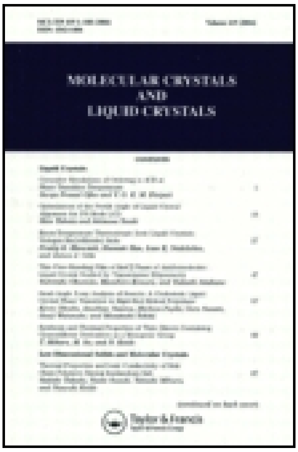

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# Study and Characterization of Double Hydrogen-Bonded Liquid Crystals Comprising p-n Alkoxy Benzoic Acids with Azelaic and Dodecane Dicarboxlic Acids

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# Study and Characterization of Double Hydrogen-Bonded Liquid Crystals Comprising p-n Alkoxy Benzoic Acids with Azelaic and Dodecane Dicarboxlic Acids

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*Two series of double hydrogen-bonded liquid-crystalline complexes have been designed and synthesized. Dodecane dicarboxlic acid (DDC) and azelaic dicarboxlic acid (AC) belong to the same family of dicarboxlic acids having similar structural properties but with increasing H-C-H spacer groups. A successful attempt has been made to form hydrogen bonding between DDC and AC with p-n-alkyloxy benzoic acids (nOBA) by varying the respective alkyloxy carbon number and the physical properties exhibited by the individual series. The first series comprises DDC and p-n-alkyloxy benzoic acids (nOBA) and the other series is formed between AC and nOBA, where n represents the alkyloxy carbon numbers from 5 to 12 (except 6). These two homologous series are analyzed by polarizing optical microscopy (POM), differential scanning colorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, and proton nuclear magnetic resonance (NMR) studies. The formation of an inter-hydrogen bond is evinced through FTIR and* $^1H$ *NMR. An interesting feature of DDC + nOBA homologues series is the stabilization of the higher order smectic C phase with increasing chain length. In the AC + nOBA homologues series a smectic G phase is induced with the increment of alkyloxy number. Phase diagrams of the above complexes are computed and compared. An even–odd effect in both series is discussed with respect to the enthalpy values at the isotropic to nematic phase.*

**Keywords** FTIR; hydrogen bonded liquid crystal; optical textures; NMR

## Introduction

The use of noncovalent interactions has great potential in the design of functional organic liquid-crystalline materials. Due to the demand for a wide variety of electro-optic materials with properties suitable for the display applications [1–4], research activity has grown in this area. Although the first reports of hydrogen bonding in liquid crystals (HBLC) dates back to the 1960s [5,6], much research has taken place

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in the last two decades [7–20]. It is noticed that in HBLC lower bonding and activation energies showed a profound influence on their thermal properties, viz. clearing points, enthalpies, and mesomorphic phase behaviors. Hydrogen bonding is a powerful tool for assembling molecules for noncovalent interactions in nature. The main advantage of hydrogen-bonded mesogens is that their liquid crystal (LC) properties can be tuned easily by changing the H-bond donor/acceptor or percentage of molar composition. Stable and dynamic molecular complexes can be prepared by simple molecular self-assembly processes using such hydrogen bonding. A conventional low-molar-mass liquid-crystal comprises molecules consisting of a rigid core attached normally to one or two flexible alkyl end chains [21]. A number of such liquid crystal systems have been investigated following the reports of Kato *et al.* [8–10,22–24], which indicates that the mesomorphism results from a proper combination of molecular interactions and shape of the molecules.

Many reports in the current literature involve the formation of LCs through the H-bonding of aromatic carboxylic acids, as well as from mixtures of unlike molecules capable of interacting through H-bonding [1–4,12,15–19,24]. The uniqueness of double hydrogen-bonded liquid crystals is a central rigid core not only built by covalent bonds but supported by noncovalent bond interactions (*i.e.,* H-bonding extends along the length of the rigid core). Hence, a distinctly tunable LC phase abundance and molecular dynamics different from those of traditional covalently bonded LCs are expected to be exhibited by these HBLC complexes [24].

In the literature, self-assembly in living nematics [25,26] has been reported, which are essentially low-molecular-weight liquid crystals. The mechanism of hydrogen bonding for the case of self-assembling systems formed by polymer liquid crystals and extended chain polymer liquid crystals has been extensively studied [27]. The influence of photo-polymerization in self-organizing systems comprising benzoic acid were also investigated. It is inferred that hydrogen bonding has an influence on crystallization and phase behaviors of multicomponent supramolecular complexes formed by benzoic acids [28]. Heteromeric liquid-crystalline association chain polymers comprising carboxylic acids and the effect of hydrogen bonding as a function temperature have been reported [29].

In continuation of our work on design, synthesis [30–35], and characterization [36–40] of various types of HBLCs, in this article we present the results of a double HBLC possessing a mesogenic ligand (n-p alkyloxy benzoic acids, nOBAs) and a nonmesogenic moiety of aliphatic carboxylic acid.

## Experimental

### Characterization

Optical textural observations were made by a Nikon polarizing microscope equipped with a Nikon digital CCD camera system (Nikon, Japan) having 5 megapixels and 2560 × 1920 pixel resolutions. The liquid-crystalline textures were processed, analyzed, and stored with the aid of ACT-2U (Nikon, Japan) imaging software system. The temperature control of the liquid crystal cell was equipped by an Instec HCS402-STC 200 temperature controller (Instec (Colorado, USA)) to a temperature resolution of ±0.1°C. This unit was interfaced to a Pentium computer by an IEEE–STC 200 to control and monitor the temperature. The

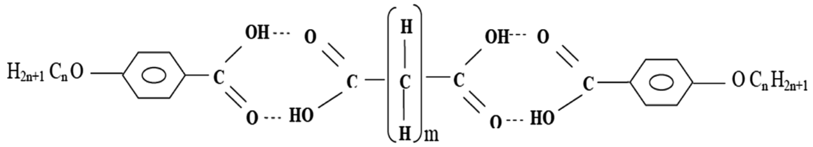


**Figure 1.** Molecular structure of X + nOBA (where X = DDC when m = 12 and X = AC when m = 7).

liquid-crystal sample was filled by capillary action in its isotropic state into a commercially available polyamide buffed cell (Instec) of about 4 μm spacer. The transition temperatures and corresponding enthalpy values were experimentally obtained by differential scanning calorimetry (DSC; Shimadzu DSC-60). The Fourier transform infrared spectroscopy (FTIR) spectra were recorded using KBr pellets (ABB FTIR MB3000) and analyzed with the MB3000 software. The complexes were analyzed with proton nuclear magnetic resonance spectroscopy (p-NMR; Brucker International, Ultra Shield model). The 300 MHz NMR spectrum of complexes was recorded in $CDCl_3$ with Tetra Methyl Sylene (TMS) as an internal standard. The p-n-alkyloxybenzoic acids (nOBA) and dodecane dicarboxlic acid were supplied by Sigma Aldrich (Munich, Germany) and all solvents used were high-performance liquid chromatography (HPLC) grade.

### *Synthesis of Hydrogen-Bonded Liquid-Crystal Homologous Series*

*DDC + nOBA and AC + nOBA Series:* Intermolecular double hydrogen-bonded mesogens were synthesized by the addition of 2 mol of p-n-alkoxybenzoic acids (nOBA) with one mole of dodecane dicarboxlic acid/azelaic dicarboxlic acid in N, N-dimethyl formamide (DMF) respectively. They were subject to constant stirring for 12 h at ambient temperature (30°C) until a white precipitate in a dense solution was formed. The white crystalline crude complexes obtained by removing excess DMF were recrystallized with dimethyl sulfoxide (DMSO) and the yield varied from 75 to 99%. The yield of higher homologue complexes were observed to be greater (99%) compared to their lower homologue counterparts (75%). The molecular structures of the present homologous series of p-n-alkoxy benzoic acids with dodecane dicarboxlic acid/azelaic dicarboxlic acid are depicted in Figure 1, where n represents the alkyloxy carbon number and m is the number of H-C-H spacers.

## Results and Discussion

All of the mesogens isolated under the present investigation are white crystalline solids and are stable at room temperature (30°C). They are insoluble in water and sparingly soluble in common organic solvents such as methanol, ethanol, benzene, and dichloro methane. However, they show a high degree of solubility in coordinating solvents like DMSO and pyridine. All of these mesogens melt at specific temperatures below 125°C (Tables 1 and 2). They show high thermal and chemical stability when subjected to repeated thermal scans performed during polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) studies.

**Table 1.** Phase transition temperatures of DDC + nOBA homologous series obtained by DSC. Enthalpy values in J/g are given in parentheses

| n | Phase variance | Study | Crystal melt | N | C | F | Crystal |
|---|---|---|---|---|---|---|---|
| 12 | NCF | DSC (h) | 94.3 (59.58) | 108.4 (52.8) | [a] | [a] | |
| | | DSC (c) | | 91.8 (1.53) | 78.2 (12.94) | 72.5 (3.27) | 54.3 (22.88) |
| | | POM (c) | | 92.3 | 78.9 | 73.1 | 54.8 |
| 11 | NCF | DSC (h) | 97.3 (22.23) | 108.6 (22.3) | 116.5 (0.34) | [a] | |
| | | DSC (c) | | 127.0 (0.97) | 90.9 (34.92) | 79.8 (6.51) | 69.3 (4.43) |
| | | POM (c) | | 127.8 | 91.5 | 80.2 | 69.9 |
| 10 | NCF | DSC (h) | 86.7 (40.4) | 95.0 (18.23) | 108.5 (20.02) | [a] | |
| | | DSC (c) | | 116.2 (2.21) | 114.2 (2.49) | 85.4 (1.26) | 71.3 (13.03) |
| | | POM (c) | | 116.9 | 114.8 | 85.8 | 71.9 |
| 9 | NCF | DSC (h) | 92.9 (74.65) | [a] | 106.4 (50.41) | [a] | |
| | | DSC (c) | | 99.3 (1.13) | 93.5 (32.2) | 84.7 (16.01) | 61.4 (43.82) |
| | | POM (c) | | 99.8 | 106.8 | 84.9 | 61.8 |
| 8 | NC | DSC (h) | 107.5 (33.73) | [a] | [a] | | |
| | | DSC (c) | | 124.8 (3.79) | 90.3[b] | | 87.4 (75.09) |
| | | POM (c) | | 125.3 | 90.5 | | 87.9 |
| 7 | NC | DSC (h) | 91.2 (64.72) | [a] | 106.8 (30.07) | | |
| | | DSC (c) | | 112.8 (0.87) | 81.4 (25.8) | | 66.5 (27.45) |
| | | POM (c) | | 113.2 | 81.9 | | 66.9 |
| 5 | N | DSC (h) | 109.1 (140.3) | [a] | | | |
| | | DSC (c) | | 96.9 (0.46) | | | 90.9 (119.38) |
| | | POM (c) | | 97.3 | | | 91.3 |

[a] Phase not observed.
[b] Merged with crystal.

**Table 2.** Phase transition temperatures of AC + nOBA homologous series obtained by DSC. Enthalpy values in J/g are given in parentheses

| n | Phase variance | Study | Crystal melt | N | G | Crystal |
|---|---|---|---|---|---|---|
| 12 | NG | DSC (h) | 94.4 (84.50) | [a] | [a] | |
| | | DSC (c) | | 114.6 (5.05) | 79.9[b] | 77.5 (73.83) |
| | | POM (c) | | 112.0 | 80.5 | 77.9 |
| 11 | NG | DSC (h) | 96.1 (117.92) | [a] | [a] | |
| | | DSC (c) | | 105.5 (1.14) | 76.0 (7.55) | 75.1 (78.24) |
| | | POM (c) | | 105.9 | 76.5 | 75.6 |
| 10 | NG | DSC (h) | 94.1 (50.57) | [a] | [a] | |
| | | DSC (c) | | 109.2 (3.23) | 82.1 (13.35) | 69.5 (58.38) |
| | | POM (c) | | 109.8 | 82.5 | 69.9 |
| 9 | NG | DSC (h) | 92.9 (151.55) | [a] | [a] | |
| | | DSC (c) | | 123.3 (2.15) | 77.9 (21.98) | 66.4 (99.92) |
| | | POM (c) | | 123.8 | 78.2 | 66.8 |
| 8 | NG | DSC (h) | 92.1 (68.42) | [a] | [a] | |
| | | DSC (c) | | 124.5 (2.41) | 80.2 (10.58) | 69.6 (35.00) |
| | | POM (c) | | 124.8 | 80.7 | 70.1 |
| 7 | NG | DSC (h) | 89.9 (83.8) | [a] | [a] | |
| | | DSC (c) | | 123.5 (1.80) | 72.0 (2.95) | 67.8 (53.84) |
| | | POM (c) | | 123.9 | 72.6 | 68.1 |
| 5 | G | DSC (h) | 96.6 (60.28) | | 109.4 (13.73) | |
| | | DSC (c) | | | 100.1 (30.12) | 76.4 (44.33) |
| | | POM (c) | | | 100.6 | 76.8 |

[a] Phase not observed.
[b] Merged with crystal.

### *Infrared Spectroscopy (FTIR)*

Infrared spectra of free p-n-alkoxybenzoic acid, 1,12 dodecane dicarboxlic acid, azelaic acid, and their intermolecular H-bonded complexes were recorded in the solid state (KBr) at room temperature. As a representative case, Figure 2 illustrates the FTIR spectra of the hydrogen-bonded complex of DDC + 12OBA and AC + 12OBA 12OBA in a solid state at room temperature (31°C). The solid-state spectra of free alkoxybenzoic acid was reported [41] to have two sharp bands at 1685 and 1695 $\mathrm{cm}^{-1}$ due to the frequency $\nu$(C=O) mode. The doubling feature of this symmetrical stretching mode confirms the dimeric nature of alkoxybenzoic acid at room temperature [41].

*DDC + 12OBA and AC + 120BA.* The absorption peak at 3106 $\mathrm{cm}^{-1}$ is due to the C–H stretching of the aromatic systems. The absorption at 1427 $\mathrm{cm}^{-1}$ is attributed to the O–H in plane bending coupled with C–O stretching vibrations. In DDC + 12OBA and AC + 12OBA, the O–H stretching absorption band appeared at 2924 $\mathrm{cm}^{-1}$. The presence of H-bonding in the present complexes is further inferred by the appearance of a new band diagnostic of $\nu$(O–H) at 2561 $\mathrm{cm}^{-1}$. The doubling nature of the $\nu$(C=O) mode may be attributed to the

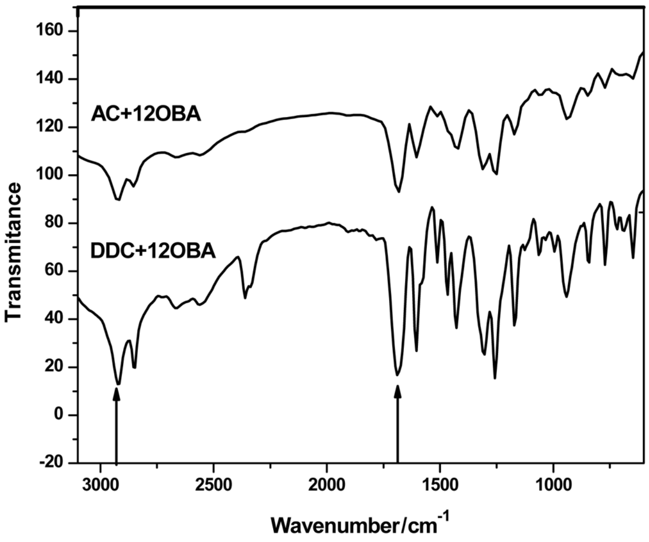


**Figure 2.** FTIR spectra of DDC + 12OBA and AC + 12OBA.

dimeric nature of the acid group at room temperature [41]. The corresponding spectrum of solution state (chloroform) shows a strong intense band, suggesting the existence of a monomeric form of benzoic acid. A noteworthy feature in the spectra of DDC + 12OBA and AC + 120BA series is the appearance of a broad band at 1690 $\mathrm{cm}^{-1}$ and nonappearance of the doubling nature of the $\nu$(C=O) mode of the benzoic acid moiety. This clearly suggests that the dimeric nature of the benzoic acid dissociates and prefers to exist in a monomeric form upon complexation. Thus, from FTIR studies the hydrogen bond formation in both of the above series has been evinced.

## *$^1$H-NMR*

The proposed structure of DDC + nOBA and AC + nOBA complexes has been verified by $^1$H NMR studies. As a representative case, $^1$H NMR for the DDC + 12OBA complex is discussed. The complexes were analyzed using NMR (Bruker International (Coventry, UK), model Ultra Shield, 300 MHz). NMR spectrum of the complex was recorded in $CDCl_3$ with TMS as the internal standard. The recorded spectra are shown in Figure 3 and the following chemical shifts were observed.

(a) Broad resonance signals were observed approximately in the range of 0.5–2.8 ppm for the methylene group. In the DDC + 12OBA complex these signals were observed between 2.969 and 0.793 ppm, which has been attributed [42] to the existence of the backbone methylene.
(b) Two sets of multiplets between 6.848 and 7.011 ppm and 7.968 and 8.132 ppm are equivalent to 2H and were attributed [42] to aromatic protons.
(c) The existence of the methoxy proton unit resonance showed a signal between 3.933 and 4.043 ppm.

The proposed structure of the complex was confirmed the NMR study.

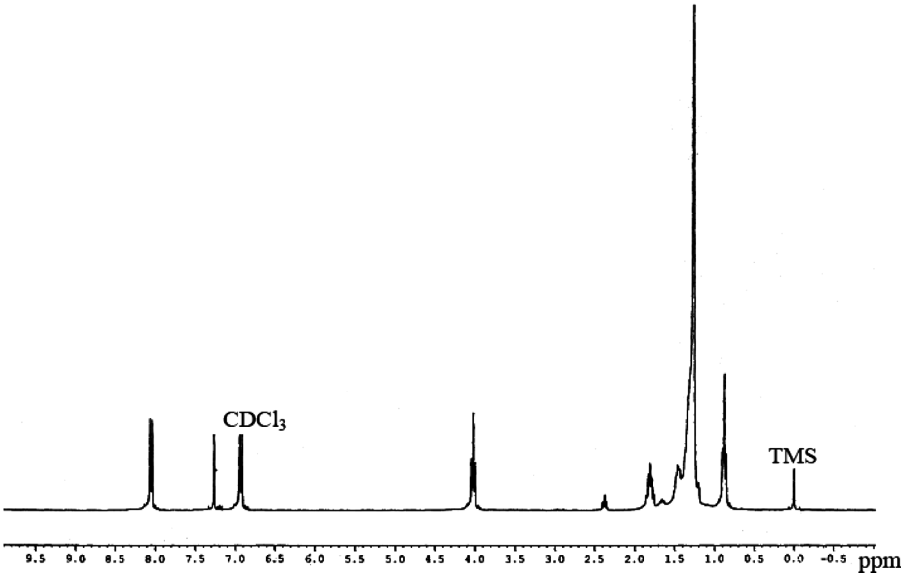


**Figure 3.** P-NMR spectra of DDC + 12OBA.

### *DDC + nOBA Homologous Series*

The mesogens of the dodecane dicarboxlic acid and alkoxy benzoic acid homologous series were found to exhibit three phases with characteristic textures [43], viz. nematic (droplets, Figure 4), smectic C (broken focal conic, Figure 5) and smectic F (checkerboard texture, Figure 6), respectively. The general phase sequence of the dodecane dicarboxlic acid and alkyloxy benzoic acids in the cooling run can be shown as:

$$Isotropic \rightleftharpoons N \rightleftharpoons Crystal \qquad (DDC + 5OBA)$$

$$Isotropic \rightleftharpoons N \rightleftharpoons Sm\ F \rightleftharpoons Crystal \qquad (DDC + 7, 8OBA)$$

$$Isotropic \rightleftharpoons N \rightleftharpoons Sm\ C \rightleftharpoons Sm\ F \rightleftharpoons Crystal \quad (DDC + nOBA, n = 9\ to\ 12)$$

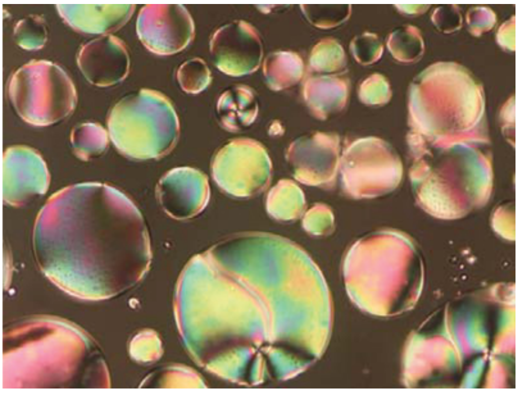


**Figure 4.** Nematic droplets texture in DDC + nOBA complex (recorded at 10×).

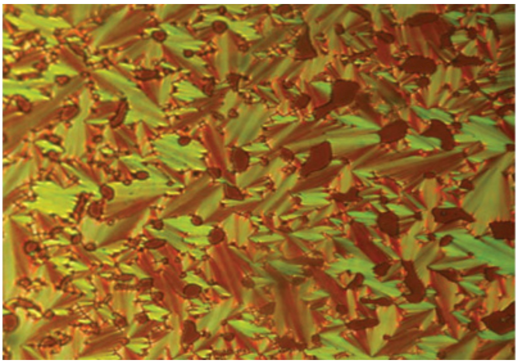


**Figure 5.** Broken focal conic texture of smectic C in DDC + nOBA complex (recorded at 10×).

*AC + nOBA Homologous Series.* The mesogens of the azelaic dicarboxlic acid and alkoxy benzoic acid homologous series were found to exhibit two phases with characteristic textures [43], viz. nematic (threaded texture, Figure 7) and smectic G

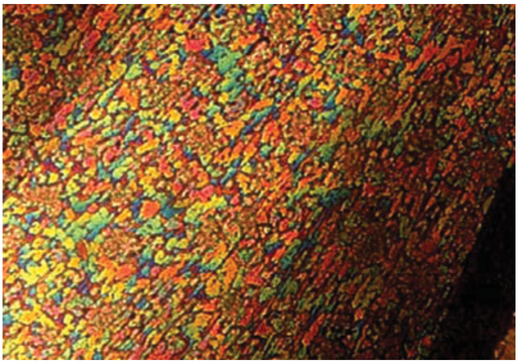


**Figure 6.** Checker board texture of smectic F in DDC + nOBA complex (recorded at 10×).

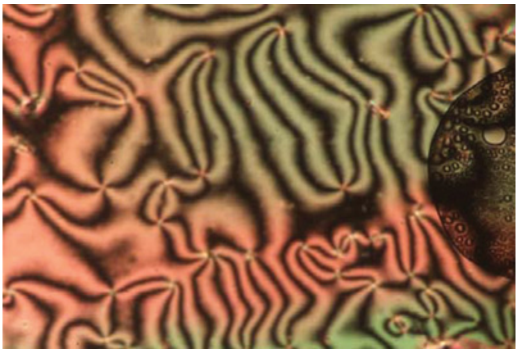


**Figure 7.** Threaded nematic texture in AC + nOBA complex (recorded at 10×).

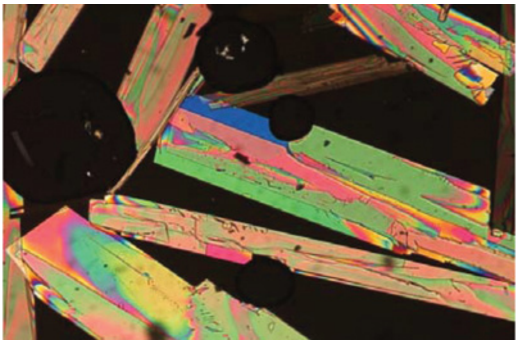


**Figure 8.** Smooth, multicolored mosaic texture of smectic G in AC + nOBA complex (recorded at 10×).

(multicolored mosaic texture, Figure 8), respectively. The general phase sequence of the azelaic dicarboxlic acid and alkyloxy benzoic acids in the cooling run can be shown as:

$$Isotropic \rightleftharpoons G \rightleftharpoons Crystal \qquad (AC + 5OBA)$$

$$Isotropic \rightleftharpoons N \rightleftharpoons Sm\ G \rightleftharpoons Crystal \qquad (AC + nOBA, n = 7\ to\ 12)$$

### *DSC Studies*

DSC thermograms were obtained in heating and cooling cycles. The sample was heated with a scan rate of 10°C/min in an $N_2$ atmosphere and held at its isotropic temperature for one minute to attain thermal stability. The cooling run was performed with the same scan rate of 10°C/min. The respective equilibrium transition temperatures and corresponding enthalpy values of the mesogens of the homologous series were recorded. POM studies also confirmed these DSC results along with the results of monotropic transition.

*DSC Studies of DDC + 9 OBA.* As a representative case, the phase transition temperatures and enthalpy values of nonyloxybenzoic acid and dodecane dicarboxlic acid mesogen (DDC + 9OBA) are discussed and are tabulated in Table 1. Figure 9 illustrates the thermogram of the DDC + 9OBA hydrogen-bonded complex recorded at a scan rate of 10°C/min for the heating and cooling runs. The cooling run of the DSC thermogram shows four distinct transitions, namely, isotropic to nematic, nematic to smectic C, smectic C to smectic F, and smectic F, to crystal with transition temperatures 99.3°C, 93.5°C, 84.7°C, and 61.4°C and corresponding enthalpy values 1.13, 32.2, 16.01, and 43.82 J/g. In the heating cycle two distinct transitions, namely, crystal to melt and melt to smectic C, were obtained at 92.9°C and 106.4°C with corresponding enthalpy values of 74.65 and 50.41 J/g.

All of these transition temperatures of the present homologous series concur with optical polarizing microscopy studies.

*DSC Studies of AC + 7 0BA.* As a representative case, the phase transition temperatures and enthalpy values of heptyloxybenzoic acid and dodecane dicarboxlic acid mesogen (AC + 7OBA) are discussed and are tabulated in Table 2.

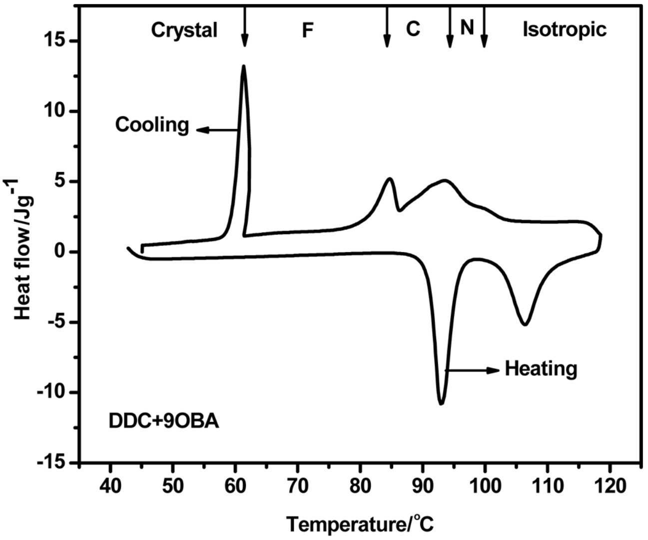


**Figure 9.** DSC thermogram of DDC + 9OBA.

Figure 10 illustrates the thermogram of the AC + 7OBA hydrogen-bonded complex recorded at a scan rate of 10°C/min for the heating and cooling runs. In the cooling run the DSC thermogram shows three distinct transitions, namely, isotropic to nematic, nematic to smectic G, and smectic G to crystal with transition temperatures 123.5°C, 72.0°C, and 67.8°C and corresponding enthalpy values 1.80, 2.95, and 53.84 J/g. In the heating cycle one transition, namely, crystal to melt, obtained at 89.9°C with corresponding enthalpy value of 83.8 J/g was monotropic, whereas the melt to nematic and nematic to smectic G were observed to be enantiotropic transitions in the heating run.

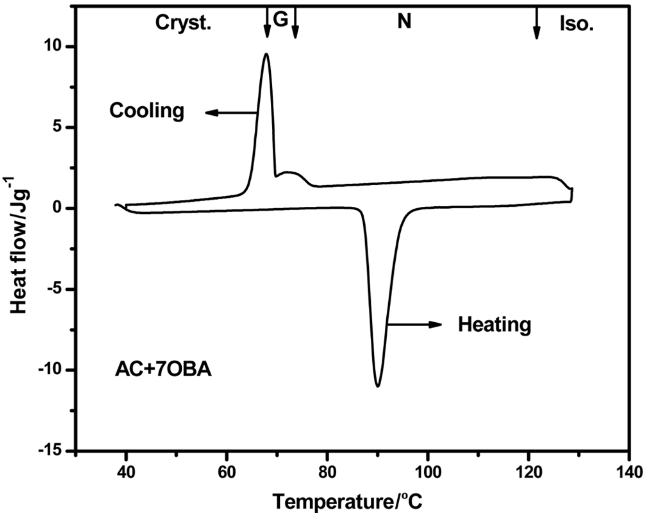


**Figure 10.** DSC thermogram of AC + 7OBA.

### *Phase Diagram of p-n-Alkoxybenzoic Acid*

The phase diagram of a dodecane dicarboxlic acid with p-n-alkoxybenzoic acid complexes was reported earlier [30] by us to be composed of nematic and smectic phases.

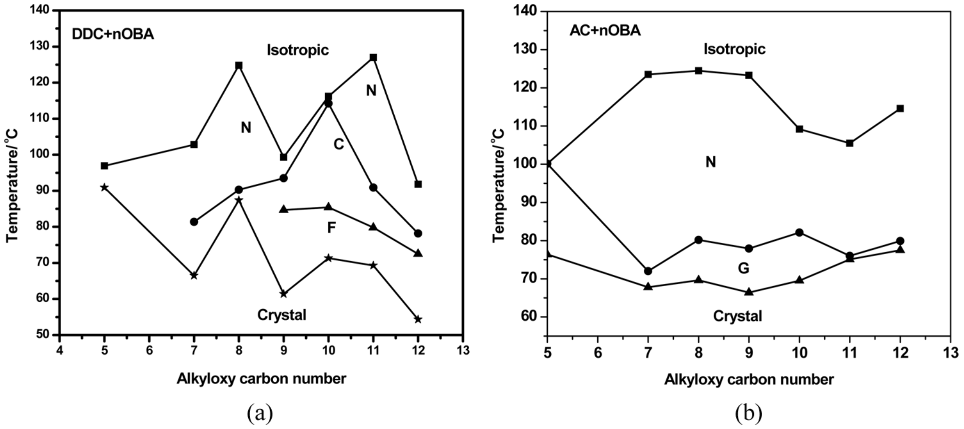
*Phase Diagram of DDC + nOBA Homologous Series.* The phase diagram of a dodecane dicarboxlic acid with p-n-alkoxybenzoic acid complex is depicted in Figure 11a. A careful observation of the figure 6a reveals the following points:

(a) The phase diagram is composed of three phases, namely, nematic, smectic C, and smectic F.
(b) The nematic phase is present in all of the homologues and the higher ordered smectic F phase is induced in higher homologues starting from DDC + 9OBA.
(c) It is interesting to note that DDC + 9, 10, 11, 12OBA exhibit all the three phases (NCF), whereas DDC + 5OBA exhibits only the nematic phase.
(d) In general, DDC + 5OBA have the least mesogenic thermal range and DDC + 10OBA have the largest mesogenic thermal range.
(e) The lower homologues (DDC + nOBA, n = 5, 7, and 8) exhibit mono/biphase variance with the phase being either nematic or smectic C or both.
(f) In contrast, the higher homologues (DDC + nOBA n = 9 to 12) exhibit three phase variances, with the phases being nematic, smectic C, and smectic F.

New phases are also induced at regular increments of odd alkyloxy carbon number. As an example, in DDC + 7OBA the smectic C phase is induced and in DDC + 9OBA the smectic F phase is induced.

*Phase Diagram of AC + nOBA Homologous Series.* The phase diagram of azelaic dicarboxlic acid with p-n-alkoxybenzoic acid complexes is depicted in Figure 11b. A careful observation of Figure 11b reveals the following points:

(a) The phase diagram is composed of two phases, namely, nematic and smectic G.
(b) The nematic phase is present in all of the homologues except in AC + 5OBA.
(c) In the entire homologous series, in all complexes, the thermal range of the nematic phase is much larger compared to the smectic G phase.



(a) (b)

**Figure 11.** (a) Phase diagram of DDC + nOBA homologous series; (b) Phase diagram of AC + nOBA homologous series.

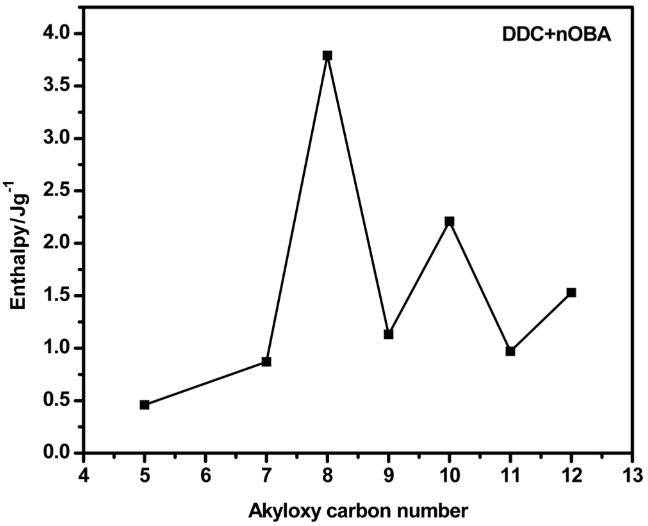


**Figure 12.** Odd–even effect in DDC + nOBA homologous series.

(d) The least mesogenic thermal range is observed in the AC + 5OBA complex and AC + nOBA (n = 7, 8, and 9) possesses the maximum mesogenic thermal range.

## Odd–Even Effect in DDC + nOBA and AC + nOBA Homologous Series

In the present homologous series, an odd–even effect is noticed. A plot is constructed with the enthalpy values corresponding to the isotropic to the first mesomorphic phase transition, mostly isotropic to nematic transition in the present case, and the alkyloxy carbon number. Figures 12 and 13 depict the variation of enthalpy values with carbon numbers in DDC + nOBA and AC + nOBA homologous series,

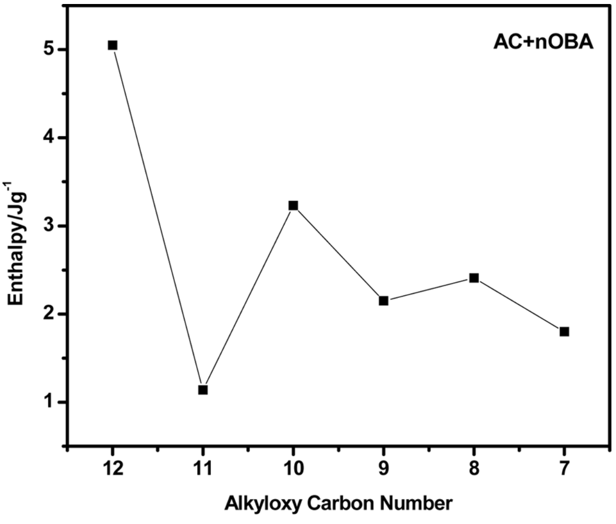


**Figure 13.** Odd–even effect in AC + nOBA homologous series.

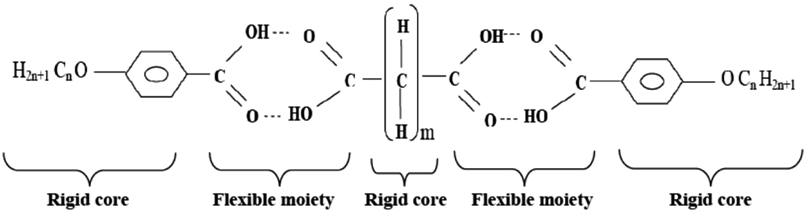


**Figure 14.** Molecular modeling indicating various types of cores in X + nOBA series.

respectively. From Figures 12 and 13 it can be observed that the magnitudes of the enthalpy values corresponding to the even homologous carbon number exhibit one type of behavior, whereas the odd counterparts show a different increment. In the literature, such behavior has been reported [44] and is referred to as the odd–even effect.

It may be noted that the present liquid-crystalline molecule is composed of rigid and flexible parts as depicted in Figure 14. The rigid part is the alkyloxy benzoic acid moiety and the flexible moiety is mostly composed of the hydrogen-bonded frame. The rigid core length varies with increment in the benzoic acid carbon number. The rich liquid-crystalline phase polymorphism and the associated enthalpy values with increment of alkyloxy carbon number are thus attributed to this part of the chemical structure. Hence, the rigid core plays a vital role in establishing the pronounced odd–even effect as evinced in the present homologous series.

## Influence of Spacer Groups on Liquid Crystallinity

Homologous series DDC + nOBA and AC + nOBA have different numbers of spacer group H-C-H. The number of the spacer group H-C-H in the DDC + nOBA nOBA series is 12 whereas it is 7 in AC + nOBA. The increment in spacer groups influenced phase variants and liquid crystallinity. Comparing DDC + nOBA and AC + nOBA series, the increment in the spacer group H-C-H has the following effects:

(a) DDC + nOBA has three phase variants, namely, nematic, smectic C, and smectic F, whereas AC + nOBA has only two phase variants, namely nematic and smectic G. Thus, the phase variants increased with increased number of spacer groups.
(b) Increased spacer groups induced two highly ordered phases, namely, smectic C and smectic F, in DDC + nOBA compared to AC + nOBA.
(c) The clearing temperatures (isotropic to nematic) in both series (DDC + nOBA and AC + nOBA) were almost unaltered. Thus, the increased spacer groups had no influence on the clearing temperatures.
(d) The crystallization temperatures were relatively low in DDC + nOBA compared to the AC + nOBA series. Thus, the increased spacer groups considerably decreased the crystallization temperatures.
(e) With the increment in the spacer groups, the length of the molecule (l) increased for the same interplanar distance (d), which in turn influenced the l/d ratio. This altered l/d ratio of DDC + nOBA favored inducement of the tilted phases.

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