A study of the thermodynamical interactions with solvents and surface characterisation of liquid crystalline 5-((S)-3,7-dimethyloctyloxy)-2-[[[4-(dodecyloxy)phenyl]imino]-methyl]phenol by inverse gas chromatography

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ABSTRACT

An inverse gas chromatography (IGC) study of thermodynamic interactions of a new chiral calamitic liquid crystalline 5-((S)-3,7-Dimethyloctyloxy)-2-[[[4-(dodecyloxy)phenyl]imino]methyl]phenol (**DODPIMP**) with some solvents was presented. The retention diagrams of the solvents on the **DODPIMP** were plotted by specific retention volumes, V_g^0 at temperatures between 373.2 and 393.2 K. The Flory-Huggins interaction parameter, χ_{12}^∞, the weight fraction activity coefficient, Ω_1^∞ and selectivity coefficients, α, of the structural isomers were determined for the **DODPIMP** liquid crystal.

To characterize the surface properties of, retention diagrams of several non-polar and polar solvents on the **DODPIMP** were plotted by net retention volumes, V_N in the temperature range from 303.2 to 318.2 K. The dispersive surface energy, the thermodynamic adsorption parameters and the acid–base constants of the compound in the crystalline phase were determined. The results indicated a basic character for the surface of **DODPIMP** at the studied conditions.

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1. Introduction

Liquid crystals (LC)'s are finding increasing application in advanced technologies such as LC displays, fast switching ferroelectric materials, sensors, high-performance polymers, transporting of electron, ion or molecule and drug-delivery systems [1–3]. However, it is needed their thermodynamic characteristics related to their interaction with various nonmesogenes for the further development of the multicomponent LC compositions in various technologies. It is not easy to obtain these data experimentally since LC generally has complex morphologies and a limited solubility in solvents [4–6]. Fortunately, inverse gas chromatography (IGC) yields valuable information about the thermodynamic characteristics of a LC. The interaction between a LC and a solvent (probe) is usually characterized by the value of Flory-Huggins interaction parameter [7,8]. On the other hand, LC materials have a great potential in use as isomer-selective stationary phases for gas chromatography columns. Certainly, IGC studies serve to reveal the selectivity of a LC for the structural isomers.

In this study, we reported the synthesis of a new chiral calamitic LC, 5-((S)-3,7-Dimethyloctyloxy)-2-[[[4-(dodecyloxy)phenyl]imino] methyl]phenol (**DODPIMP**) and the data on its thermodynamic interactions, selectivity coefficients, dispersive surface energy and acid–base properties determined by IGC.

2. Inverse gas chromatography

2.1. Thermodynamic characterization

The primary data measured by IGC are the retention times of the solvent (probe) and air. Then, specific retention volume, V_g^0 is determined from the following [9] equation;

$$V_g^0 = Q(t_R - t_A)J273.2/(T_r w) \tag{1}$$

where Q is the carrier gas flow rate measured at room temperature T_r; J is the pressure correction factor, w is the weight of liquid crystal in the column.

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The interaction between two components in a mixture can be evaluated by Flory-Huggins interaction parameters, χ_{12}^{∞}

$$\chi_{12}^{\infty} = \mathrm{Ln}\left(\frac{273.2 R v_2}{p_1^0 V_g^0 V_1^0}\right) - \left(1 - \frac{V_1^0}{M_2 v_2}\right) - \frac{p_1^0\left(B_{11} - V_1^0\right)}{RT} \tag{2}$$

where, V_1^0, B_{11} and p_1^0 are the molar volume, the second virial coefficient and the saturated vapor pressure of the solvent, respectively, at temperature T, v_2 is specific volume of the material in the column.

The weight fraction activity coefficient, Ω_1^{∞} given in the following should be a more reliable parameter compared to the χ_{12}^{∞} in terms of thermodynamic interactions since it is derived from the fundamental relations of physical chemistry and consequently does not include any uncertainty coming from the theoretical assumptions.

$$\Omega_1^{\infty} = \mathrm{Ln}\left(273.2 R / V_g^0 p_1^0 M_1\right) - p_1^0\left(B_{11} - V_1^0\right)/RT \tag{3}$$

where; M_1 is the molecular weight of the solvent.

2.2. The selectivity coefficient

The difference between the retention times of two solvents which are obtained at the same condition determines the selectivity of the stationary phase [10]. This selectivity is called as selectivity coefficient (or separation factor), α which is defined the ratio of $(t_R - t_A)$ values of two solvent peaks obtained under the same condition:

$$\alpha = \frac{(t_{R(2)} - t_A)}{(t_{R(1)} - t_A)} = \frac{V_{g,2}^0}{V_{g,1}^0} \tag{4}$$

The bigger this ratio, the better is the selectivity of the stationary phase for the solvent pair of the solvents.

2.3. Surface characterization [11–13]

2.3.1. Dispersive surface interactions

The surface energies and acidity/basicity of the solid materials in the column can be determined from the net retention volume of the solvents, V_N:

$$V_N = QJ(t_R - t_A)T_c/(T_r) \tag{5}$$

where T_c is the column temperature (K). If the IGC experiments are conducted at infinite dilution of the solvents, the molar free energy of adsorption, ΔG_A is related to V_N according to:

$$\Delta G_A = -RT\mathrm{Ln}(V_N) + K \tag{6}$$

where K is a constant for a given column.

The adsorption between a solid surface and solvent vapor is mainly governed by dispersive (nonpolar) and specific (polar, hydrogen bonding, etc.) interactions [14]. Thus, surface energy of the solid, γ_S is considered to be sum of dispersive, γ_S^D and specific, γ_S^S components:

$$\gamma_S = \gamma_S^D + \gamma_S^S \tag{7}$$

γ_S^D can be determined by retention data of n-alkanes on the stationary phase in the column since n-alkanes cannot apply any specific interaction. Schultz [15] determined the dispersive surface energy from the slope of the straight line between RTLnV_N and $a(\gamma_L^D)^{0.5}$ for each probe according to the following equation;

$$-\Delta G_A = RT\,\mathrm{Ln}\,(V_N) = 2N\,a\,\left(\gamma_S^D\right)^{1/2}\left(\gamma_L^D\right)^{1/2} + C \tag{8}$$

where a is surface area of the solvent molecule, N is Avogadro's number and C is constant.

γ_S^D can also be determined by the method proposed by Dorris and Gray [16] following the Eq. (9);

$$\gamma_S^D = \frac{\left(-\Delta G_{CH_2}\right)^2}{4(N)^2 a_{CH_2}^2 \gamma_{L[CH_2]}} \tag{9}$$

where,

$$\Delta G_{CH_2} = -RT\mathrm{Ln}\left(\frac{V_N\,(n+1)}{V_N\,(n)}\right) \tag{10}$$

ΔG_{CH_2} represents the Gibbs free energy of a single methylene group adsorption and determined from the slope of a linear line plotted by RTLnV$_N$ of n-alkanes against their carbon atom number, n; $a_{[CH_2]}$ is the cross-sectional area of an adsorbed methylene group (0.06 nm^2) and $\gamma_{L[CH_2]}$ is the surface energy of a solid material consisting of only methylene groups given as $\gamma_{L[CH_2]}$ (mJ/m^2) = 35.6 + 0.058(293.2-T) where T is the temperature in K.

2.3.2. Specific surface interactions

The specific component of the free energy of adsorption, $-\Delta G_A^S$ is related to the solid phase's ability to act as a donor or acceptor toward to electrons. The difference between the ordinate values of the polar solvent datum point and the n-alkane reference line in the plot of RTLnV$_N$ against $a(\gamma_L^D)^{0.5}$ gives the specific component of the surface free energy, $-\Delta G_A^S$ for each solvent at a given temperature. An equation may be written for this procedure,

$$-\Delta G_A^S = RT\mathrm{Ln}\left(\frac{V_{N,n}}{V_{N,ref}}\right) \tag{11}$$

where $V_{N,n}$ and $V_{N,ref}$ are the retention volumes of the polar solvent and the n-alkane which has the same abscissa value in the n-alkane reference line, respectively.

ΔG_A^S is related to the enthalpy, ΔH_A^S and entropy, ΔS_A^S of the specific adsorption:

$$\Delta G_A^S = \Delta H_A^S - T\Delta S_A^S \tag{12}$$

ΔH_A^S can be determined for each polar probe from the slope by plotting $\Delta G_A^S/T$ against $1/T$.

Then, the ΔH_A^S data are related to the acidic or the basic character through the equation:

$$-\Delta H_A^S = K_A.DN + K_D AN^* \tag{13}$$

where, DN and AN^* are Gutmann's donor and modified acceptor numbers, respectively, whereas K_A and K_D are indicators reflecting acidity and basicity of the solid surface in the column. The values of DN and AN* are present in the literature [17,18].

Consequently, K_A and K_D can be determined from the slope and intercept, respectively, of the straight line obtained by plotting $-\Delta H_A^S$/AN* versus DN/AN*. The ratio K_D/K_A provides an empirical basis for the classification of a surface with respect to acidity-basicity. If $K_D/K_A > 1$, the surface is considered to be basic, or vice versa.

3. Experimental

3.1. Materials and instrumentation

For synthesis, (S)-(−)-β-citronellol (Aldrich, ≥99.0%, $[\alpha]_D^{20}$-5.3°, hydrobromic acid (ABCR, 48% aqueous solution), sulfuric acid (Merck, 95–98%), tetrabutylammonium hydrogensulfate (Sigma-Aldrich, 97%), 4-(dodecyloxy)aniline (Sigma-Aldrich), potassium hydrogen carbonate (Merck) and p-toluenesulfonic acid monohydrate (Merck) were purchased commercially. Solvents were purchased or distilled. MeOH

(Merck), DMF (Merck) and Toluene (Merck) were purchased commercially and used without further purification. Analytical thin-layer chromatography (TLC) was carried out on aluminum plates coated with silica gel 60F254 (Merck).

n-Hexane (Hx), n-heptane (Hp), n-octane (O), n-nonane (N) and n-decane (D), n-undecane (UD), n-dodecane (DD), n-tridecane (TD), ethyl acetate (EAc), n-butyl acetate (nBAc), isobutyl acetate (IBAc), toluene (T), ethylbenzene (EB), isopropylbenzene (IPB), n-propylbenzene (nPB), chlorobenzene (ClB), diethylether (DEE) tetrahydrofurane (THF), dichloromethane (DCM), chloroform (TCM), acetone (ACe) were purchased from Merck AG Inc. for inverse gas chromatography measurements.

3.2. Synthesis and characterization of DODPIMP

The synthesis of the new salicylaldimine based chiral calamitic liquid crystal DODPIMP is shown in Scheme 1. In the first step of the synthesis of DODPIMP, (S)-(−)-β-Citronellol was reduced to (S)-3,7-dimethyl-1-octanol under catalytic hydrogenation conditions (H$_2$, 10% Pd/C in MeOH). As reported previously [19], (S)-3,7-Dimethyloctyl bromide was prepared from (S)-3,7-dimethyl-1-octanol by reaction with 48% aq. HBr/conc. H$_2$SO$_4$ using tetrabutylammonium hydrogensulfate (TBAHS) as catalyst. Etherification of the obtained (S)-3,7-Dimethyloctyl bromide with 2,4-dihydroxybenzaldehyde using KHCO$_3$ as base in DMF solvent, followed by the condensation reaction with 4-(dodecyloxy)aniline in toluene using p-toluene sulfonic acid monohydrate as catalyst yield the final compound DODPIMP.

The characterization of the DODPIMP is based on ^{1}H NMR and APT-^{13}C NMR (Bruker Avance III 500 spectrometer in CDCl$_3$ solutions, with tetramethylsilane as internal standard). The proposed structure is in full agreement with the spectroscopic data.

3.3. The procedure for 5-((S)-3,7-Dimethyloctyloxy)-2-[[[4-(dodecyloxy)phenyl]imino]methyl]phenol (DODPIMP) (C$_{35}$H$_{55}$NO$_3$; 537.82 g/mol)

The compound DODPIMP was prepared as reported previously [20–22]. Into a 100 mL round-bottomed flask which was connected to the Dean-Stark apparatus, 4-((S)-3,7-dimethyloctyloxy)-2-hydroxybenzaldehyde (0.69 g, 2.5 mmol) and 4-(dodecyloxy)aniline (0.83 g, 3 mmol) were dissolved in 25 mL toluene. To this solution, p-toluenesulfonic acid (40 mg) was added and the reaction mixture was refluxed for 4 h at 160 °C under argon atmosphere. The end of reaction was monitored by TLC (hexane:ethyl acetate/10:1). After cooling, the reaction mixture was extracted into diethyl ether (3×) and the combined organic phases were washed with saturated solution of NaHCO$_3$ and brine, respectively. The organic solution was dried over Na$_2$SO$_4$ and then removed in vacuo. The crude product was purified by recrystallization from acetone/methanol. **Yield:** 0.94 g (70%); yellow crystals. **^{1}H NMR** (500 MHz, CDCl$_3$) δ (ppm) = 13.88 (s; OH), 8.43 (s; HC=N), 7.26–7.23 (m, 3 arom. H), 6.85 (d, J ≈ 8.9 Hz; 2 arom. H), 6.42–6.38
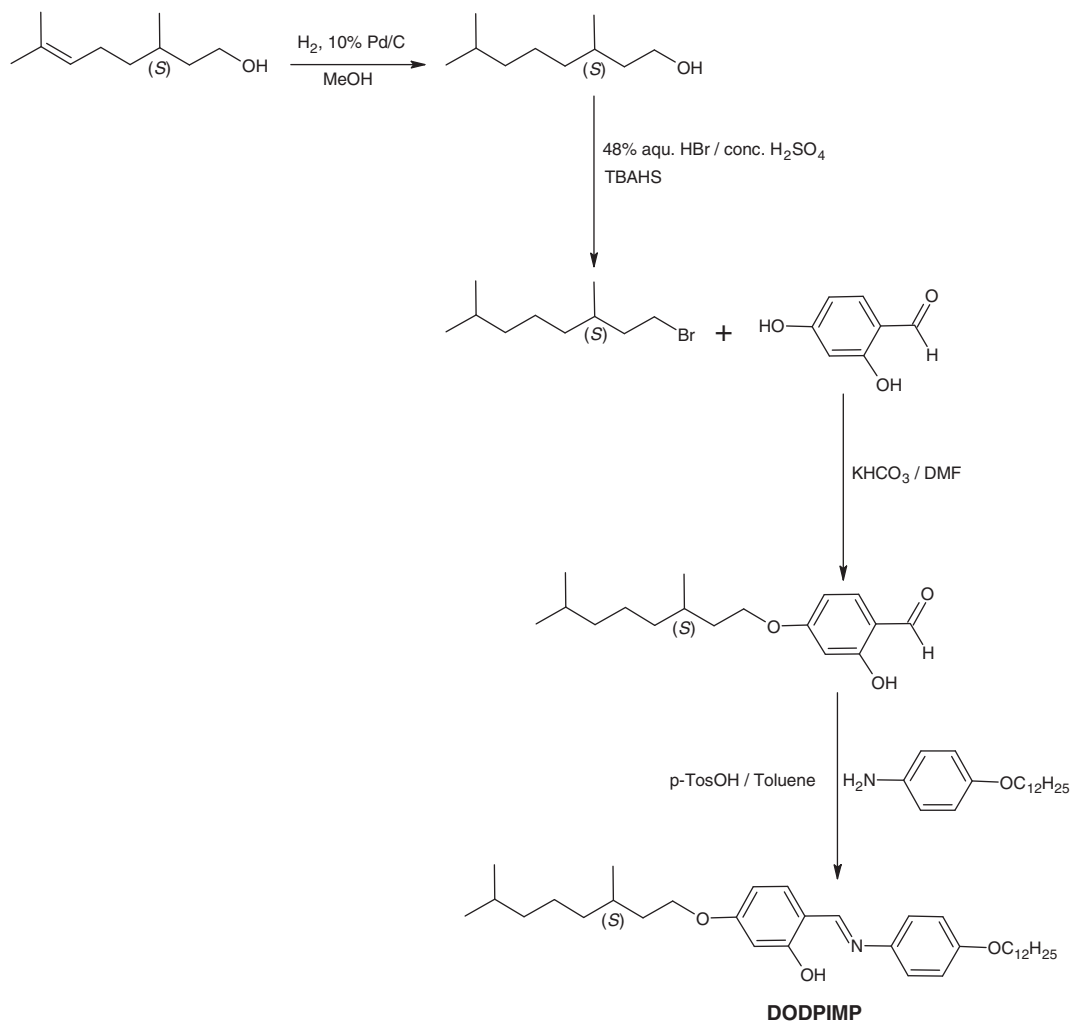
Scheme 1. The synthesis of the new salicylaldimine compound DODPIMP.

(m; 2 arom. H), 3.99–3.93 (m, 2H, OCH$_2$), 3.89 (t, $J \approx$ 6.6 Hz; 2H, OCH$_2$), 1.80–1.69 (m; 3H, CH$_2$, CH), 1.63–1.36, 1.31–1.06 (2 m; 27H, 1 CH, 13 CH$_2$), 0.87 (d; $J \approx$ 6.5 Hz; 3H, CH$_3$), 0.82–0.79 (m, 9H, 3 CH$_3$). **APT-^{13}C NMR** (125 MHz, CDCl$_3$) δ (ppm) = 163.76, 163.21, 157.99, 141.20, 113.10 (arom. C) 159.46 (H$\underline{C}$ = N), 133.11, 121.97, 115.16, 107.41, 101.58 (arom. CH), 68.35, 66.57 (OCH$_2$), 39.24, 37.27, 36.01, 31.94, 29.68, 29.66, 29.62, 29.60, 29.42, 29.37, 29.29, 26.06, 24.66, 22.71 (CH$_2$), 29.85, 27.98 (CH), 22.73, 22.62, 19.65, 14.15 (CH$_3$).

The **DODPIMP** was coated on the support material (Chromosorb W (AW-DMCS-treated) with 80–100 mesh size, Merck AG Inc.) as a stationary phase by slow evaporation of TCM as stirring the support in LC solution. The amount of coated **DODPIMP** on the support was determined as 9.42% by calcination. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc. A Hewlett-Packard 6890N model gas chromatograph with a thermal conductivity detector was used to measure the retention times of the solvents and air. The column was made of stainless steel tubing with 3.2 mm outside diameter and 1 m length. A trace amount of solvent was injected into the chromatograph. The column was conditioned at 373 K for 24 h under a helium atmosphere. Transition temperatures were measured and optical investigations were carried out using a Mettler FP-82 HT hot stage and a control unit in conjunction with a Leica DM2700P polarizing microscope and Leica DMC2900 Digital Camera. The associated enthalpies were obtained from DSC-thermograms which were recorded on a Perkin-Elmer DSC-6, heating and cooling rate: 10 °C min^{-1}.

4. Result and discussion

4.1. Liquid crystalline properties

The transition temperatures, corresponding enthalpy values and mesophase type observed for **DODPIMP** by polarizing microscope (PM) and differential scanning calorimetry (DSC) are given in Table 1.

The new chiral salicylaldimine compound **DODPIMP** exhibits enantiotropic chiral smectic C (SmC*) mesophase with finger print and broken fan-shaped texture. The introduction of a chiral branched unit at one of the terminals of the rod-like salicylaldimine molecule leads to a significant chirality effect on the formation of the tilted smectic phase. A comparison of the mesomorphic properties of **DODPIMP** with those of related non-branched compound C/8 [23] with the same alkyl chain length shows that transition temperatures clearly decrease by chain branching. C/8 carrying a *n*-octyloxy chain instead of (S)-3,7-dimethyloctyloxy chain only exhibits the tilted smectic phase (SmC) as a result of the absence of a chiral moiety (see Table 1).

The texture of SmC* mesophase on cooling and DSC-traces (second heating and cooling, 10 °C min^{-1}) of **DODPIMP** are shown in Figs. 1 and 2, respectively.

4.2. Thermodynamic interactions of Liquid **DODPIMP**

The V_g^0 values of the solvents on **DODPIMP** were determined by using Eq. (1). Figs. 3 and 4 show the variation of the specific retention volumes of n-alkanes, nBAc, IBAc, EAc, nPB, IPB, EB, T and ClB with temperature between 373.2 and 393.2 K, respectively.

Table 1
The phase transition temperatures of the **DODPIMP**.

Compound	T/°C [ΔH kJ mol^{-1}][a]
DODPIMP	Cr 53.2 [*30.9*] SmC* 93.0 [*7.0*] Iso
[23]**C/8**	Cr 76.5 [*49.0*] SmC 125.6 [*7.9*] Iso

^{a} Enthalpy values in italics in brackets; Abbreviations: Cr = crystalline, Sm C* = chiral smectic C phase, Iso = isotropic liquid phase.
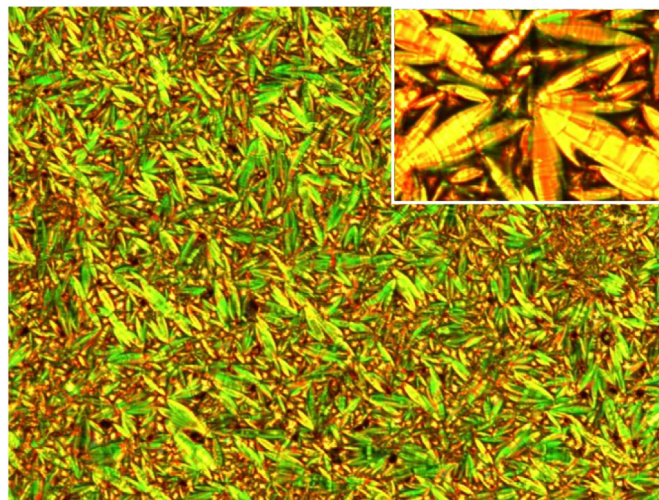

Fig. 1. The broken fan-shaped texture of the SmC* phase obtained between crossed polarizers at 68 °C on cooling; the inset shows the finger-print texture of the SmC* phase at 61 °C.

When transitions such as melting, glass and nematic–isotropic transitions occur, generating an aggregation change for the stationary phase, a break in the linear variations appears [24]. Linearity is observed when the stationary phase remains at the same thermodynamic equilibrium state. Thermodynamic interaction of **DODPIMP** in the liquid state is meaningful at the linear thermodynamic equilibrium region. Since the linearity occurred at the temperatures between 373.2 and 398.2 K, the Flory-Huggins interaction parameters, χ_{12}^{∞} of **DODPIMP** were determined at this temperature range and given in Table 2.

The values $\chi_{12}^{\infty} < 0.5$ represent favorable interaction of LC with the solvent whereas the values $\chi_{12}^{\infty} > 0.5$ indicate favorable interactions at infinitely lower solvent concentration. The values of χ_{12}^{∞} in Table 2 suggest that n-alkanes and aliphatic acetates are poor; however benzene derivatives are good solvents for **DODPIMP**. It can be said from data in Table 1 that toluene is the best solvent. All of the parameters decrease with temperature indicating endothermic solubility.

The parameter Ω_1^{∞} indicating the thermodynamic interaction of **DODPIMP** with solvents were also determined from the same raw retention data and given in Table 3.
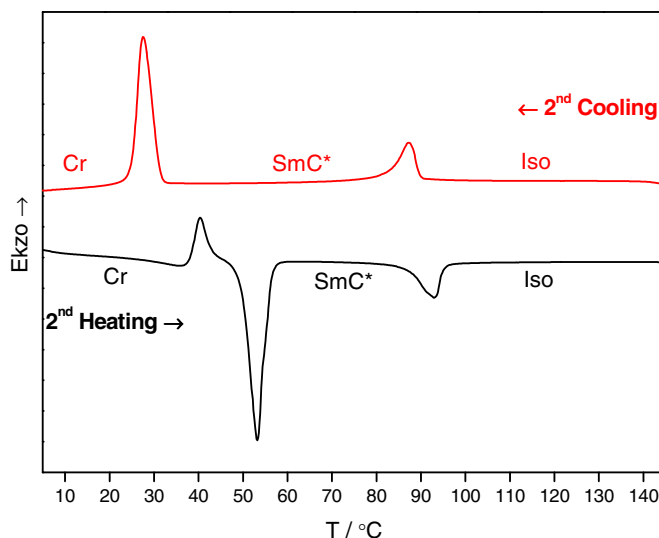

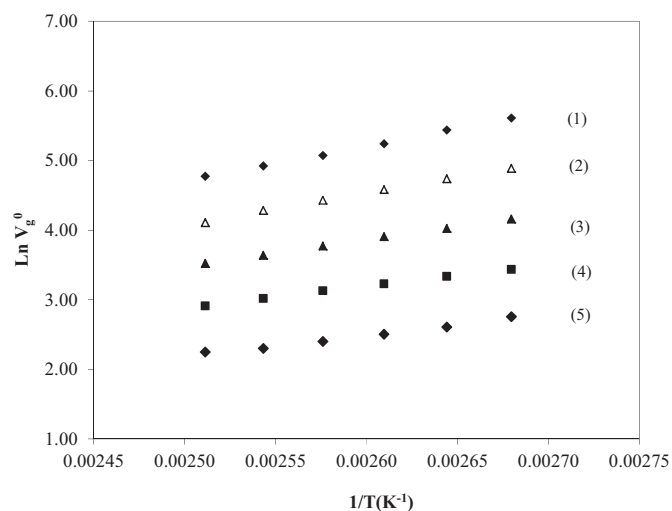**Fig. 2.** DSC-traces (second heating and cooling, 10 °C min^{-1}) of **DODPIMP**.

Fig. 3. The specific retention volume diagrams, V_g^0, of D (1), N (2), O (3), Hx (4) and Hp (5) on **DODPIMP**.
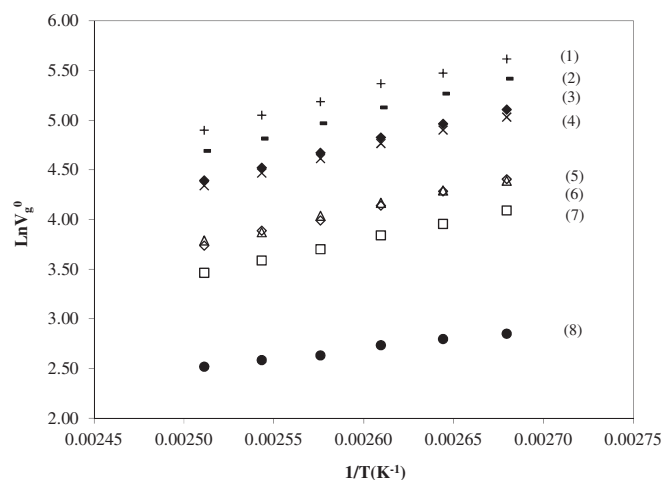

Fig. 4. The specific retention volume diagrams, V_g^0, of nPB (1), IPB (2), ClB (3), EB (4), nBAc (5), T (6), IBAc (7) and EAc (8) on **DODPIMP**.

According to Guillet, the solvent is good if $\Omega_1^\infty < 5$ and poor if $\Omega_1^\infty > 10$. The values between 5 and 10 indicate moderately good solubility. The values in Table 3 suggest n-alkanes and aliphatic acetates are moderately good; while benzene derivatives are good solvents for **DODPIMP**. The values of Ω_1^∞ suggest the best solvent is ClB for **DODPIMP** unlike to the suggestion of χ_{12}^∞. It might be expected that ClB is better solvent than T since electron attractive chlorine atoms can make favorable interactions with unbounded electrons of **DODPIMP**. This suggests that Ω_1^∞ values are more reliable than χ_{12}^∞ values to reveal the thermodynamical interactions of a LC with solvents. It should be also noted the definition of Ω_1^∞ based on the fundamental physical chemistry laws.

Table 3
The weight fraction activity coefficients, Ω_1^∞, of **DODPIMP**.

T(K)	Hx	Hp	O	N	D	nBAc	IBAc	EAc	nPB	IPB	EB	T	ClB
373.2	7.5	7.3	6.8	6.5	6.2	5.5	5.7	7.9	4.2	3.8	4.2	3.6	3.2
378.2	7.7	7.0	6.7	6.3	6.0	5.2	5.6	7.3	4.0	3.8	4.0	3.4	3.1
383.2	7.7	6.9	6.5	6.2	6.1	5.2	5.4	6.9	3.8	3.7	3.9	3.4	3.1
388.2	7.6	6.6	6.4	6.1	6.0	5.1	5.4	6.8	3.8	3.7	3.9	3.4	3.1
393.2	7.6	6.6	6.4	6.1	5.9	4.9	5.2	6.3	3.8	3.7	3.9	3.5	3.1
398.2	7.2	6.5	6.2	6.2	5.7	5.0	5.1	6.0	3.7	3.6	3.9	3.4	3.1

Table 4
The selectivity coefficients of the **DODPIMP** for the structural isomer pairs: nBAc/IBAc and nPB/IPB.

T(K)	$\alpha = (t_{R(1)} - t_A)/(t_{R(2)} - t_A)$	
	$t_{R(nBAc)}/t_{R(IBAc)}$	$t_{R(nPB)}/t_{R(IPB)}$
373.2	1.3	1.2
378.2	1.3	1.2
383.2	1.3	1.2
388.2	1.2	1.2
393.2	1.2	1.2
398.2	1.2	1.2

4.3. The selectivity coefficients of liquid *DODPIMP* to the structural isomers

The selectivity coefficients, α of the pairs of nBAc/IBAc and nPB/IPB were obtained using their retention times in order to reveal the usage of **DODPIMP** as the isomer selective stationary phase in a gas–liquid chromatography column. The values given in the Table 4 suggest a good separation can be reached for the pairs of nBAc/IBAc and nPB/IPB if longer columns are used although the separation coefficients are not so high.
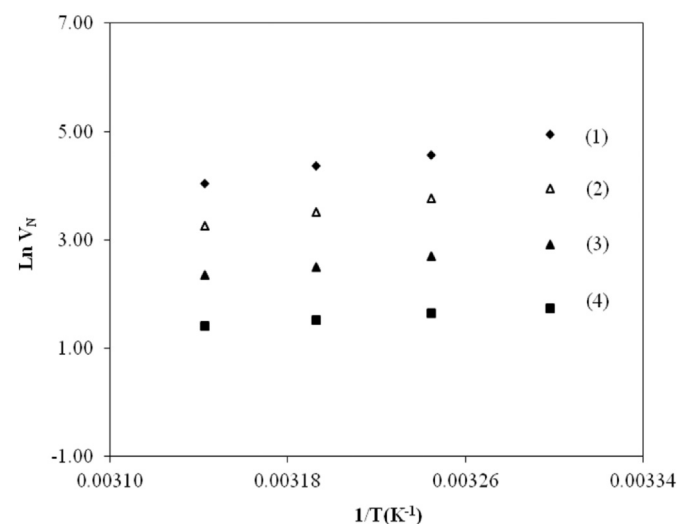

Fig. 5. The net retention volumes, V_N, of nonpolar solvents: D (1), N (2), O (3) and Hp (4).

Table 2
Flory-Huggins interaction parameters, χ_{12}^∞, of **DODPIMP** with solvents.

T(K)	Hx	Hp	O	N	D	nBAc	IBAc	EAc	nPB	IPB	EB	T	ClB
373.2	0.61	0.80	0.80	0.80	0.81	0.75	0.73	1.07	0.47	0.40	0.45	0.28	0.39
378.2	0.65	0.76	0.78	0.78	0.79	0.71	0.71	0.99	0.44	0.38	0.42	0.23	0.37
383.2	0.64	0.73	0.75	0.76	0.80	0.69	0.67	0.92	0.37	0.36	0.40	0.22	0.36
388.2	0.64	0.70	0.74	0.75	0.79	0.69	0.66	0.90	0.39	0.36	0.40	0.21	0.36
393.2	0.63	0.69	0.73	0.74	0.76	0.64	0.63	0.83	0.36	0.36	0.40	0.25	0.37
398.2	0.59	0.67	0.71	0.76	0.74	0.65	0.61	0.77	0.36	0.33	0.38	0.20	0.36

Table 5
The dispersive surface energy, γ_S^D of **DODPIMP** determined by the methods of Schultz and Dorris-Gray.

T (K)	γ_S^D (mJ/m²)	
	Schultz	Dorris-Gray
303.2	39.3	40.8
308.2	34.6	36.2
313.2	33.7	35.5
318.2	29.5	31.3

Fig. 8. The plot of $-\Delta H_A^S/AN^*$ versus DN/AN*.

The dispersive component of the surface energy of **DODPIMP** was determined using both Schultz and Dorris-Gray methods and given in Table 5.

Dispersive surface energy of **DODPIMP** was found approximately 40 mJ/m² around room temperature and decreased with temperature. The dispersive surface energies of some LCs were reported around 35 mJ/m² in the literature [25,26]. Our value is comparable with literature data. As it can be observed from Table 5, Dorris-Gray method gives a little bit higher values than other one although they are very close to each other.

4.5. Acidity-basicity of crystalline **DODPIMP** surface

The V_N diagrams of polar solvents were given in the Fig. 6. It can be seen the logarithm of V_N change linearly with the reciprocal of the absolute temperature. This suggests any thermal transition does not occur at this temperature range.

The specific component of adsorption free energy, $-\Delta G_A^S$, was calculated using the difference between the $RT\ln V_N$ values of the polar solvent and hypothetical n-alkane which was derived by the linear fit of the nonpolar reference line at a given temperature, according to the Eq. (11) at the corresponding temperature. The plot at 303.2 K was given as an example in Fig. 7.

The values of K_A and K_D were calculated from the slope and intercept, respectively, of the plot of $-\Delta H_A^S/AN^*$ versus DN/AN* as shown in Fig. 8.

Fig. 6. The net retention volumes, V_N of polar solvents: THF (1), TCM (2), DCM (3), ACe (4) and DEE (5).

4.4. Dispersive surface energy of crystalline **DODPIMP**

The adsorption properties of **DODPIMP** surface were investigated by IGC technique between 303.2 K and 318.2 K, which it is crystalline state. Dispersive component of the surface energy of **DODPIMP** can be obtained using V_N data of only nonpolar probes such as n-alkanes since they cannot make specific interactions with the stationary phase. The V_N values of n-alkanes on the **DODPIMP** were obtained using Eq. (5) and given in Fig. 5 as the plots of $\ln V_N$ versus 1/T.
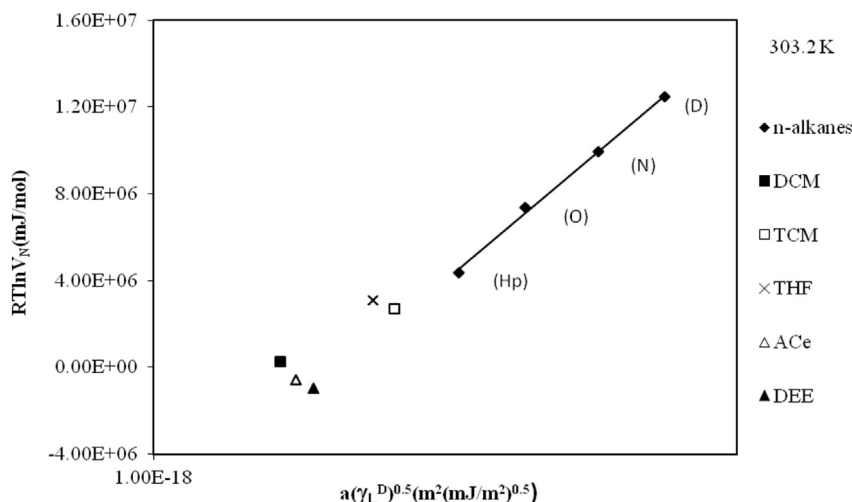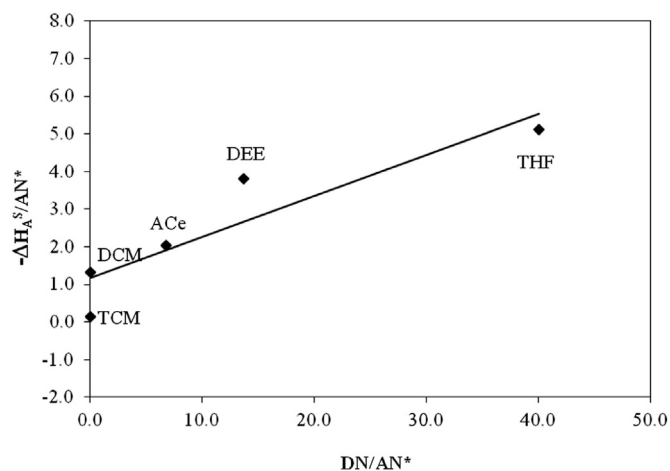

Fig. 7. A plot of $RT\ln V_N$ vs. $a(\gamma_L^D)^{0.5}$ for n-alkanes and the polar solvents adsorbed on **DODPIMP** at 303.2 K.

The values of K_A and K_D are found to be 0.11 and 1.17, respectively. The ratio of K_D/K_A which is 10.6, suggests the surface of **DODPIMP** has basic character in nature.

5. Conclusions

We have synthesized and characterized a new chiral calamitic liquid crystalline compound **DODPIMP** and investigated its mesomorphic. Phase transition temperatures and heats of **DODPIMP** were determined by PM and DSC. For this compound, the transition of crystal-SmC* phase at 53.2 °C occurred while the SmC*-isotropic phase transition occurred at 93.0 °C.

The thermodynamic interactions of **DODPIMP** with various solvents were characterized by IGC technique. The results are used to evaluate its solubility properties. The values of χ_{12}^{∞} suggest aromatic solvents are good while n-alkanes and aliphatic acetates are poor solvents. However the values of Ω_1^{∞} suggest n-alkanes and acetates are moderately good solvents while aromatic solvents are good for **DODPIMP**. This study suggests Ω_1^{∞} is more reliable than χ_{12}^{∞} in determination of the quality of a solvent for a LC, at least in this study.

The selectivity coefficients of **DODPIMP** to the structural isomers studied in this study were found around 1.2 at temperatures between 373.2 and 398.2 K, which the LC is in the liquid state. The dispersive surface energy, γ_S^D of **DODPIMP** was found as 40 mJ m^{-2} as a mean of the two methods at 30 °C by means of V_N data of n-alkanes. The surface of **DODPIMP** was estimated as a basic character according to the value of $K_D/K_A = 10.6$ by means of V_N data of TCM, DCM, ACe, DEE and THF.

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