} \tag{3}$$



Fig. 11. HOMO, LUMO plot of 3-NO2 and 3-Cl in both gas and solvent phase (a) 3-Cl in gas phase; (b) 3-Cl in chloroform; (c) 3-NO2 in gas phase; (d) 3-NO2 in chloroform.

$$\eta = IP - EA \tag{4}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{5}$$

These reactivity parameters not only describe the ground state behavior of the system but also explain the excited state phenomena [44–48]. Reactivity parameters are also helpful to analyze toxicity [49,50]. Table 5 presents the calculated values of μ , η and ω .

Table 5

Calculated values of chemical potential (μ), chemical hardness (η) and electrophilicity index (ω) of bent core compounds (**3-NO**₂ and **3-Cl**) in gas medium and chloroform.

Compounds	Medium	μ (eV)	η (eV)	$\Omega (eV)$
3-NO ₂	Gas	-4.027	5.991	1.353
	Chloroform	-4.141	4.303	1.993
3-Cl	Gas	-3.708	6.108	1.126
	Chloroform	-3.869	4.428	1.690

Chemical potential measures the electron escaping tendency from the system. Electrons tend to flow from systems with higher chemical potential to systems with lower chemical potential. Thus, systems having lower chemical potential values have higher electron attracting power. **3-NO**₂ has lower μ values than **3-Cl** *i.e.*, the presence of nitro group (NO₂) makes the compound **3-NO₂** more electrons attracting in nature compared to 3-Cl compound. Moreover, μ value in solvent phase is lower than in the gas phase. Chemical hardness indicates resistance to charge transfer and can give a measure of the chemical stability of the system. It is obvious from Table 5 that among the two compounds, 3-Cl has higher hardness value than 3-NO2 which indicates that the compound 3-Cl is chemically more inert. The chemical hardness value decreases in the solvent phase suggests that the compounds become more reactive in the solvent phase. Electrophilicity index is an important reactivity descriptor which gives a measure of the stabilization in energy when the system acquires electrons from surrounding [51]. Electrophilicity index is a quantity which contains kinetic and thermodynamic information of the system [52–55]. Among the two compounds, **3-NO**₂ has higher ω *i.e.*, the nitro substituted

compound **3-NO**₂ has higher tendency to accept electrons than chloro substituted compound **3-Cl**. Also the tendency of the compounds to acquire electrons also increases in solvent phase.

4. Conclusion

New five ring bent core molecule derived from 4-substituted 1,3-phenylenediamine with ester imine linkage have been synthesized and characterized. The influence of polar substitution at the central bent core was investigated with respect to its effects upon the structures of the mesophases. The nitro group substitution at the 4-position of the bent core unit of the bent core molecule exhibited tilted SmC and unidentified SmX phase. The replacement of the nitro group by the chloro group leads to a drastic change in the mesophase behaviors and displayed orthogonal SmA phase. Both the bent core mesogens are fluorescent in nature with large stoke shift. The bent core mesogens possess nitro and chloro substitution at the central bent core unit display interesting intrinsic light generating ability. The nitro substituted bent core mesogen emits in the region Ultra-Violet (280-400 nm) region whereas chloro substitution at the central bent core emits in the 350–600 nm region. Theoretical calculation predicts the greater stability and less reactivity of 3-Cl compound over 3-NO2 compound and shed insights on the higher dipole moment, polarizability and electron attracting power of 3-NO2 compound than 3-Cl compound. Moreover the inclusion of solvent makes these systems more reactive and increases the dipole moment and polarizability. Based on the results obtained from TD-DFT calculation, it is clear that, accurate prediction of the excitation energy does not require the inclusion of solvent. The solvent phase calculation underestimate the value of λ_{max} compare to experiment, but gas phase calculated value is near the experimentally observed one. Our calculated UV-visible spectra of compound **3-Cl** in gas phase has highest peak at 289.755 nm which matches well with experimental value.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.04.060.

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