

Article

Nematogenic Laterally Substituted Supramolecular H-Bonded Complexes Based on Flexible Core

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Abstract: New laterally CH₃-substituted series of 1:2 hydrogen-bonded supramolecular complexes (HBSMCs) based on flexible acid core were prepared and mesomorphically investigated. Mixtures were formed through H-bonded interactions between adipic acid (A) and 4-(2-(pyridin-4-yl)diazenyl-(3-methylphenyl) 4-alkoxybenzoate (Bn). Mesomorphic and optical properties were investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM), X-ray diffraction (XRD), and UV-spectroscopy. HBSMCs formed from 1:2 mol mixture of A:2Bn, where the base component (B) bearing different alkoxy chain lengths from n = 8 to 14. The new HBSMCs (A/2B) interactions were confirmed by Fermi-bands formation via FT-IR spectroscopy measurements. Results revealed that all prepared HBSMCs are enantiotropic, exhibiting induced nematic (N) phase. The XRD pattern confirmed the POM texture results. Moreover, a comparison was made between the new laterally HBSMC series based on flexible core and the previously analyzed laterally neat complexes.

Keywords: lateral-group; supramolecular H-bonding complexes; X-ray diffraction; induced phase; adipic acid; flexible core

1. Introduction

An interesting study was undertaken to prepare and design enormous new mesogenic liquid crystal (LC) structures for display applications and technologies [1–6]. Kato et al. [7] reported in 1989 the first hydrogen-bonded supramolecular liquid crystal complex (HBSMCs) induced via intermolecular hydrogen-bonding (H-bonding) interactions between pyridine derivative and a carboxylic acid. H-bonding interactions are power tools for forming and inducing new mesophases [7–13]. Thus, HBSMCs have been attracting considerable attention based on the preparation of new geometrical molecules, as well as the mesomorphic characterizations and the structure–property relationships of them [1–6,14–18].

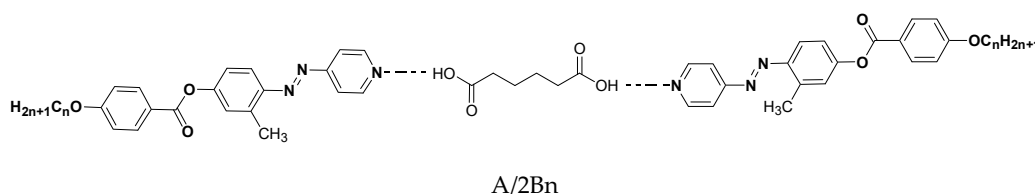
The introduction of azo-pyridine derivatives in the synthesized complexes enhances the powerful polar induction [19] and influences the conjugation power of the mesogenic cores, which offer photonic application [20]. In addition, the *trans-cis*-isomerization ability of azo-linkage makes it a suitable candidate for photo-responsive property [21,22].

LC substituent in the lateral position decreases the melting temperature of solid states and the thermal stability of the mesophase due to the steric effects and the intramolecular hindering of the lateral substituent [23–30]. Moreover, the lateral substituent makes molecules broad, having an effective

role in the mesomorphic characters of the resulting derivatives. Furthermore, the lateral moiety in the rigid core can destroy the molecular closed packing of liquid crystalline materials.

Geometry and terminal chain length of the LC molecule play an important role in the formation, type, thermal stability, and range of the mesophase. The molecules tend to be oriented in a parallel arrangement as the length of the terminal chain increases [31]. Moreover, the lengths of terminals can influence the twist-bend and heliconical N mesophases [32,33].

For further established structure–property relationships of HBSMCs, and due to the H-bonding interactions effects on the molecular association leading to increase the mesogenic core moiety length, we increased molecular biaxiality of the HBSMCs by introducing a lateral methyl group on the complex skeleton. From this point of view, the goal of our work is to synthesize new structural symmetrical 1:2 lateral HBSMCs based on the H-bonding interactions between the flexible core adipic acid (A) and the lateral CH₃ azo-pyridine base derivatives (Bn) [30], with changeable terminal alkoxy chain length (n). The aim of the study is also to investigate their mesomorphic, optical properties, and photo-physical behavior of prepared HBSMCs (A/2Bn, Scheme 1), and to estimate the effect of the terminal length of alkoxy chain (n) on the mesomorphic and optical behaviors of complexes. Further, a comparison is constructed between the present lateral HBSMCs and the previously reported laterally neat complexes [34] to investigate the effect of the position and orientation of lateral CH₃-group on mesomorphic characters.



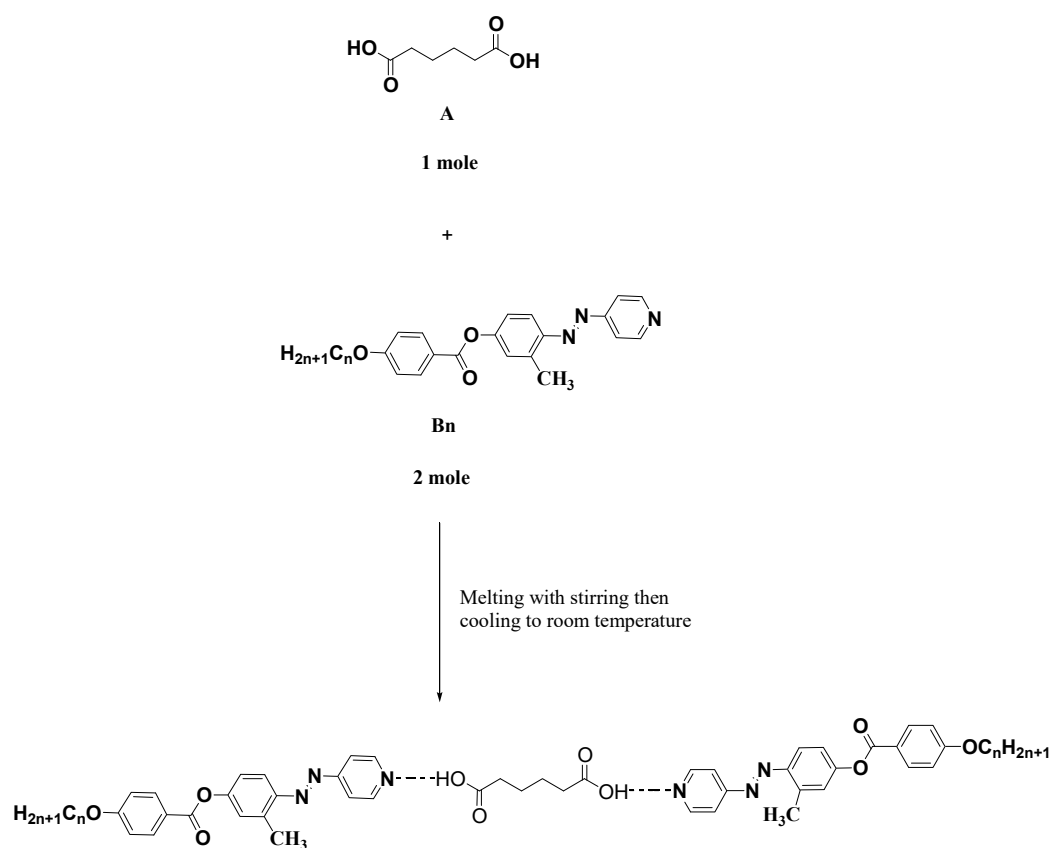
Scheme 1. 1:2 hydrogen-bonded supramolecular complex (HBSMC), A/2Bn.

2. Experimental

4-(2-(pyridin-4-yl)diazenyl-(3-methylphenyl)) 4-alkoxybenzoate (Bn) were prepared according to the previous method [30] that is attached in Supplementary Materials (Table S1, Figures S1 and S2).

Preparation of 1:2 HBSMCs Complexes

HBSMCs (A/2Bn) were formed from one mole of adipic acid (A) and two moles of 4-(2-(pyridin-4-yl)diazenyl-(3-methylphenyl)) 4-alkoxybenzoate (Bn), with n values between n = 8 and 16 for carbons. The solid mixture was melted with stirring to form an intimate blend and then allowed to cool to room temperature (Scheme 2). The formations of the HBSMCs (A/2Bn) were confirmed via differential scanning calorimetry (DSC) and FT-IR spectroscopy.



Scheme 2. Preparation of 1:2 hydrogen-bonded supramolecular complexes (A/2Bn).

3. Results and Discussion

3.1. FT-IR Characterizations of 1:2 HBSMCs Complexes

FT-IR spectroscopy was used to confirm the formation of H-bonded intermolecular interactions of present HBSMCs (A/2Bn) between the adipic acid component (A) and laterally azopyridine-based components (Bn). Measurements were performed for the individual components and their 1:2 HBSMCs. The alkoxy chain length (n) was not significantly affected by the mesomeric absorption value of the C=O group of azopyridine compounds B8, B10, B12, and B16 before complexation. FT-IR spectrum of adipic acid (A), lateral azopyridine homologue (B12), and their HBSMC A/2B12 are shown in Figure 1 as examples and Figure S3 in Supplementary Materials.

As shown in Figure 1, the spectrum of B12 has an ester carbonyl band at 1727.0 cm^{-1} , which changes in the FT-IR spectrum due to the complexation to 1735.0 cm^{-1} , and at the same time the carboxylic carbonyl peak of acid A changes from 1631.0 to 1651.0 cm^{-1} . These results confirm the intermolecular H-interactions between them. Moreover, the observation of three Fermi-resonance vibration bands of the H-bonded OH groups A-, B-, and C-types is also confirmation of the HBSMCs formation [35–42]. The A-type Fermi-band of complex A/2B12 is overlapped with that of the C-H vibrational peaks at 2920.0 to 2853.0 cm^{-1} . The observed peak at 2348.0 cm^{-1} for (A/2B12) could be assigned to B-type of the in-plane bending vibration of the O-H group. On the other hand, the band at 1914.0 cm^{-1} corresponds to C-type Fermi-band due to the interaction between the fundamental stretching vibration of the OH group and the overtone of the torsional effect.

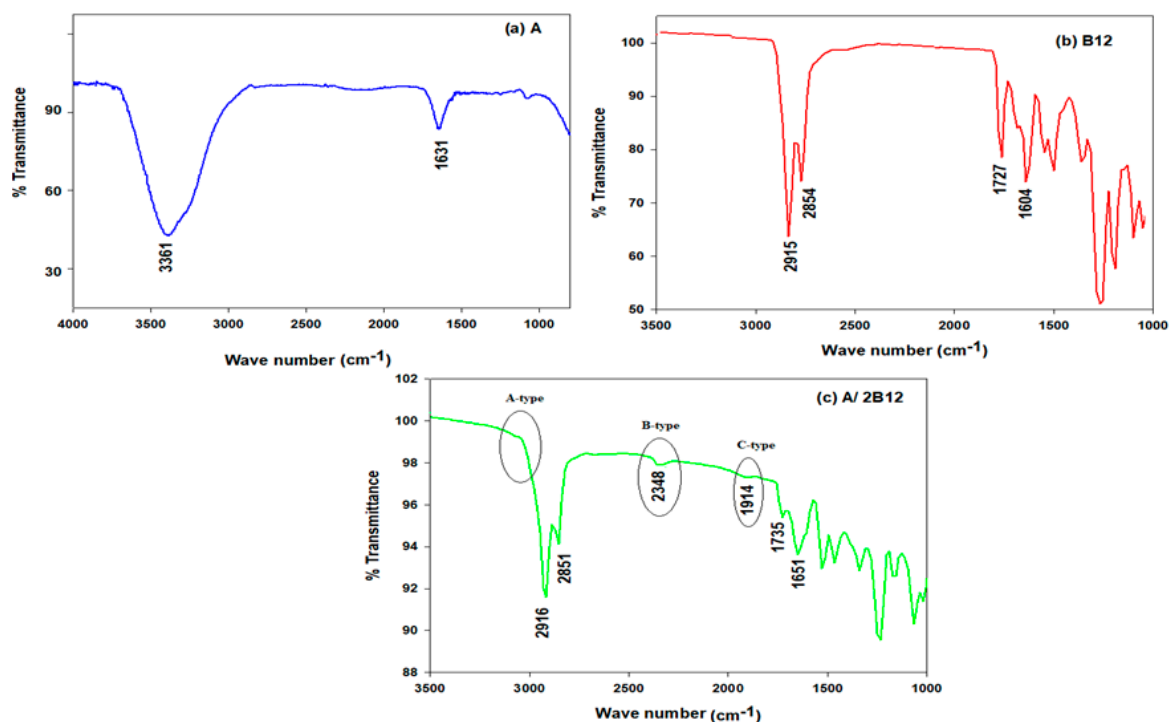


Figure 1. FT-IR spectra of (a) acid, A, (b) base, B12, and (c) complex, A/2B12.

3.2. Mesomorphic Studies of 1:2 HBSMCs, A/2Bn

All prepared supramolecular mixtures (A/2Bn) were investigated by DSC and polarized optical microscopy (POM) to evaluate their thermal and mesomorphic properties. DSC results, given as transition temperatures as well as enthalpy and normalized entropy, are collected in Table 1. All thermal measurements were recorded from the second heating scan. DSC thermogram taken from the second heating/cooling scans for A/2B12 complex is represented in Figure 2 as an example (Figures S4 and S5, Supplementary Materials). In order to ensure the stability of the formed 1:2 mixtures, measurements were performed for two heating/cooling scans and found to be the same. Only one mesomorphic peak was observed in the DSC thermogram upon both the heating and cooling cycles. Examples of observed textures of nematic mesophases under POM are depicted in Figure 3. Nematic phase was only observed upon heating and cooling rounds, indicating that the textures are confirming the DSC measurements. Dependency relation of transition temperatures on the length of alkoxy terminal chain (n), for the characterized HBSMCs A/2Bn, was represented graphically in Figure 4. That relation was constructed in order to evaluate the impact of the terminal chain lengths of the base moieties on the mesomorphic property.

It should be noted that the flexible core adipic acid (A) is non-mesomorphic with melting temperature $\approx 152^\circ\text{C}$, whereas the lateral CH_3 azo-pyridines (Bn) are monomorphic exhibiting smectic C (SmC) phase, except the homologue B10 which has very narrow enantiotropic SmC phase [30,43]. Therefore, it was interesting to study the mesophase property by incorporating a polar lateral group, with spatial orientation angle, of present HBSMCs and compare their mesomorphic results with the previous laterally neat synthesized complexes [34].

Generally, for H-bonded complexes, the lateral group, mesogenic linkage, and terminal chain length have a shared impact on the thermal stability of the formed mesophase. Moreover, the polarity changes between H-donors and H-acceptors affect the H-bonding strength and enhancement of the molecular anisotropy, resulting in the promotion of the broadening of the mesomorphic range [44]. However, the terminal length of the alkoxy chain of the complex does not affect the polarity of either individual. The attachment of heterocyclic moiety in the mesomorphic compounds strongly affects

polarity and/or polarizability, as well as the geometric arrangement. In addition, the molecular size and shape of the lateral group affects the mesophase stability and the polarizability [45,46].

Table 1. Phase transition temperatures (T , °C), enthalpy of transitions (ΔH , kJ/mol), and normalized transition entropy ($\Delta S/R$) of HBSMCs, A/2Bn.

System	T_{Cr-N}	ΔH_{Cr-N}	T_{N-I}	ΔH_{N-I}	$\Delta S_{N-I}/R$
A/2B8	83.5	71.40	100.4	1.11	0.36
A/2B10	81.0	76.11	99.2	1.99	0.64
A/2B12	81.4	80.81	95.9	2.34	0.76
A/2B16	77.2	73.65	66.0	2.45	0.87

Abbreviations: Cr-N = solid to nematic phase transition; N-I = nematic to isotropic liquid transition.

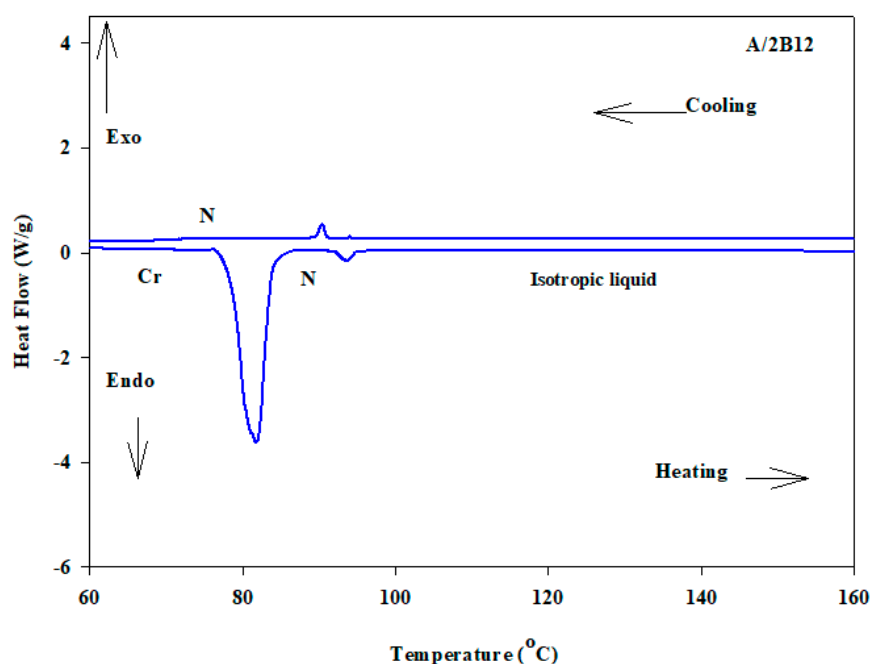


Figure 2. Differential scanning calorimetry (DSC) curve at rate 10 °C/min for 1:2 HBSMC, A/2B12 upon the second heating/cooling cycles.



Figure 3. Nematic phase textures during heating under polarized optical microscopy (POM) of 1:2 HBSMC, A/2B12 (a) at 83.0 °C, (b) at 91.0 °C, and (c) at 95.0 °C.

It could be seen from Table 1 and Figure 4 that the nematic mesophase is exhibited by all 1:2 supramolecular complexes, independent of the length of terminal alkoxy chain (n). In addition, the N phase stability is affected by the increase of n ; it decreases as n increases. The melting point transitions of the investigated 1:2 HBSMCs (A/2Bn) are related randomly with n . Therefore, despite the fact that the lateral methyl-azopyridines possess only less stable SmC phases and the adipic acid is non-mesomorphic, all synthesized 1:2 complexes (A/2Bn) exhibit unique induced N mesophase with

enantiotropic ranges, except the mixture A/2B16, which is monomorphic. The higher N stability value is observed for the complex A/2B8 (≈ 100.4 °C) and the lower value for A/2B16 (≈ 66.0 °C); the higher N range value is observed for the mixture A/2B10 (≈ 18.2 °C) and the lower range for A/2B16 (≈ 11.2 °C). Additionally, the nematic stability enhancement decreases with the increment of the chain length (n), thus the stability of the N phase is affected by the length of alkoxy chain. It was reported that as the molecular anisotropy increases in the HBSMCs, the broadening of N phases will be promoted [34], which revealed that the increment of the length of mesogenic core will increase the stability of N phase.

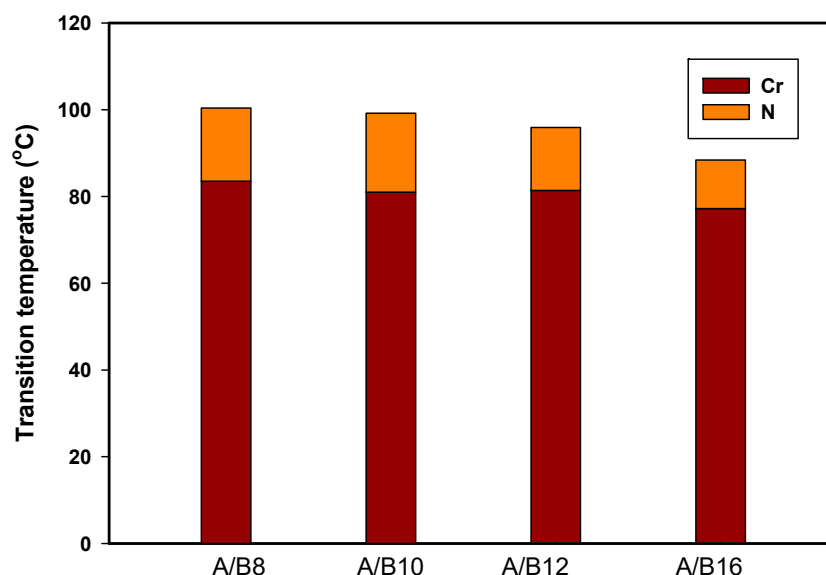


Figure 4. DSC transitions of 1:2 HBSMCs series, A/2Bn.

The monotropic N phase at terminal chain length $n = 16$ can be attributed to the dilution of the rigid mesogenic core [33]. Moreover, the higher value of Van der Waals attraction forces between the longer terminal chains enhances the terminal interactions and aggregation of alkyl groups, that attraction forces an effect on the formation of N phase. The mesomorphic properties of HBSMCs depend mainly on various factors: (1) Lateral adhesion interaction of molecules that increases with the increment of the terminal-chain length or aspect ratio. (2) Molecular geometry, which is affected by the steric hindrance of the terminal and lateral groups. (3) End-to-end interaction, which depends on the polarity and/or polarizability of terminal and lateral substituents. Furthermore, the linking groups highly impact the conjugation within the mesogenic core of the molecule.

3.3. Entropy Changes, $\Delta S/R$

Terminal alkoxy-chains are very labile and can make multi-conformational changes. Therefore, they play a dominant role in entropy changes ($\Delta S/R$). An influence of entropy change is observed in all investigated HBSMCs A/2Bn, suggesting the increment in the conformational and orientational changes of the complex compared with its pure individuals. The normalized transition entropies ($\Delta S/R$) were estimated for the present symmetric 1:2 HBSMCs (A/2Bn), as driven from DSC results and tabulated in Table 1, as well as represented graphically as function of n , in Figure 5. It can be concluded that the increment of the entropy changes, with increasing the terminal alkoxy-chain length (n), is due to the increase in the biaxiality of the mesogenic part due to the incorporation of the lateral CH_3 group. In addition, this may be further attributed to the change in geometrical interactions between individuals of the mixtures, which is accordingly affected by the polarizability and the molecular shape of the terminal and lateral substituents.

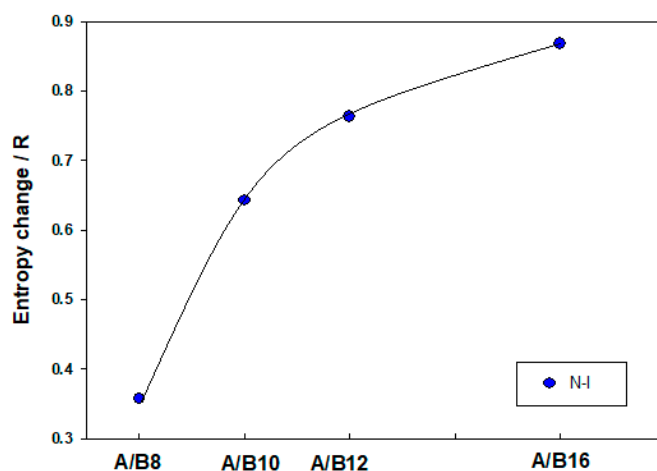


Figure 5. Entropy changes as a function of chain length (n) of present HBSMCs A/2Bn.

3.4. Effect of Incorporation of Lateral Group in HBSMCs

In order to study the effect of addition of a lateral methyl group in the mesogenic core of the HBSMCs on the mesomorphic behavior, a comparison was established between the mesomorphic behavior of present HBSMCs, A/2Bn, and our previously investigated laterally neat complexes, A/2Cn [34]. Figure 6 represents the graphical comparison, which indicates that the mesophase stabilities of laterally neat mixtures (A/2Cn) are relatively higher than those of the present HBSMCs (A/2Bn), i.e., attachment of lateral CH_3 group, in meta-position with respect to the ester moiety of the base component, in the molecular structure, has destabilized the N stability. Thus, it seems that the incorporation of lateral CH_3 moiety into azopyridine derivatives decreases the polarizability of the whole molecule and consequently disrupts the intermolecular interactions between individual molecules.

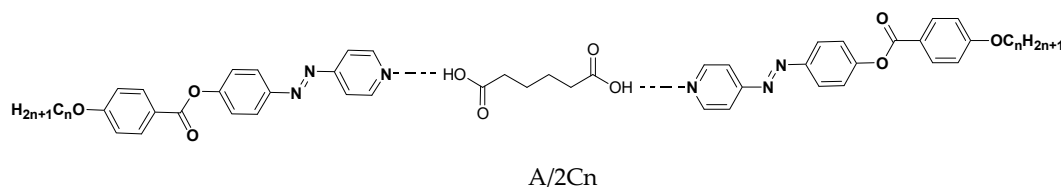


Figure 6. 1:2 HBSMCs A/2Cn [34].

3.5. Photo-Physical Investigation

Azopyridine compounds undergo *trans-cis* isomerization when irradiated with light of an appropriate wavelength. Those phenomena make it an essential component of various molecular devices as well as functional materials [47,48]. The photo-physical measurements of the present lateral CH_3 -HBSMCs, A/2Bn, were carried out by measuring UV-vis spectra. To evaluate the spectrophotometric absorption spectra, a solution of concentration $C = 1.8 \times 10^{-6}$ mol/L in chloroform was prepared. Figure 7 represents the resulting absorption bands graphically. It could be found from Figure 7, the light radiation in the wavelength range 380–800 nm for present 1:2 lateral CH_3 -HBSMCs is found to be strongly absorbed with the maximum at ≈ 456 –457 nm, according to the terminal alkoxy chain (n), which can be attributed to the π – π^* transition of the chromophore in the molecule. The absorbance values at the maximum wavelength increased in an irregular manner independent of the alkoxy chain (n). In addition, the intensity and absorption of the peak in the absorption spectrum are dependent on the molecular geometry of the material that absorbs the light at the given wavelength. Furthermore, the absorption spectra of the present HBSMC, A/2Bn, showed the maximum bands at 457 nm, which also attributed to the π – π electronic transitions from the HOMO (highest occupied molecular orbitals) to LUMO (lowest unoccupied molecular orbitals) [49–51].

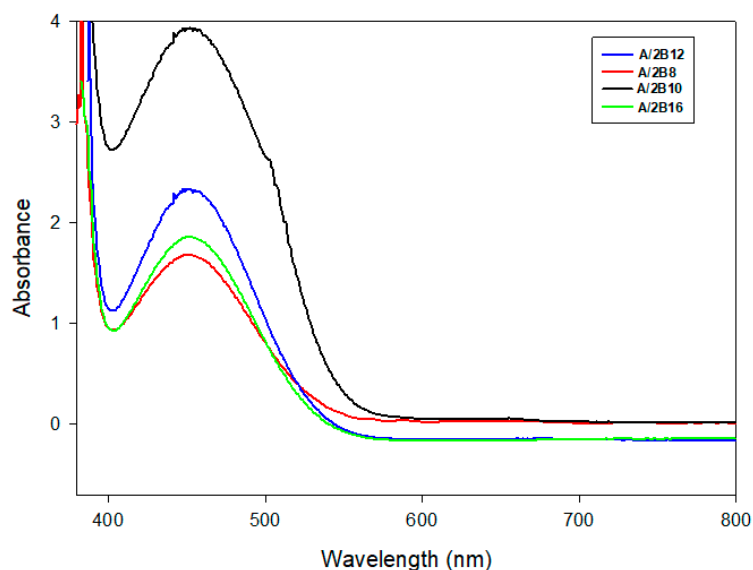


Figure 7. UV-absorption spectrum of present HBSMCs, A/2Bn, in chloroform.

3.6. X-ray Diffraction Investigation

The mesomorphic properties of the present prepared HBSMCs (A/2Bn) were confirmed by X-ray diffraction (XRD) measurements. XRD is another tool to confirm the mesophase assignments [34,52]. XRD experiments were performed at different temperatures upon cooling of the sample from the isotropic liquid mesophase. Figure 8 shows the homologue A/2B8 as a representative example for the present 1:2 laterally substituted HBSMCs series (A/2Bn). It can be seen from Figure 8, XRD analysis pattern at all recorded temperatures showed only one peak at angle $2\theta = 25^\circ$, assigned to the presence of nematic transition phase upon cooling for all recorded temperatures, which related to the lateral interactions between mesogenic groups. Thus, the temperature dependent XRD investigations of the present lateral CH_3 -HBSMCs confirmed the presence of a monomorphic broad peak of N mesophase. After comparing the XRD and POM results, the existence of only N mesophases in all formed HBSMCs A/2Bn were assigned.

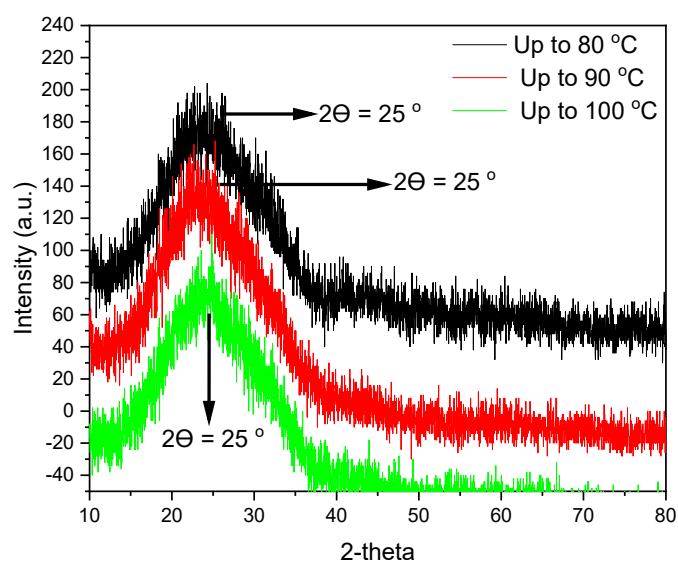


Figure 8. X-ray diffraction (XRD) patterns of A/2B8 at different temperatures upon cooling from the isotropic liquid mesophase.

4. Conclusions

New 1:2 symmetrical homologues of lateral methyl HBSCMs, bearing different lengths of terminal alkoxy groups, were synthesized and evaluated by different tools. Appearance of Fermi-bands in FT-IR spectroscopic analysis confirmed the presence of H-bonding interactions. Mesomorphic properties of present 1:2 HBSCMs were investigated by DSC, POM, and XRD measurements. UV-spectroscopy was performed to evaluate the photo-physical characters of the complexes. Results revealed that all prepared complexes that are nematogenic exhibit induced enantiotropic N phase except for the complex of longer terminal alkoxy chain at $n = 16$, which possess monotropic nematogenic phase. In addition, the temperature-dependent XRD pattern was consistent with the intrinsic character of N mesophase and that is in agreement with both the DSC and POM results. A comparative study was established between the present HBSCMs and their corresponding laterally neat complexes, resulting that the attaching of the lateral CH_3 group decreases the mesophase stability with only an N phase obtained. Finally, the increment in the biaxiality of the mesogenic part due to the addition of a lateral CH_3 group leads to increases in the entropy changes of present complexes with terminal chain length.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/10/10/878/s1>, Figure S1: The mass spectrum of B16, Figure S2: The ^1H -NMR spectrum of B10, Figure S3: FT-IR spectra of (a) B8; (b) B10; (c) A/2B8 and (d) A/2B10, Figure S4: DSC curve at rate $10\text{ }^\circ\text{C/min}$ for 1:2 HBSCM, A/2B8 upon the second heating/cooling cycles, Figure S5: DSC curve at rate $10\text{ }^\circ\text{C/min}$ for 1:2 HBSCM, A/2B16 upon the second heating/cooling cycles, Table S1: Mass spectra (m/z) of the Azopyridine derivatives (Bn).

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