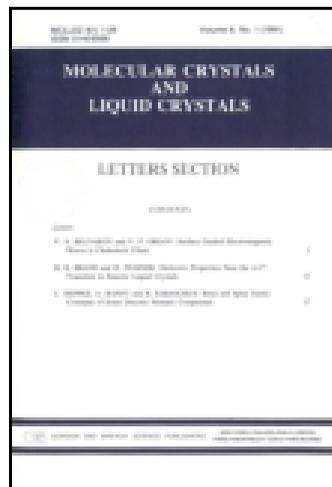


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Synthesis and Mesomorphic Properties of New Methylene-Linked Linear Symmetrical Liquid Crystal Dimers

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A series of methylene-linked symmetrical liquid crystal dimers were synthesized. Their structures were confirmed by physicochemical techniques. Differential scanning calorimetry and polarizing optical microscopy verified the liquid crystal behaviors and their transition temperatures. The thermodynamic data for phase transition, melting transition (T_m), and isotropic transition temperatures (T_i) of the dimers were decreased with increasing the length of spacer. Both T_m and T_i and enthalpy change for isotropic transition (δH_i) for dimers with even numbers of methylene units were higher than those with odd numbers. Dimers AC-OnO-AC ($n = 2-10$) formed enantiotropic nematic phase only, while the unsymmetrical dimer formed a smectic phase.

Keywords Liquid crystal; mesogenic properties; symmetric dimers, thermodynamic data

1. Introduction

Low molar mass liquid crystals were discovered in 1888. Liquid crystal dimers are one class among other classes that attracted particular attention due to their unique thermal behavior and structural features as model compounds similar to polymeric liquid crystals and that still remain the focus of much research [1].

Of all the important low molar mass liquid crystals discovered, one class, the so-called liquid crystal dimers, have great potential. Liquid crystal dimers comprise molecules containing two conventional single semi-rigid mesogenic groups linked by a flexible spacer, which is most commonly an alkyl chain. [2, 3].

In essence, it is the anisotropic interaction between the cores, normally comprising phenyl rings linked through short unsaturated linkages, that give rise to the observation of liquid crystalline behavior while the alkyl chains tend to lower the melting point. Indeed, for many years it was widely assumed that such a molecular structure was a prerequisite

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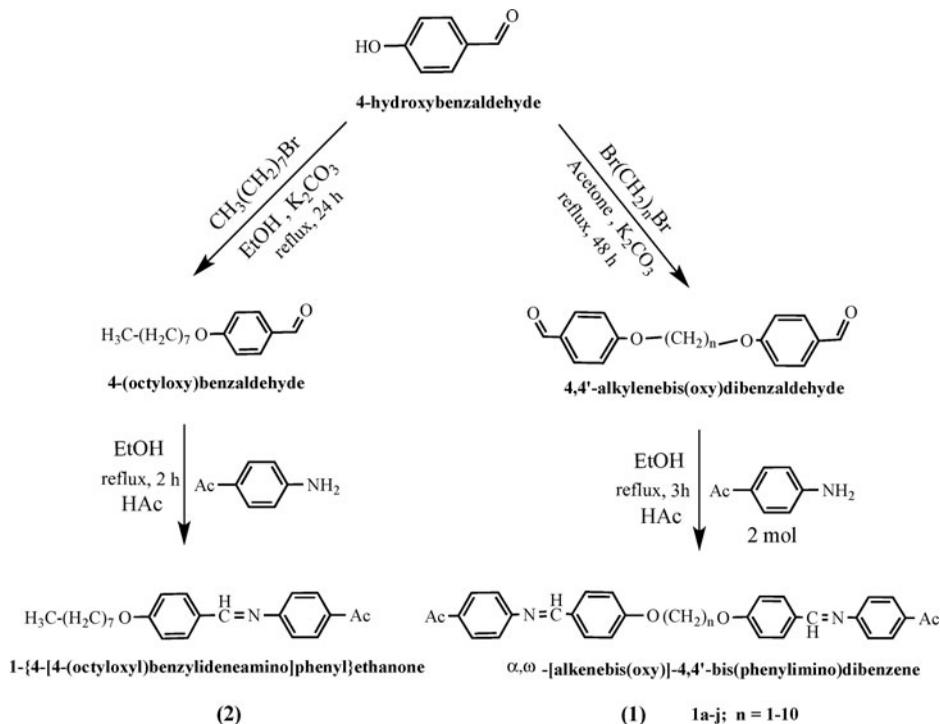
for liquid crystallinity [2]. During the 1970s, a wide range of unconventional molecular structures were prepared and shown to support liquid crystallinity [2].

Liquid crystal dimers are classified into two categories, viz., symmetric and non-symmetric dimers. In the former class of dimers, the mesogenic groups are identical, and in the later, the mesogenic groups are not identical.

The liquid crystalline properties as well as the structure of different mesophases of these classes of compounds are found to be dependent on the length and the parity of the spacer, as it strongly affects the overall shape of the molecule. Depending on the number of atoms in the spacer, the molecule adopts a bent or linear shape [4] and this then influences not only the isotropization temperatures but also the type of liquid crystal phase formed.

The nematic–isotropic transition temperatures are found to exhibit a dramatic alternation as the number of carbon atoms in the alkyl spacer changes from odd to even. However, the alternation is attenuated as the spacer grows in length [5].

In this study, a new series of linear symmetric dimers with general formula of AC-OnO-AC has been synthesized and their mesomorphic properties were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy. The mesomorphic properties of the symmetrical compounds (AC-OnO-AC) derived from 4-hydroxybenzaldehyde and different α,ω -dibromoalkanes followed by the Schiff base condensation with 4-aminoacetophenone were compared with unsymmetrical compound **2** derived from 4-(octyloxy)benzaldehyde and the symmetrical analogues, viz. **3** and **4**, which were derived from 4-formylbenzoic acid with 4-aminoacetophenone and 4-hydroxyacetophenone respectively (Schemes 1 and 2). This was done to investigate the



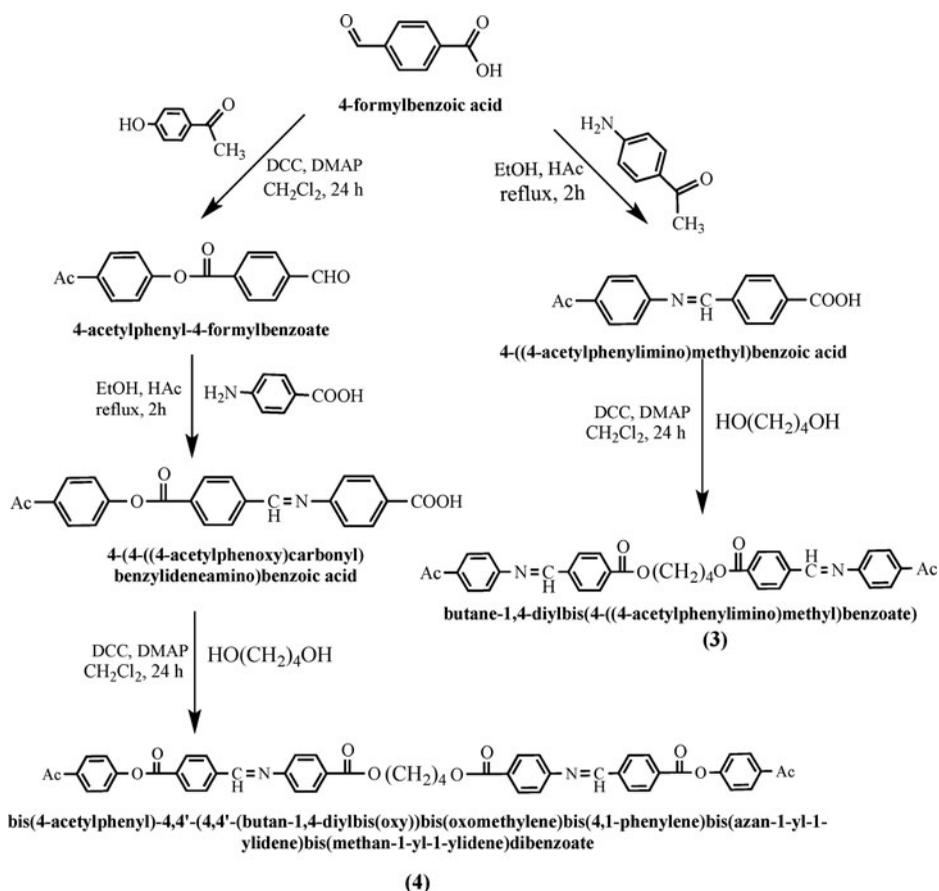
Scheme 1. Synthesis steps of prepared dimers in series AC-OnO-AC ($n = 1-10$) and compound **2**.

influence of the length and type of spacer on the mesomorphic properties of symmetric dimers and comparing it with low molecular weight molecular analogues.

2. Results and Discussion

A series of linear symmetric dimers (AC-OnO-AC dimers; $n = 1-10$) are synthesized in two steps: ether formation reaction of 4-hydroxybenzaldehyde and different α,ω -dibromoalkanes followed by the Schiff base condensation with 4-aminoacetophenone as shown in Scheme 1. The unsymmetrical compound **2** was derived from 4-(octyloxy)benzaldehyde as shown in Scheme 1, and the symmetrical analogues **3** and **4**, derived from 4-formylbenzoic acid with 4-aminoacetophenone and 4-hydroxyacetophenone, respectively, were synthesized as shown in Scheme 2.

The new dimers are characterized by Fourier transform infrared (FT-IR) spectroscopy, Hydrogen-1 Nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), and mass spectroscopy. The FT-IR and $^1\text{H-NMR}$ spectral data confirm the formation of these compounds. Mass spectra also verify the structures of these compounds through their molecular ion peak $[\text{M}^+]$. Figure 1 shows representative mass spectrum of AC-O8O-AC dimer. The phase



Scheme 2. Synthesis steps of prepared dimers **3** and **4**.



Figure 1. Mass spectra for AC-O8O-AC dimer.

transitions were observed with an optical microscope with polarized light in conjunction with a Leitz 350 hot stage equipped with a Vario-Orthomat camera.

The thermal mesomorphic phases of the AC-OnO-AC series (except when $n = 1$) and compounds **2–4** were analyzed by DSC and hot stage polarizing microscopy. The mesomorphic properties of these compounds were investigated thru the DSC analyses and polarizing optical microscopy, which affirm liquid crystal behaviors and their transition temperatures. Figures 2 and 3 present the DSC thermograms of AC-O4O-AC and AC-O5O-AC dimers respectively.

All the compounds of series AC-OnO-AC ($n = 2–10$) (except AC-O1O-AC) and the dimer **4** formed enantiotropic nematic phase only, whereas compound dimer **3** showed this phase only upon cooling. On the other hand, compound **2** formed a smectic phase. The AC-O1O-AC was directly transformed into isotropic melt from the solid crystal on heating at 163°C .

The thermodynamic data for the phase transition are presented in Table 1. The melting temperature (T_m : transition temperature to liquid crystal phase) as well as the isotropic

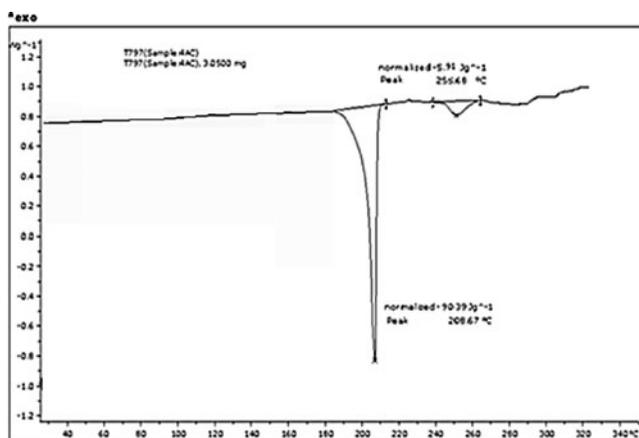


Figure 2. DSC thermogram for AC-O4O-AC dimer.

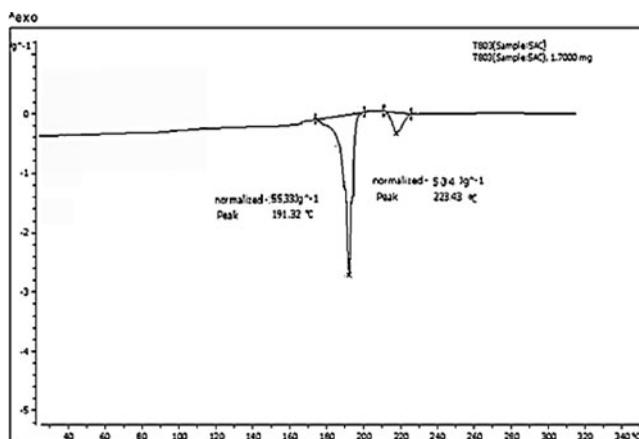


Figure 3. DSC thermogram for AC-O5O-AC dimer.

transition temperatures (T_i : transition temperature to isotropic state) of the dimer compounds in the series AC-OnO-AC were decreased in a zigzag manner (Fig. 4) as the length of spacer (n) increased. Both T_m and T_i for the dimeric compounds with an even number of methylene units were higher than those with an odd number of methylene units. Similar trends were reported for many other series of low molecular liquid crystal compounds and dimers [6, 7].

Another interesting point is that the values of ΔH_i (enthalpy change value for isotropic transition) for the dimers with an even number of methylene units were generally higher than those for the odd-numbered dimeric compounds [8]. It appeared that the mesophases of the dimeric compounds with spacers of even-numbered methylene units were generally

Table 1. The phase transitions temperatures (K) of series AC-OnO-AC ($n = 2-10$) and associated (ΔH), (ΔS), and ($\Delta S/R$) data

Dimer	C \rightarrow N				N \rightarrow I			
	T (K)	ΔH kJ- mol $^{-1}$	ΔS Jmol $^{-1}$ K $^{-1}$	$\Delta S/R$	T (K)	ΔH kJ- mol $^{-1}$	ΔS Jmol $^{-1}$ K $^{-1}$	$\Delta S/R$
AC-O2O-AC	485.20	46.30	95.42	11.47	536.31	6.22	11.59	1.39
AC-O3O-AC	478.00	30.02	62.80	7.55	514.01	5.01	9.74	1.17
AC-O4O-AC	481.67	48.08	99.81	12.00	528.68	5.91	11.17	1.34
AC-O5O-AC	464.32	30.21	65.06	7.82	496.43	5.34	10.75	1.29
AC-O6O-AC	473.01	49.81	105.30	12.66	511.52	5.52	10.79	1.29
AC-O7O-AC	457.00	30.45	66.63	8.01	473.11	4.03	8.51	1.02
AC-O8O-AC	459.81	51.26	111.48	13.40	484.91	5.62	11.59	1.39
AC-O9O-AC	451.21	51.31	113.71	13.67	463.33	5.83	12.58	1.51
AC-O10O-AC	448.48	52.75	117.63	14.14	458.55	6.23	13.58	1.63

Note. C: crystals, N: nematic, I: isotropic, R: 8.314 Jmol $^{-1}$ K $^{-1}$.

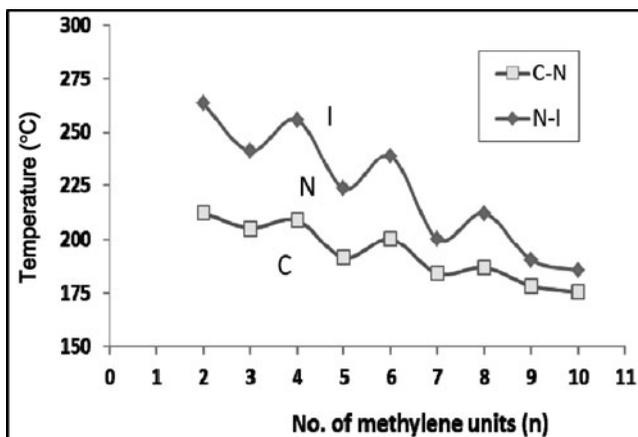


Figure 4. Phase transition temperatures as a function of the number of methylene units in the spacer; C: crystal, N: nematic, I: isotropic.

of a higher degree of order than those with odd-numbered ones [7, 8]. The melting entropy values ($\Delta S/R$) increase with increasing the length of spacer, as the contributions to the conformational entropy change associated with methylene units in the spacer are higher. This can also describe the decrease in the melting point with increasing the methylene units [9].

The polarizing microscopic studies for dimer **1** revealed that it was directly transformed into the isotropic melt from solid crystal on heating and its melting point (160°C) was lower than AC-O8O-AC. This behavior was attributed to the effect of the dipole moment of the acetyl group, which is substituted at the terminal position of the AC-O8O-AC molecule which enhances the mesogenic properties [10].

The mesogenic phases of AC-O8O-AC were compared with compound **2** since it is known that compound **2** shows a smectic phase, while AC-O8O-AC is a nematogen. The difference between compound **2** and AC-O8O-AC can be attributed to the disrupted conjugation and flexibility due to the aliphatic spacer (octane group), which disallows smectic phase to occur [11].

The polarizing microscope studies for dimer **3** revealed that this compound was directly transformed into the isotropic melt from the solid crystal on heating, while on cooling, nematic liquid crystal phase was formed before transition to solid state from the isotropic melt. Therefore, dimer **3** is monotropic. The comparison between the structures of the dimer of AC-O8O-AC and dimer **3** indicate that the magnitude of the dipole moment should be taken into account. By considering the electron arrangement in the mesogenic moieties of dimer AC-O8O-AC and **3**, the dipole moment of dimer **3** is expected to be greater than that of AC-O8O-AC because of the influence of the dipole moment of the carbonyl group

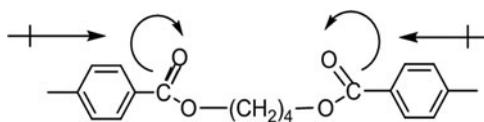


Figure 5. Dipole moment of carbonyl group in the spacer.

Table 2. The phase transitions temperatures (K) of compounds **2**, **3**, and dimer **4** and associated (ΔH), (ΔS), and ($\Delta S/R$) data

Compound	Phase transition	T (K)	ΔH kJmol ⁻¹	ΔS Jmol ⁻¹ K ⁻¹	$\Delta S/R$
2	C-S	433.34	31.61	72.94	8.77
	S-I	389.34	4.36	11.19	1.34
3	C-I	—	—	—	—
	I-N	—	—	—	—
	N-C	—	—	—	—
4	C-N	462.61	80.37	173.74	20.89
	N-I	591.94	5.65	9.55	1.14

Note. C: crystals, N: nematic, I: isotropic, S: smectic, R: 8.314 J.mol⁻¹.K⁻¹.

in the spacer. The greater local dipole moment in the spacer (Fig. 5) hinders the parallel arrangement of molecules in liquid crystal phases [5].

Dimer **4**, in which the carbonyl groups are substituted in the mesogenic unit of the molecule, formed enantiotropic nematic, whereas dimer **3** is monotropic (Table 2). The carbonyl group found in the mesogenic unit (in the terminal group) confers a dipole moment on dimer **4** in the mesogenic unit that is equal to the greater dipole moment in the spacer that enhances the attraction between the molecules and, in addition, demonstrates mesomorphic phases on heating and cooling [5].

Under polarizing optical microscopy, the nematic phase reflects a marbled texture on heating and the Schlieren texture on cooling. The smectic (S_A) phase was clearly characterized by its typical focal conic texture on heating and cooling (Fig. 6).

3. Experimental

3.1. General

Infrared spectra were recorded as KBr pellets on a Buck-M500 spectrometer (Buck Scientific, USA). ¹H-NMR spectra were recorded on Bruker-300 using CDCl₃ as a solvent and TMS as internal standard. Mass spectra were recorded on an Agilent technologies 5957C spectrometer. The phase transitions were observed with a Leitz Laborlux 12 Pol optical microscope with polarized light in conjunction with a Leitz 350 hot stage equipped with a Vario-Orthomat camera. Transition temperatures were determined using a Shimadzu 24 DSC-50 DSC with a heating rate of 10°C min⁻¹.

3.2. Synthesis

3.2.1. Synthesis of α , ω -[alkenebis(oxy)]-4,4'-bis(phenylimino)dibenzene (AC-OnO-AC); $n = 1-10$. 4,4-alkylenebis(oxy)dibenzaldehydes ($n = 1-10$) were synthesized according to the literature procedure [12] by adding a solution of 2 mmol of 4-hydroxybenzaldehyde in acetone to 2 mmol of potassium carbonate and 1 mmol of appropriate α,ω -dibromoalkane, and the reaction mixture was refluxed with stirring for 48 hr. The reaction mixture was filtered when hot and the solvent was evaporated. The obtained white solid was purified by recrystallization from ethanol (Scheme 1).

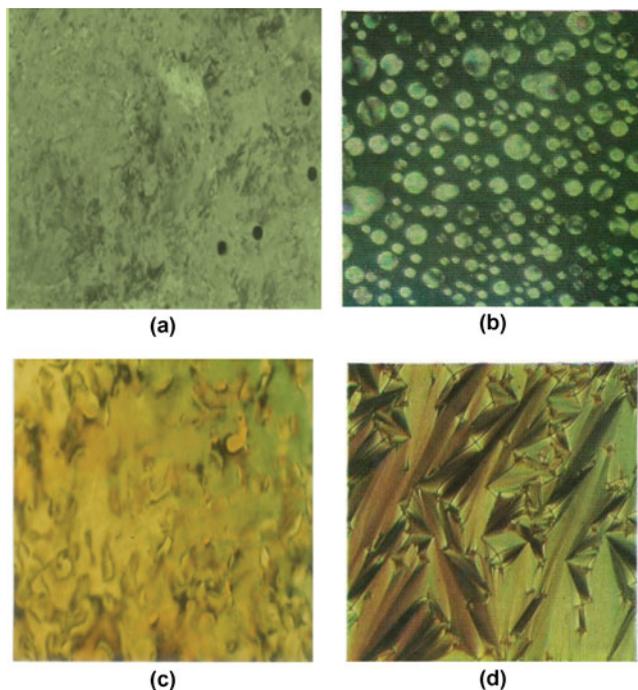


Figure 6. (a) Marble texture for nematic phase on heating for AC-O8O-AC, (b) nematic droplet for AC-O8O-AC, (c) Schlieren texture for nematic phase on cooling for AC-O8O-AC, (d) focal conic texture of smectic A on heating of compound **2**.

The Schiff base dimers were synthesized by the reaction of 4,4'-alkylene-bis(oxy)dibenzaldehyde with 4-aminoacetophenone (1:2 molar ratio) in absolute ethanol and three drops of acetic acid (Scheme 1). The reaction mixture was refluxed for 3 hr with stirring. The reaction mixture was allowed to cool and the product was filtered and recrystallized from ethanol.

3.2.2. Synthesis of 1-(4-(4-(octyloxy)benzylideneamino)phenyl)ethanone (2). This compound was prepared following the reported method [13]. 4-(octyloxy)benzaldehyde was synthesized accordingly in Section 3.2.1 with 1:1 molar ratio. The resulting compound was further reacted with 4-aminobenzophenone to obtain the Schiff base compound **2** (Scheme 1).

3.2.3. Synthesis of butane-1,4-diyl bis(4-(4-acetylphenylimino)methyl)benzoate (3). The dimer compound **3** was synthesized following the reported method with slight modification [14]. The Schiff base was synthesized by mixing equimolar amounts of 4-formylbenzoic acid with 4-aminoacetophenone in absolute ethanol and drops of acetic acid. The product (4-((2-acetylphenylimino)methyl)benzoic acid) obtained after 3-hr reaction time was then reacted with 1,4-dihydroxybutane in dichloromethane in the presence of dicyclohexylcarbodiimide (DCC) 4-dimethylaminopyridine (DMAP) to produce dimer **3** (Scheme 2).

3.2.4. Synthesis of Esters (4). The ester was synthesized by following the reported method with a slight modification [15, 16].

Esterification reaction was performed by the slow addition of equimolar quantities of 4-formylbenzoic acid to a solution of 4-hydroxy acetophenone in presence of dicyclohexylcarbodiimide (DCC)/4-dimethylaminopyridine (DMAP). The reaction was stirred for 30 min. The pH of the solution was adjusted with dilute HCl or NaOH solution to induce precipitation. The product was filtered, washed, and dried. The solid obtained was reacted with 4-aminobenzoic acid. The final product was further reacted with 1,4-dihydroxybutane to obtain the desired dimer (**4**) (Scheme 2).

4. Characterization

AC-O10-AC: Yellow solid; yield 55.3%; $^1\text{H-NMR}$: 4.16 (s, 2H, $-\text{OCH}_2\text{O}-$), 2.51 (s, 6H, $-\text{COCH}_3$), 7.06–8.05 (m, 16H, Ar–H), 8.63 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1673 (C=O), 1627 (C=N); MS m/z: 490.4 [M] $^+$.

AC-O20-AC: Yellow solid; yield 50.4%; $^1\text{H-NMR}$: 2.62 (s, 6H, $-\text{COCH}_3$), 4.45 (s, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 7.06–7.99 (m, 16H, Ar–H), 8.38 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1677 (C=O), 1622 (C=N); MS m/z 504.4 [M] $^+$.

AC-O30-AC: Yellow solid; yield 51.30%; $^1\text{H-NMR}$: 2.25 (p, 2H, $-\text{CH}_2-$), 4.16 (t, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 2.50 (s, 6H, $-\text{COCH}_3$), 7.07–8.06 (m, 16H, Ar–H), 8.66 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1680 (C=O), 1622 (C=N); MS m/z: 518.4 [M] $^+$.

AC-O40-AC: Yellow solid; yield 63.20%; $^1\text{H-NMR}$: 1.92 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 2.50 (s, 6H, $-\text{COCH}_3$), 4.16 (s, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 7.09–8.01 (m, 16H, Ar–H), 8.56 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1676 (C=O), 1624 (C=N); MS m/z: 532.4 [M] $^+$.

AC-O50-AC: Yellow solid; yield 73.79%; $^1\text{H-NMR}$: 1.60 (m, 2H, $-\text{CH}_2\text{CH}_2-$), 1.79 (pentate, 4H, $-\text{CH}_2\text{CH}_2-$), 2.53 (s, 6H, $-\text{COCH}_3$), 7.04–8.03 (m, 16H, Ar–H), 8.55 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1676 (C=O), 1624 (C=N); MS m/z: 546.1 [M] $^+$.

AC-O60-AC: Yellow solid; yield 75.4%; $^1\text{H-NMR}$: 1.52 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 1.79 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 2.64 (s, 6H, $-\text{COCH}_3$), 7.08–8.00 (m, 16H, Ar–H), 8.55 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1678 (C=O), 1622 (C=N); MS m/z: 560.5 [M] $^+$.

AC-O70-AC: Yellow solid; yield 77.35%; $^1\text{H-NMR}$: 1.72 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 1.30 (pentat, 4H, $-\text{CH}_2\text{CH}_2-$), 1.42 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 1.27 (p, 2H, $-\text{CH}_2\text{CH}_2-$), 2.51 (s, 6H, $-\text{COCH}_3$), 7.04–8.00 (m, 16H, Ar–H), 8.66 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1676 (C=O), 1620 (C=N); MS m/z: 574.1 [M] $^+$.

AC-O80-AC: Yellow solid; yield 80.20%; $^1\text{H-NMR}$: 1.45 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 1.53 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 1.87 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 4.07 (t, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 2.63 (s, 6H, $-\text{COCH}_3$), 7.01–8.03 (m, 16H, Ar–H), 8.41 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1676 (C=O), 1622 (C=N); MS m/z: 588.5 [M] $^+$.

AC-O90-AC: Yellow solid; yield 81.35%; $^1\text{H-NMR}$: 1.32 (m, 6H, $-(\text{CH}_2)_3-$), 1.46 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 1.79 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 4.07 (t, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 2.50 (s, 6H, $-\text{COCH}_3$), 7.02–8.03 (m, 16H, Ar–H), 8.51 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1677 (C=O), 1621 (C=N); MS m/z : 602.1 [M] $^+$.

AC-O100-AC: Yellow solid; yield 81.4%; $^1\text{H-NMR}$: 1.32 (m, 8H, $-(\text{CH}_2)_4-$), 1.459 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 1.79 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 4.07 (t, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 2.53 (s, 3H, $-\text{COCH}_3$), 7.03–8.08 (m, 16H, Ar–H), 8.66 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1676 (C=O), 1620 (C=N); MS m/z: 616.1 [M] $^+$.

Compound 2: Yellow solid; yield 65.01%; $^1\text{H-NMR}$: 0.91 (t, 3H, $-\text{CH}_3$), 1.32 (m, 8H, $-(\text{CH}_2)_4-$), 1.50 (m, 2H, $-\text{CH}_2-$), 1.80 (m, 2H, $-\text{CH}_2-$), 4.05 (t, 2H, $-\text{OCH}_2-$), 2.64 (s, 6H, $-\text{COCH}_3$), 6.99–8.00 (m, 18H, Ar–H), 8.38 (s, 1H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1680 (C=O) ketone, 1624 (C=N); MS m/z: 351.1 [M] $^+$.

Dimer 3: Yellow solid; yield 60.65%; $^1\text{H-NMR}$: 1.43 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 2.50 (s, 6H, $-\text{COCH}_3$), 4.30 (t, 4H, $-(\text{OCH}_2)_2-$); 7.06–8.05 (m, 16H, Ar–H), 8.66 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1701 (C=O) ester, 1670 (C=O) ketone, 1627 (C=N); MS m/z : 588.4 $[\text{M}]^+$.

Dimer 4: Yellow solid; yield 45.7%; $^1\text{H-NMR}$: 1.877 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 3.10 (s, 6H, $-\text{COCH}_3$), 4.42 (t, 4H, $-\text{OCH}_2-$), 7.79–8.34 (m, 24H, Ar–H), 8.35 (s, 2H, $-\text{CH}=\text{N}$); IR (cm^{-1}): 1708 (C=O) ester, 1676 (C=O) ketone, 1627 (C=N); MS m/z : 828.5 $[\text{M}]^+$.

5. Conclusions

A series of linear symmetrical liquid crystal dimers (AC-OnO-AC) with methylene spacer ($n = 1-10$) were synthesized. The structures of these crystal liquid dimers are confirmed by FT-IR, $^1\text{H-NMR}$, and mass spectroscopy and DSC analyses. The thermodynamic data for the phase transition, i.e., the melting transition temperature (T_m) and the isotropic transition temperatures (T_i) of the dimer compounds in the series (AC-OnO-AC) were decreased in a zigzag fashion as the length of spacer (n) increased. Both T_m and T_i for dimeric compounds with an even number of methylene units were higher than those with an odd number. The enthalpy change values for isotropic transition of δH_i for the dimers with an even number of methylene units were generally higher than those for the odd-numbered dimeric compounds. Dimers AC-OnO-AC ($n = 2-10$) and the dimer **4** formed enantiotropic nematic phase only, dimer **3** showed this phase only upon cooling whereas compound **2** formed a smectic phase.

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