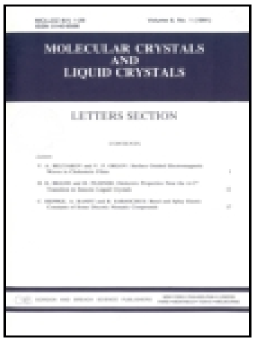

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Linear Double Hydrogen-bonded Thermotropic Liquid Crystals Formed Between Oxaloacetic Acid and *p*-*n*- Alkyloxy Benzoic Acids

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ABSTRACT

Double hydrogen-bonded thermotropic liquid crystal complexes (DHBLC) have been isolated from molar ratios of Oxaloacetic acid (OAC) and eight alkyloxy benzoic acids (nBAO) whose carbon number varied from pentyloxy to dodecyloxy. The complexes are referred as OAC+nBAO where n varied from 5 to 12. In each of the synthesized complexes, complementary hydrogen bonds formed are confirmed by FTIR study and the complexes are further investigated by Polarizing Optical Microscopy (POM), Differential Scanning Calorimetry (DSC) for the construction of phase diagram. Characteristic phases like nematic, smectic C, smectic F, and smectic G are characterized by various textures. From DSC studies, odd–even effect is evinced in transition temperatures across isotropic to nematic phase transition and across smectic F to smectic G phase transition in enthalpy values. The order of all transitions observed in eight complexes is calculated by thermal analysis. The magnitude of optical tilt angle in smectic C is fitted to a power law and the scale of critical exponent is found to concur with the Mean Field theory predicted value.

KEYWORDS

Double hydrogen-bonded liquid crystals; odd-even effect; optical tilt angle; thermal analysis

1. Introduction

Liquid crystals (LC) are the thermotropic mesogenic material that forms intermediate state of liquid and solid. LC has an orientational ordering that depends on external conditions, such as temperature or electric fields [1, 2]. Liquid crystal device technology paved way for its extensive implementation in the field of Science and Technology [3]. Synthesis of LC involves many established routes. One among them is liquid crystal synthesized by formation of hydrogen bonds and are referred as hydrogen bonded liquid crystals (HBLC). Hydrogen bond is materialized between hydrogen atom and other electronegative atoms which is stronger than van der Waals force but weaker than covalent bond [4–8]. For the formation of hydrogen bond it is necessary to have interaction between two functional groups, one group act as donor of proton and the another group act as accepter of electron [9, 10]. Examples of donor of protons are carboxy, hydroxy, amino, amido groups, and the acceptor of electrons are carbonoyle, ethers and hydroxyl groups. Hydrogen bond plays vital role in molecular self-assembly [11]. Self-assembly manifest in two types, static and dynamic. Most researchers has focused on static

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type self-assembly systems [12]. In liquid crystals, single hydrogen bond shares one pair of electron and proton with respective atoms in complimentary manner [13], while in double hydrogen-bonded LC [14] two pairs of electrons and protons are shared between respective atoms and it is experimentally possible to obtain multiple hydrogen bonds also [15]. Phase polymorphism and the role of hydrogen bonding in liquid crystals had been recently reviewed by research groups of Paleos [15, 16] and Kato [17–21]. Few of the shapes of hydrogen-bonded reported are linear [22], Banana/bent shaped [23–25], T shaped [26–28], W shaped [29], Y shaped [30–32] zigzag [33–35], and U shaped [36]. The inducement of smectic phases in hydrogen-bonded liquid crystals is an interesting phenomena and is reported in the recent literature [37–41].

The aim of the present work is to design, synthesize, and characterization of eight novel homologues of DHBLC where the hydrogen bond is formed between *p*-*n* alkyloxy benzoic acids (nBAO) and Oxaloacetic acid (OAC). Smectic F is found to induce in the present DHBLC.

2. Experimental

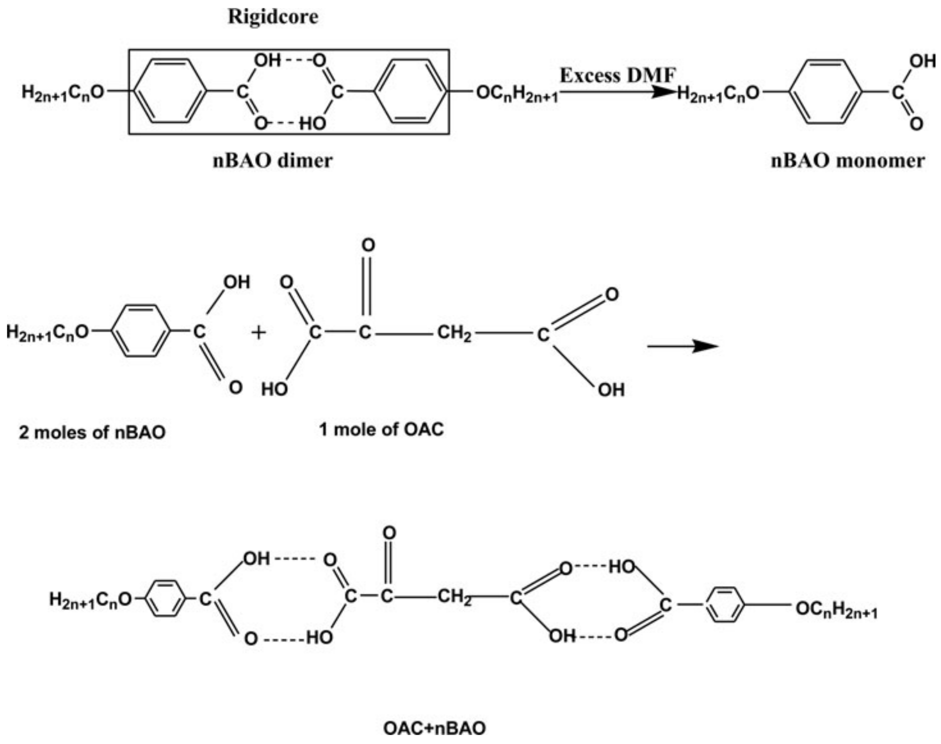
Observations of optical textural are made with a Nikon polarizing microscope (Nikon, Japan) equipped with Nikon digital CCD camera system with 5 mega pixels and 2560 × 1920 pixel resolutions. The liquid crystalline textures are analyzed and stored with the assist of NIS system. The temperature control of the liquid crystal cell is equipped with HCS402-STC 200 temperature controller (Instec, USA) to a temperature resolution of ±0.1°C. This unit is interfaced to a computer by IEEE–STC 200 to control and monitor the temperature. Optical extinction technique is used for the determination of tilt angle in smectic C phase. Transition temperatures and corresponding enthalpy values are obtained by DSC (Shimadzu DSC-60, Japan). FTIR spectra are recorded (ABB FTIR MB3000) and analyzed with the MB3000 software. Oxaloacetic acid and *p*-*n*-alkyloxy benzoic acids (nBAO) are supplied by Sigma Aldrich, (Germany) and all the solvents used are of High-Performance Liquid Chromatography (HPLC) grade.

3. Synthesis of DHBLC

DHBLC complexes examined in the present study are obtained by mixing 1:2 molar ratio of Oxaloacetic acid with various alkyloxy benzoic acids separately in DMF and reprecipitating after the evaporation as described in the reported literature [42, 43]. The synthesis scheme of present homologous series of Oxaloacetic acid with *p*-*n*-alkyloxy benzoic acids is depicted in scheme 1 along with the proposed atomic structure for all the eight homologues (Fig. 1a–h). The chemical linear structure of OAC+5BAO can be shown as:

4. Results and discussion

DHBLC isolated under the present investigation are white crystalline solids and are stable at room temperature (∼30°C). They are insoluble in water and are soluble in common organic solvents such as methanol, ethanol, benzene, and dichloro methane. However, a high degree of solubility is found in coordinating solvents like dimethyl formamide (DMF). They show high thermal and chemical stability when subjected to repeated thermal scans performed during POM and DSC studies. The transition temperatures obtained for individual mesogenic phases



Scheme 1. Synthesis scheme representing the formation of OAC+nBAO Hydrogen-bonded series.

from POM and DSC along with their enthalpy values (from DSC) for all the complexes of OAC+nBAO homologous series are depicted in Table 1.

4.1. Phase identification

The observed phase variance, transition temperatures and corresponding enthalpy values obtained by DSC in the cooling and heating cycles for the OAC+nBAO complexes are presented in Table 1. It is found that these data are in good agreement with POM data. The present homologous series is found to exhibit characteristic textures [44], viz., nematic (N) (four brushes, Plate 1), smectic C (broken focal conic, Plate 2), smectic F (broken focal conic fan texture, Plate 3). The fans in the smectic C are usually sanded and broken (Plate 2), the breaks being ill defined and having a shaded appearance. On cooling to a smectic F phase, the sanding disappears and breaks become well defined (Plate 3). Smectic G is observed as smooth multi colored mosaic, Plate 4 i.e., mosaic platelets separated by very fine lines containing schlieren-like brushes, but does not show actual intersections in the form of crosses.

The general phase sequence of various homologues of OAC+nBAO series in cooling and heating run of POM and DSC can be shown as:

Iso. ↔ N ↔ Crystal (OAC + 5BAO, OAC + 6BAO)
Iso. ↔ N ↔ Sm C ↔ Sm G ↔ Crystal (OAC + 7BAO, OAC + 8BAO)
Iso. ↔ N ↔ Sm C ↔ Sm F ↔ Sm G → Crystal (OAC + 9BAO)
Iso. → N ↔ Sm C ↔ Sm F ↔ Sm G ↔ Crystal (OAC + 10BAO, OAC + 11BAO)
Iso. ↔ N → Sm C ↔ Sm F ↔ Sm G → Crystal (OAC + 12BAO)

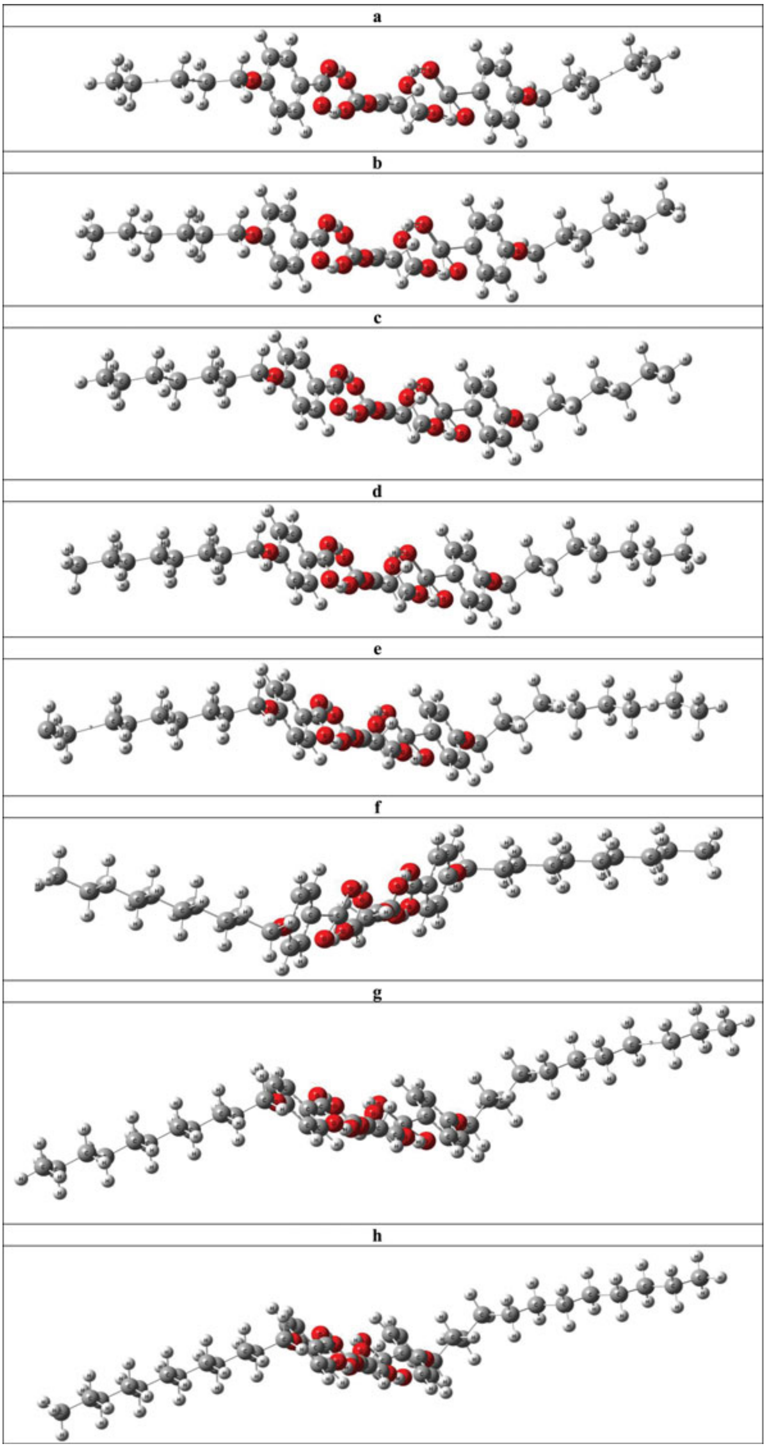


Figure 1. **(a-h)** Atomic structure of OAC+nBAO complexes (where $n = 5$–12).

Table 1. Transition temperatures and corresponding enthalpy values obtained by POM and DSC techniques for OAC+nBAO homologues.

Complex	Phase variance	Technique	N	C	F	G	K
OAC+12BAO	N C F G	DSC (h)	140.4 (6.31)	#	134.1 (4.62)	98.3 (104.03)	
		DSC (c)	139.1 (4.69)	135.9 (6.28)	129.8 (5.18)	86.5 (30.69)	68.0 (16.59)
		POM	139.6	136.4	130.3	86.9	68.3
OAC+11BAO	N C F G	DSC (h)	#	140.0 (6.02)	128.6) (5.17	90.4 (19.67)	82.0 (13.08)
		DSC (c)	140.9 (0.29)	138.2 (5.17)	126.2 (4.51)	84.0 (21.41)	70.8 (14.30)
		POM	142.1	139.4	127.3	84.5	71.5
OAC+10BAO	N C F G	DSC (h)	#	139.6 (6.55)	120.5 (4.07)	96.4 (32.54)	88.1 (21.55)
		DSC (c)	139.9 (6.67)	138.0 (8.94)	116.7 (4.0)	91.0 (28.89)	72.2 (23.83)
		POM	141.8	139.1	117.7	92.1	72.8
OAC+9BAO	N C F G	DSC (h)	142.6 (merged)	139.8 (10.19)	118.7 (4.96)	96.6 (104.39)	
		DSC (c)	137.3 (4.07)	131.0 (3.61)	114.9 (4.41)	89.5 (30.77)	65.7 (67.92)
		POM	138.5	132.3	115.9	90.2	66.1
OAC+8BAO	N C G	DSC (h)	148.0 (8.74)	107.1 (1.32)		102.2 (28.65)	76.1 (45.62)
		DSC (c)	145.0 (11.20)	103.3 (3.55)		94.2 (32.68)	57.4 (44.28)
		POM	146.8	104.5		95.2	58.4
OAC+7BAO	N C G	DSC (h)	141.4 (4.19)			94.9 (81.04)	
		DSC (c)	139.7 (5.87)	91.6 (3.40)		87.3 (28.21)	68.5 (37.91)
		POM	140.8	92.7		88.5	69.3
OAC+6BAO	N	DSC (h)					107.5 (45.1) 71.1*(20.1)
		DSC (c)	142.1 (16.0)				94.3 (40.36)
		POM	143.5				95.2
OAC+5BAO	N	DSC (h)	150.7 (43.5)				126.1 (58.66)
		DSC (c)	147.0 (4.51)				116.7 (55.8)
		POM	148.1				117.2

Monotropic transition, * Crystal to crystal transition.

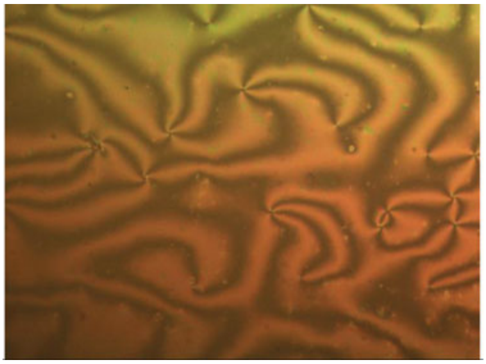


Plate 1. Schlieren four brush texture of nematic phase.

Plate 2. Broken focal conic texture of smectic C phase.

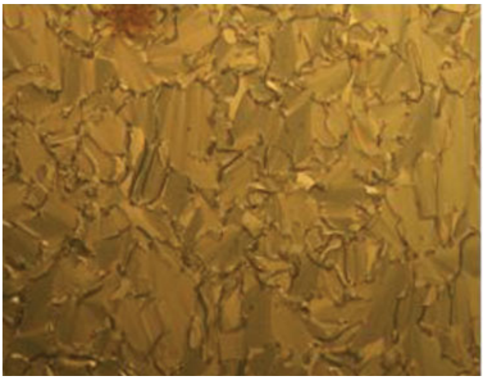


Plate 3. Platelet texture in yellowish color of Smectic F phase.

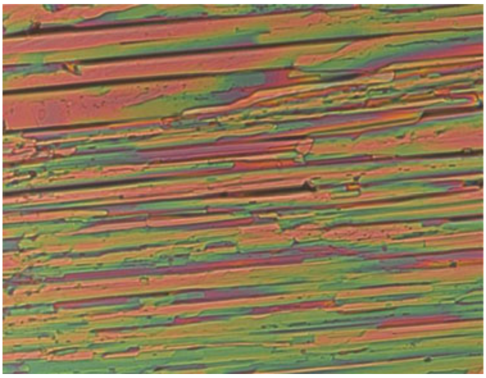


Plate 4. Multi-colored smooth mosaic like texture of Smectic G phase.

Monotropic and enantiotropic transitions are depicted as single and double arrows respectively.

4.2. Fourier transform infrared spectroscopy (FTIR)

At room temperature, FTIR spectra of all the DHBLC along with the precursors of alkyloxy benzoic acid are recorded in the solid state (KBr). As a representative case, the FTIR spectrum of OAC+10BAO is illustrated in Fig. 2. In the alkyloxy benzoic acids, carboxylic acid exists in monomeric form and the stretching vibration of C=O is observed at 1674 cm^{-1}. Further it is reported [45] that when a hydrogen bond is formed between carboxylic acids it results in lowering of the carbonyl frequency which has been detected in the present hydrogen bonded complexes. A noteworthy feature in the spectrum of the OAC+10BAO is the appearance of sharp peak at 1682 cm^{-1} which clearly suggests the dimmer formation, in particular the carbonyl group vibration [45–48]. A carboxylic acid existing in monomeric form in dilute solution absorbs at about 1760 cm^{-1} because of the electron withdrawing effect. However, acids in concentrated solution or in solid state tend to dimerize through hydrogen bonding. It is reported [49] that this dimerization weakens the C=O bond and lowers the stretching force constant K, resulting in lowering of the carbonyl frequency of saturated acids to ∼1674 to 1690 cm^{-1}. The frequencies of C=O and O-H pertaining to various homologues

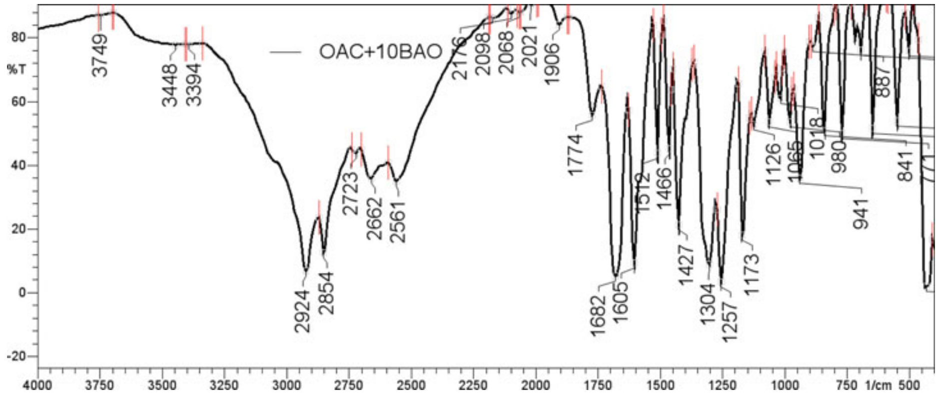


Figure 2. FTIR spectrum of OAC+10BAO complex.

of OAC+nBAO are listed in Table 2. Hence, in the present complexes the formation of hydrogen bonding is established by FTIR peak assignments. A similar trend of result is followed in all the other homologues.

4.3. DSC studies

DSC thermograms of all the eight DHBLC are recorded in heating and cooling cycle. The accurately weighed individual sample is crimped in aluminum pan and loaded into the heating chamber. The instrument is programmed to heat the sample with a predetermined scan rate (5°C/min and 10°C/min) and held at its respective isotropic temperature for two minutes so as to attain thermal stability. Nitrogen gas is continuously purged inside the heating chamber. Cooling run is programmed with identical scan rate (5°C/min and 10°C/min). The respective resultant equilibrium transition temperatures and corresponding enthalpy values of the mesogens of the homologous series are listed separately in Table 1. POM studies also concur with the DSC transition temperatures. As a representative case, DSC thermogram in both the heating and cooling cycles of OAC+12BAO is depicted in Figure 3 which shows various mesogenic transitions. In addition, the well resolved phase transitions of sample OAC+12BAO, corresponding to isotropic to nematic, nematic to smectic C, smectic C to smectic F and smectic F to smectic G in the cooling cycle are depicted in Fig. 3.

Table 2. FTIR spectral data obtained for OAC+nBAO complexes.

Complex	ν for (C=O)	ν for (OH)
OAC+12BAO	2924	1682
OAC+11BAO	2924	1674
OAC+10BAO	2924	1682
OAC+9BAO	2924	1674
OAC+8BAO	2932	1690
OAC+7BAO	2932	1682
OAC+6BAO	2939	1682
OAC+5BAO	2955	1674

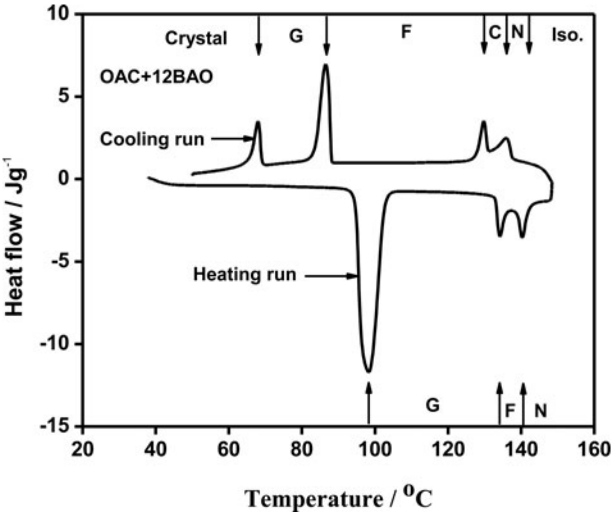


Figure 3. DSC thermogram of OAC+12BAO complex.

4.3.1. Thermal analysis

Landau theory and Mean Field theory [50] are the theories which discuss the phase transitions in liquid crystalline substance. Two theories on the whole can be summarized as, a physical system in which phase transition can occur is usually characterized by one or more long range order parameters. A phase transition can be accompanied either by a continuous change or by a discontinuous change in the equilibrium value of the order parameter when the system transforms from one phase to the other. It is said to be the first order transition when it is discontinuous and if the state is continuous it is assigned to be second order transition. Thus the theoretical description of a phase transition is equivalent to the determination of the free energy density as a function of the order parameter, its spatial derivatives and the temperature. Determination of phase transition order by experimental technique carried out by Navard and Cox [51] supplements the above mentioned arguments.

Navard and Cox [51] utilized thermal analysis for the differentiation of first and second order transitions of liquid crystal complexes basing on DSC thermograms. The DSC scanning rate or the weight of the sample measured can be varied for this purpose but for the accurate results and for the convenience the former is preferred in the present study. Transition peaks obtained by DSC studies at two scan rates, one being twice the other, are measured and their ratio (Cox parameter, N_C) is employed for this purpose. The first and the second order transitions can be classified basing on the ratio (N_C) of the measured heights, $1 < N_C \geq \sqrt{2}$ for an isothermal first order transition and $N_C = 2$ for a second order transition.

For all the homologues DSC thermograms at 5°C/min and 10°C/min are obtained and as a representative case, the thermal analysis of OAC+12BAO complex is discussed. The values of N_C for the isotropic to nematic, nematic to smectic C, smectic C to smectic F and smectic F to smectic G transitions for OAC+nBAO complexes are presented in Table 3. As a representative case the data of OAC+12BAO is discussed. In OAC+12BAO for isotropic to nematic transition the magnitude of N_C is calculated to be 2.0 indicating it to be a second order transition, for nematic to smectic C transition the value of N_C is calculated to be 1.4 indicating it to be a first-order transition and for smectic C to smectic F transition the value of N_C is calculated to be 1.9 indicating it be a second-order transition and finally the smectic F to smectic G transition yields a N_C value of 1.8 indicating a second-order transition.

Table 3. Thermal stability magnitude for the mesogenic phases observed in all the complexes of OAC+nBAO homologous series.

Complex	Phase	Cox ratio	Order of transition
OAC+12BAO	N	2.0	Second
	C	1.4	First
	F	1.9	Second
	G	1.8	Second
OAC+11BAO	N	2.1	Second
	C	2.4	Second
	F	2.2	Second
	G	1.5	Second
OAC+10BAO	N	2.2	Second
	C	2.2	Second
	F	2.2	Second
	G	1.9	Second
OAC+9BAO	N	1.8	Second
	C	1.8	Second
	F	1.9	Second
	G	1.3	First
OAC+8BAO	N	1.1	First
	C	1.7	Second
	G	1.7	Second
OAC+7BAO	N	2.1	Second
	C	1.8	Second
	G	1.8	Second
OAC+6BAO	N	1.9	Second
OAC+5BAO	N	1.1	First

4.3.2. Thermal stability of mesogenic phases

It is reported [52, 53] that when the liquid crystalline molecules have two symmetric end chains, the phase transition temperatures and the temperature ranges are affected. The molecular weights of terminal chain could be considered as the measure of balancing and if they are nearly equal, the system is balanced. In other words, the system is symmetric about its molecular short axis.

Phase stability is one of the important parameters that govern the utility of the mesogen. In the present case phase stability of nematic is discussed. The term phase stability can be attributed to isotropic to nematic transition temperature as well to the temperature range of nematic phase. It is reasonable to consider both the above factors and define a parameter called stability factor (S). As a representative case, the stability factor for nematic (S_N), is given by

$$S_N = T_{mid} * \Delta T_N$$

T_{mid} is the mid nematic temperature and ΔT_N the nematic thermal range. In this manner, the thermal stability of smectic C, smectic F, and smectic G exhibited by the complexes of OAC+nBAO homologous series are calculated and tabulated in Table 4.

Table 4. Phase transition order estimated by Navard and Cox method.

Complex	N	C	F	G
OAC+12BAO	440	810.3	4682.8	1429
OAC+11BAO	328.2	1586	4435	1021
OAC+10BAO	264	2712.5	2668.9	268.5
OAC+9BAO	845.1	1979	2595	1846.8
OAC+8BAO	5177.0	898.62	–	2789.4
OAC+7BAO	5562.1	384.6	–	1464.5
OAC+6BAO	5649.9	–	–	–
OAC+5BAO	4668.8	–	–	–

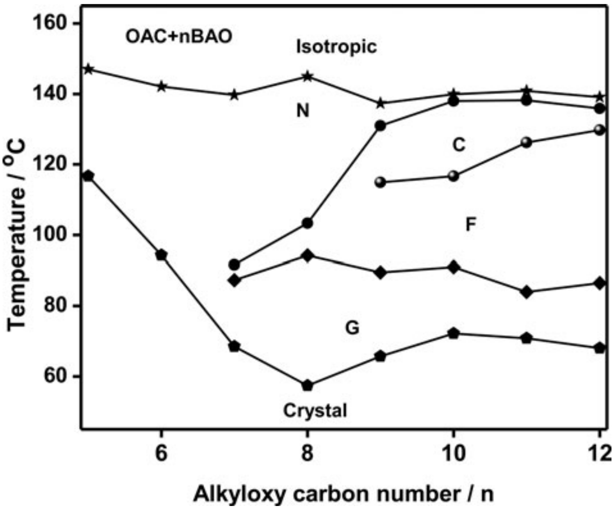


Figure 4. Phase diagram of OAC+nBAO homologous series.

4.4. Phase diagram of OAC+nBAO

Phase diagram of Oxaloacetic acid and *p*-*n*-alkyloxy benzoic acids homologues series is depicted in Fig. 4. Following points can be elucidated from Fig. 4:

A) The OAC+nBAO hydrogen-bonded homologous series exhibits nematic as orthogonal phase and smectic C, smectic F, and smectic G as tilted phases.
B) Compared to the precursors, in the present DHBLC, smectic F is induced.
C) Nematic phase is observed in all the eight homologues of OAC+nBAO series.
D) Smectic C and smectic G are induced at heptyloxy carbon number quenching the thermal range of nematic while smectic G is induced at nonyloxy carbon number quenching the thermal range of smectic C.
E) An interesting observation is the presence of odd–even effect across smectic F to smectic G enthalpy values and across isotropic to nematic phase transition temperatures.
F) In the present homologous OAC+nBAO series, the magnitude of the mesogenic range gradually increased and saturated with the increment in the alkyloxy carbon number.

4.4.1. Odd–even effect

The origin of the odd–even effect [50, 53, 54, 55] can be understood from the consideration of the molecular structure of OAC+nBAO (Figs. 1a-h). In the even numbers of the series, the disposition of the end group is to enhance the molecular anisotropy and hence molecular order, whereas in the odd number it has the opposite effect. As the chain length increase their flexibility increases and the odd–even effect observed in the present series are in accordance with the quantitative calculations proposed by Marcelja [54].

Odd–even effect is observed in the transition temperatures corresponding to isotropic to nematic phase transition. From Figure 5a, it can be observed that the magnitudes of the isotropic to nematic phase transition temperatures consistent to the even homologous carbon number exhibit one type of behavior, while the odd counter parts show a different increment and is known as odd–even effect. A similar trend is noticed for the enthalpy values obtained across smectic F to smectic G phase transition and is depicted as Fig. 5b.

Considering flexibility due to end chains, Mercelja [54] incorporated the configurational statistics of the end chains in the theory of the nematic phase in a flory-type calculation [53].

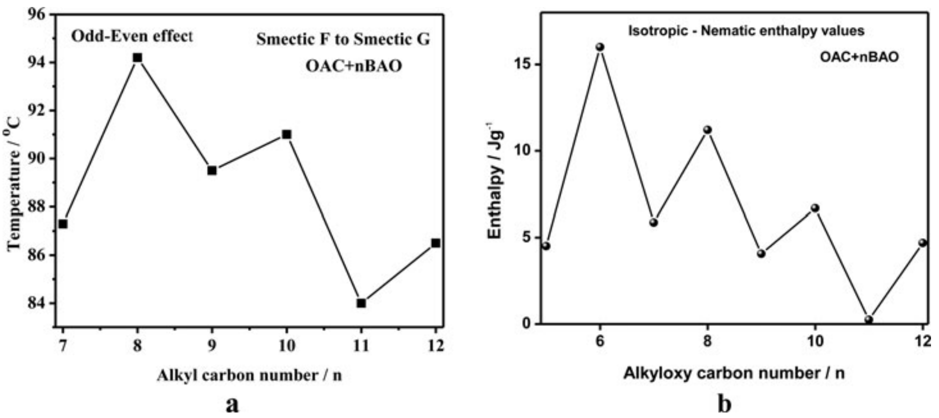


Figure 5a. Odd–even effect observed across isotropic to nematic phase transition temperatures of OAC+nBAO complexes. **b.** Odd–even effect observed across smectic F to smectic G enthalpy values Phases of OAC+ n BAO homologous series.

In addition to conformational energy, each C-C bond in the end chain is subjected to a mean field, which depends both on the orientational order of the rigid central part and that of the end chain. A high probability of occurrence of the all trans configuration for short chains is considered for the strong odd–even effect for lower homologous. The increase in conformational flexibility for the higher homologues is seen as an extension of this effect.

Luckhurst [56] refined the calculations made by Pink model which shows that, while the odd–even effect in transition temperature can be understood as a consequence of the odd–even effect in the chain order parameter with respect to the molecular axis, the odd–even effect in the rigid segment order parameter is the consequence of at least such an effect in the mean-square deviation and used to make successful calculations for compounds which have two rigid cyano biphenyl moieties linked by flexible spacers, in which the odd–even alteration in transition temperature is very strong. In compounds with alkyl and alkoxy end chains, it is already known [57] that the isotropic to nematic transition temperatures show odd–even effects.

5. Occurrence of smectic C and measurement of optical tilt angle

Smectic C phase is the first classified phase in which the molecular long axes of the constituent molecules were found to be tilted with respect to the normal of the layer planes. A large number of experimental studies are there concerning the effect of small changes in the molecular structure on the incidence and temperature dependence of the smectic C phase. The occurrence and abundance of high thermal span of smectic C in the present DHBLC can be justified by the molecular structure which is supplemented by the following arguments,

1) Molecules having two terminal alky chains especially alkyl/alkoxy groups exhibit Smectic C phase predominantly.
2) Approximately symmetrical molecular structure of the mesogens usually favors smectic C phase.
3) The molecular structure of the constituent molecules, particularly the length of the chains of the terminal alkyl or alkoxy groups influences the occurrence of smectic C phase.

The variation of tilt angle θ (T) with temperature, reflecting the growth of order parameter in smectic C phase is measured by optical extinction method [58] in all the homologues

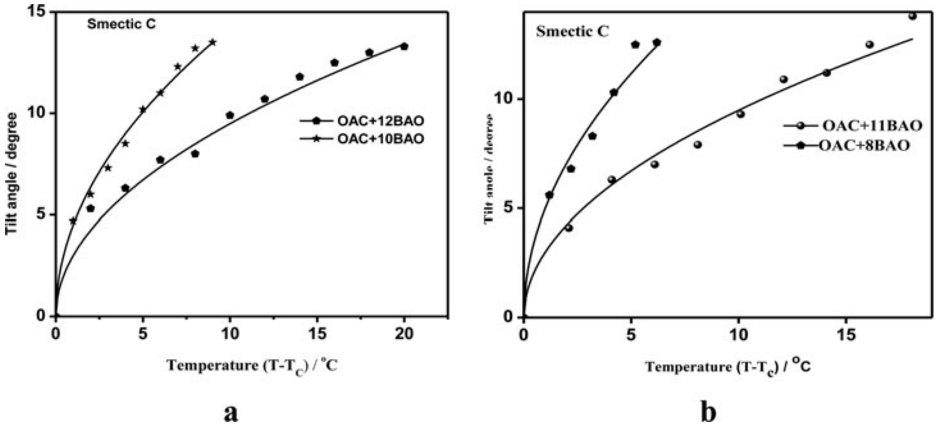


Figure 6a. Tilt angle measurement made in Smectic C phase of OAC+12BAO and OAC+10BAO complexes. **b.** Tilt angle measurement made in Smectic C phase of OAC+11BAO and OAC+8BAO complexes.

of OAC+nBAO series. The tilt angle is found to increase with decreasing temperature. It is observed from the Figures 6a and 6b that tilt angle attains a characteristic maximum value. The large magnitudes of the tilt angle in higher homologues are attributed to the enhanced orientational disorder introduced by the lengthy flexible part of the molecule. Hence, higher homologues with extended flexible part in DHBLC are argued to contribute positively to the inclined [59] soft covalent hydrogen bonding interaction for the realization of tilted phases of applicational interest.

The observed temperature variation of θ(T) appears to follow a power law relationship given by

$$\theta(\mathrm{T})\alpha(\mathrm{T_c} - \mathrm{T})^{\beta} \quad (1)$$

where, T_C represents the transition temperature,

β the critical exponent component value and

T is the temperature at which θ (T) is experimentally determined.

The data of θ (T) for the members of OAC+nBAO in Smectic C phase is fitted (Figs. 6a and 6b) to the equation 1 to study the growth of order parameter in smectic C phase. The critical exponent β value estimated by fitting the data of θ(T) to the above equation (1) is found to be 0.50 to agree with the Mean Field predicted value [50, 60] to infer the long-range interaction of transverse dipole moment for the stabilization of the tilted smectic C phase.

6. Conclusions

1) A novel series of DHBLC is designed, synthesized, and characterized by various techniques.
2) In all the eight complexes phases of nematic and smectic phase have been observed.
3) All the phases observed are confirmed by POM and DSC studies.
4) The order of transition has been analyzed by Cox's parameter N_C.
5) Optical tilt angle for all the complexes in the smectic C phase is measured and theoretical fit is performed.

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