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Synthesis and characterization of (S)-5-(2-Methylbutoxy)-2-[[[4-Hexylphenyl]Imino]Methyl]Phenol liquid crystal by inverse gas chromatography

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Liquid crystalline compound (S)-5-(2-methylbutoxy)-2-[[[4-hexylphenyl]imino]methyl]-phenol (MBHPIMP) has been prepared and characterized. Phase transition temperatures of MBHPIMP were determined by polarizing microscopy, differential scanning calorimetry and inverse gas chromatography. Trace amount of solvents such as methyl acetate, ethyl acetate, pentane, hexane, cyclopentane, cyclohexane were passed through the gas chromatography column loaded with MBHPIMP coated on Chromosorb W. MBHPIMP exhibits liquid crystal properties with calamitic molecular shape which has a chiral moiety and alkyl chain at the terminus. The retention diagrams of the solvents on the liquid crystal were plotted by means of specific retention volumes, V_g^0 at the temperatures in °C between 40 and 95 by inverse gas chromatography. The weight fraction activity coefficient, Ω_1^∞, Flory-Huggins liquid crystal-solvent interaction parameter, χ_{12}^∞, equation of state liquid crystal-solvent interaction parameter, χ_{12}^* and effective exchange energy parameter, X_{eff} related to the MBHPIMP-solvent systems were obtained. In addition, the partial molar heats of sorption, $\Delta\overline{H}_{1,\text{sorp}}$ and mixing, $\Delta\overline{H}_1^\infty$ were determined.

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1. Introduction

After the discovery of their liquid crystalline properties, especially the salicylaldimine derivatives have promoted the preparation of new anisotropic materials due to the mesogenic nature of the compounds [1]. These compounds are stabilized by intermolecular hydrogen bonding. Depending on the carbon number of the terminal alkoxyl and/or alkyl groups in the salicylaldimine core, these materials display various mesomorphic properties [1,2]. Therefore, these mesogenic compounds are very interesting subjects for scientific investigations and very perspective materials for technical and technological applications.

Application of thermotropic liquid crystal materials as stationary phases in analytical gas chromatography has been reported some years ago [3]. For these applications, knowledge of the interactions between the components is important in designing and formulating new systems.

Here, we present the preparation, characterization and mesomorphic properties of a salicylaldimine compound (S)-5-(2-methylbutoxy)-2-[[[4-hexylphenyl]imino] methyl]phenol (MBHPIMP) and the retention diagrams of some solvents on this liquid crystal compound were obtained by inverse gas chromatography (IGC). Although inverse gas chromatography method (IGC) has been widely used to investigate the interactions and phase transition temperatures of polymeric materials with various solvents [4,5], it is a new method in determination of phase transitions and interactions of a liquid crystal with solvents used as probes [6]. Therefore, the method needs lots of studies to confirm its reliability.

In this study, firstly the retention diagrams of the solvents on the MBHPIMP were determined at the temperatures in °C between 40 and 95 by inverse gas chromatography. Sorption properties of a liquid crystal in liquid state can be studied at thermodynamical equilibrium region. Thermodynamic interactions of MBHPIMP were determined at the temperatures in °C between 65 and 95 because it was seen from the retention diagram that thermodynamical equilibrium occurred at this temperature range. Then, the molar enthalpies partial sorption $\Delta\overline{H}_{1,\text{sorp}}$, partial mixing $\Delta\overline{H}_1^\infty$ and vaporization, ΔH_v were determined.

2. Experimental

2.1. Materials and instrumentation

The characterization of the MBHPIMP compound presented here are based on various spectroscopic data, e.g. ^{1}H-, ^{13}C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions) with tetramethylsilane as internal standard, UV-VIS (Agilent 8453, $CHCl_3$ solutions), FT-IR (Perkin Elmer, $CHCl_3$ solutions), MS (AMD 402 (electron impact, 70 eV)). Microanalyses were performed using a Leco CHNS-932 elemental analyzer.

The mesophases were examined by polarizing microscopy and by DSC. Microscopy was performed on a Leitz Laborlux 12 Pol polarizing microscope, equipped with a Linkam THMS 600 hot stage and a Linkam TMS93 temperature controller. DSC-termograms were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10 K min^{-1}.

Methyl acetate (MA), ethyl acetate (EA), pentane (P), hexane (Hx), cyclopentane (cP), cyclohexane (cHx) and support material being Chromosorb-W (AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG. Inc. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc.

A Hewlett-Packard 6890 N gas chromatography with a thermal conductivity detector was used to measure the retention time of the solvents. The column was stainless steel tubing with 3.2 mm o.d. and 1m in length.

2.2. Synthesis of the MBHPIMP

(S)-4-(2-methylbutoxy)-2-hydroxybenzaldehyde [7] (2.5 mmol), 3 mmol of 4-hexylaniline and *p*-toluensulfonic acid (40 mg) were dissolved in 25 ml toluene. A Dean-Stark trap was adapted to the flask and the solution was boiled for 5 h under reflux. After cooling, a yellow precipitate was obtained. The precipitate was extracted with diethylether (3 x 100 ml). The combined organic layers were washed with $NaHCO_3$ and NaCl and dried with anhydrous Na_2SO_4 before the diethyl ether was removed under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with petroleum ether (b.p. 30-70 °C) / ethyl acetate (20:1) and by crystallization from acetone/methanol.

(S)-5-(2-methylbutoxy)-2-[[[4-hexylphenyl] imino]methyl]phenol (MBHPIMP):

Yield: 0.81 g (88 %), yellow crystals. — **^{1}H NMR:** δ (ppm) = 13.88 (s; OH), 8.50 (s; HC=N), 7.24-7.14 (m; 5 arom. H), 6.52–6.46 (m; 2 aromatic H), 3.85, 3.76 (2 dd, J ≈ 9.1 Hz and J ≈ 6.5 Hz each; OCH_2 of the chiral alkyl chain), 2.62 (t, J ≈ 7.7 Hz; α-CH_2), 1.92-1.84 (m; chiral CH), 1.66-1.52 (m; CH_2), 1.39-1.22 (m; 5 CH_2), 1.02 (d, J ≈ 6.8 Hz; CH_3), 0.96, 0.90 (2 t, J ≈ 7.5 Hz and J ≈ 7.0 Hz, respectively; 2 CH_3). — **^{13}C NMR:** δ (ppm) = 163.93, 163.52, 145.88, 141.22, 112.98 (5 s; 5 arom. C), 160.46 (d, H$\underline{C}$=N), 133.19, 129.19, 120.69, 107.39, 101.62 (5 d; 1, 2, 2, 1 and 1 arom. CH, respectively), 72.98 (t; OCH_2), 35.51 (t; α-CH_2), 34.60 (d; CH), 31.73, 31.47, 28.97, 26.14, 22.63 (5t; 6 CH_2), 16.49, 14.10, 11.29 (3q; 3 CH_3). — **MS:** m/z (%) = 367 (74) [M$^+$], 297 (100) [M$^+$ - C_5H_{11}], 226 (90) [M$^+$ - C_5H_{11}- C_5H_{11}] — **UV-VIS:** λ (nm) = 341.0. — **IR**: γ = 1625 cm^{-1} (C=N). — **$C_{24}H_{33}NO_2$** (367.5): calcd. C 78.43, H 9.05, N 3.81; found C 78.68, H 9.05, N 4.08.

2.3. Theoretical Background on IGC

The specific retention volume, V_g^0 is determined experimentally from inverse gas chromatography measurements as follows [8-11]

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

where Q is carrier gas flow rate measured at the room temperature T_r; t_R and t_A are retention times of the solvent and air, respectively; J is pressure correction factor , w is weight of liquid crystal in the column.

According to the theories of Flory-Huggins and equation-of-state interaction parameters, χ_{12}^{∞} and χ_{12}^{*} are defined in the Eq.(2) and Eq.(3), respectively:

$$\chi_{12}^{\infty} = \ln\left(\frac{273.2\,Rv_2}{p_1^0 V_g^0 V_1^0}\right) - \left(1 - \frac{V_1^0}{M_2 v_2}\right) - \frac{p_1^0(B_{11} - V_1^0)}{RT} \tag{2}$$

where R is the universal gas constant; p_1^0, B_{11} and V_1^0 are saturated vapor pressure, gaseous state second virial coefficient and molar volume of the solvent at temperature T, v_2 is specific volume of the liquid crystal, M_2 is molecular weight of the liquid crystal, respectively.

$$\chi_{12}^{*} = \ln\left(\frac{273.2\,Rv_2^*}{p_1^0 V_g^0 V_1^*}\right) - \left(1 - \frac{V_1^*}{M_2 v_2^*}\right) - \frac{p_1^0(B_{11} - V_1^0)}{RT} \tag{3}$$

where v_2^* is specific hard-core volume of the liquid crystal and V_1^* is molar hard-core volume of the solvent.

The effective exchange energy parameter, X_{eff} in the equation of state theory is defined as follows,

$$\begin{aligned} RT\chi_{12}^{*} = p_1^* V_1^* \{ & 3T_{1r} \ln[(v_{1r}^{1/3} -1)/(v_{2r}^{1/3} -1)] \\ & + v_{1r}^{-1} - v_{2r}^{-1} + X_{eff}/p_1^* v_{2r} \} \end{aligned} \tag{4}$$

where p_1^* is characteristic pressure, v_{1r} and v_{2r} are reduced volume of the solvent and liquid crystal, respectively. T_{1r} is reduced temperature of the solvent. Reduced quantities in above equation are defined as:

$$v_r = \frac{V}{V^*}, \quad T_r = \frac{T}{T^*}, \quad p_r = \frac{p}{p*} \tag{5}$$

where V is the actual molar volume of the liquid at actual T, temperature in K and p, pressure. The characteristic molar volume, V^*, characteristic pressure, p^*, of a pure component can be calculated directly from experimental values of molar volume, V, thermal expansion coefficient, α and thermal pressure coefficient, γ, of the pure component, by means of the following equations

$$v_r = \left[\frac{(\alpha T/3)}{1+\alpha T}\right] + 1 \tag{6}$$

$$T_r = \frac{(v_r^{1/3} - 1)}{v^{4/3}} \tag{7}$$

$$\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_{p=0} \tag{8}$$

$$p^* = \gamma T v_r^2 \tag{9}$$

$$\gamma = \left(\frac{\partial p}{\partial T}\right)_V \tag{10}$$

The partial molar heat of sorption, $\Delta\overline{H}_{1,sorp}$, of the solvent sorbed by the liquid crystal is given as [12-16]

$$\Delta\overline{H}_{1,sorp} = -R[\partial(\mathrm{Ln}V_g^0)/\partial(1/T)] \tag{11}$$

where T is the column temperature (K) and the partial molar heat of mixing, $\Delta\overline{H}_1^\infty$ at infinite dilution of the solvent is given as

$$\Delta\overline{H}_1^\infty = R[\partial(\mathrm{Ln}\Omega_1^\infty)/\partial(1/T)] \tag{12}$$

where Ω_1^∞ is the weight fraction activity coefficient of solvents at infinite dilution, defined by the following equation,

$$\ln\Omega_1^\infty = \ln(273.2\,R / V_g^0 p_1^0 M_1) - p_1^0(B_{11} - V_1^0)/RT \tag{13}$$

where M_1 is molecular weight of the solvent.

Molar heat of vaporization, ΔH_v, of the solvent is related to $\Delta\overline{H}_{1,sorp}$ and $\Delta\overline{H}_1^\infty$ as follows:

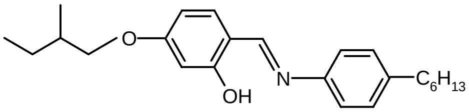
$$\Delta H_v = \Delta\overline{H}_1^\infty - \Delta\overline{H}_{1,sorp} \tag{14}$$

3. Results and discussion

The synthesis of MBHPIMP was carried out under a nitrogen atmosphere and in a three-step process [17]. The chiral moiety side of the ligand was constructed by the reacting (S)-2-methylbutanol with p-toluensulfonyl chloride to give (S)-2-methylbutyl tosylate [7]. The reaction of (S)-2-methylbutyltosylate with 2,4-dihydroxybenzaldehyde in DMF gave (S)-4-(2-methylbutoxy)-2-hydroxybenzaldehyde [7]. The condensation of 4-hexylaniline and (S)-4-(2-methylbutoxy)-2-hydroxybenzaldehyde in toluene with p-toluensulfonic acid as catalyst gave the target Schiff base MBHPIMP (81 %) [17] The MBHPIMP was purified by column chromatography and crystallization from acetone/methanol, as yellow crystals.

The MBHPIMP was characterized by various spectroscopic methods (^{1}H-, ^{13}C-NMR, UV-VIS, IR and mass) and elemental analysis. The spectroscopic data of the material is consistent with their proposed structures (see Experimental Section).

The thermal properties of the MBHPIMP which were investigated by polarizing microscopy and DSC are given in Fig. 1. The investigation suggests that MBHPIMP exhibits thermotropic mesomorphic behavior and chiral smectic mesophase. The texture of the mesophases has been detected by polarizing microscopy. For compound MBHPIMP, fingerprint texture is observed as seen in Fig. 2.



Compound	*T/°C (ΔH/kJ mol^{-1})*
MBHPIMP	*Cr* 43.9 (21.0) *SmC** 50.4 (0.5) *Iso*

^{a}Perkin-Elmer DSC-7; heating rates 10 K min^{-1} for the melting and clearing process; the enthalpies are in parentheses.

Fig. 1. Phase transition temperatures^a T (°C) and transition enthalpies^a ΔH (kJ mol^{-1}) of compound MBHPIMP. Cr: crystalline, SmC: chiral smectic and Iso: isotropic phase.*

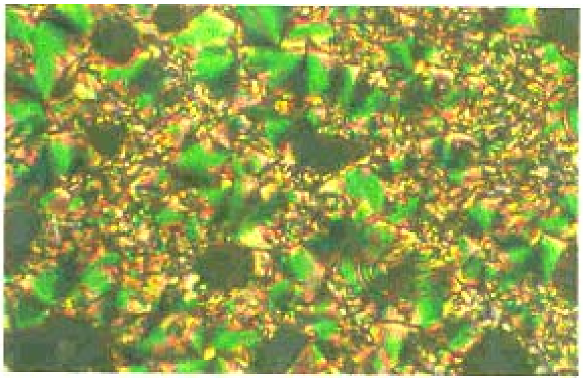


Fig. 2. Optical texture observed on cooling from isotropic phase for the MBHPIMP (smectic C phase at 45.4 ℃).*

The MBHPIMP shows only an enantiotropic *SmC** phase which occurs in the small mesomorphic temperature range. The crystal phase melting and the *SmC** phase clearing is observed at around 43.9 ºC and 50.4 ºC, respectively (see Fig. 3).

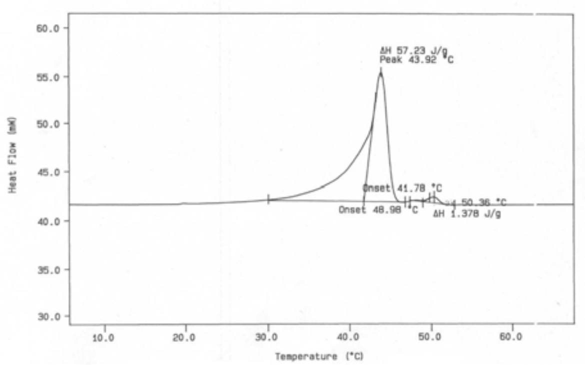


Fig. 3. DSC scans of compound MBHPIMP during the second heating process.

The specific retention volume, V_g^0 of the studied solvents on the MBHPIMP were obtained from IGC measurements at temperatures in ^{o}C between 40 and 95 using Eq.1. According to retention diagram in Fig. 4, *Cr-SmC** and *SmC*-I* transitions for MBHPIMP were found to be 43 ^{o}C and 50 ^{o}C, respectively as the point from which the deviation from linearity was first seen. The *Cr-SmC** and *SmC*-I* transition temperatures obtained by IGC technique are in good agreement with the ones obtained by DSC.

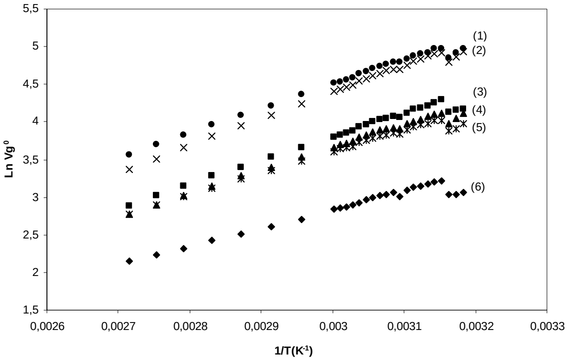


Fig. 4. Variation of specific retention volume of the cHx(1), EA(2), Hx(3), MA(4), cP(5) and P(6) and with the reciprocal of absolute column temperature.

The liquid crystal-solvent interaction parameters, χ_{12}^{∞} and χ_{12}^{*} were determined from Eq.(2) and Eq.(3) and their values were given in Table 1 and Table 2, respectively. The values of χ_{12}^{∞} greater than 0.5 represent unfavorable liquid crystal-solvent interactions while the values lower than 0.5 indicate favorable interactions in dilute liquid crystal solutions. The values of the parameters suggest that all solvents are poor for MBHPIMP.

Table 1. *Flory-Huggins liquid crystal- solvent interaction parameters, χ_{12}^{∞} of MBHPIMP with studied solvents at various column temperatures*

t(^{o}C)	MA	EA	P	Hx	cP	cHx
65	1.08	0.86	1.03	0.98	0.78	0.77
70	1.05	0.86	0.99	0.95	0.77	0.76
75	1.01	0.82	0.96	0.94	0.74	0.72
80	0.99	0.81	0.92	0.91	0.73	0.70
85	0.98	0.80	0.91	0.91	0.71	0.69
90	0.97	0.80	0.88	0.89	0.70	0.68
95	0.96	0.79	0.86	0.89	0.71	0.68

Table 2. Equation of state liquid crystal- solvent interaction parameters, χ_{12}^{*} of MBHPIMP with studied solvents at various column temperatures.

t(^{o}C)	MA	EA	P	Hx	cP	cHx
65	1.20	0.99	1.18	1.09	0.90	0.87
70	1.18	0.98	1.14	1.07	0.89	0.85
75	1.16	0.95	1.12	1.06	0.86	0.82
80	1.14	0.94	1.09	1.03	0.86	0.80
85	1.14	0.94	1.08	1.04	0.85	0.80
90	1.13	0.95	1.06	1.02	0.84	0.78
95	1.12	0.94	1.04	1.03	0.85	0.78

The effective exchange energy parameters, X_{eff} in the equation-of-state theory were obtained from Eq.4 and results were given in Table 3. It was shown that the parameters X_{eff} of all studied solvents were decreased with temperature. The higher values of X_{eff} indicate poor solubility and obtained values of X_{eff} confirm the discussion concerning χ_{12}^{∞}. These results suggest that an endothermic solubility behavior may exist between liquid crystal and studied solvents in this study.

Table 3. *The effective exchange energy parameters, X_{eff} (J/cm^3) of MBHPIMP with studied solvents at various column temperatures .*

t(^{o}C)	MA	EA	P	Hx	cP	cHx
65	40.09	20.91	24.18	19.68	23.01	20.70
70	38.43	19.71	22.71	18.74	22.38	20.24
75	36.52	18.17	21.72	18.39	21.34	19.07
80	35.72	17.47	20.80	17.55	21.30	18.50
85	35.44	17.21	20.64	17.74	20.90	18.79
90	34.84	17.27	20.05	17.36	20.19	18.15
95	34.72	16.89	18.92	17.76	21.48	18.32

$\Delta\overline{H}_{1,sorp}$ and $\Delta\overline{H}_1^{\infty}$ were determined from the slope of the logarithm of specific retention volume, $\mathrm{Ln}\,V_g^0$, versus 1/T plot and from the slope of the logarithm of the weight fraction activity coefficients, $\mathrm{Ln}\,\Omega_1^{\infty}$ which is calculated from Eq.7, versus 1/T plot (in Fig 5), respectively. ΔH_v was found by their subtraction. According to the values of $\Delta\overline{H}_1^\infty$, the solubility of liquid crystal in MA, EA, P, Hx, cP, cHx are endothermic. In Table 3, ΔH_v values obtained were compared with the $\Delta H_{v(lit)}$ values calculated according to Watson's relationship in Reference [18]. The values of solvents' ΔH_v obtained by IGC are in good agreement with the literature.

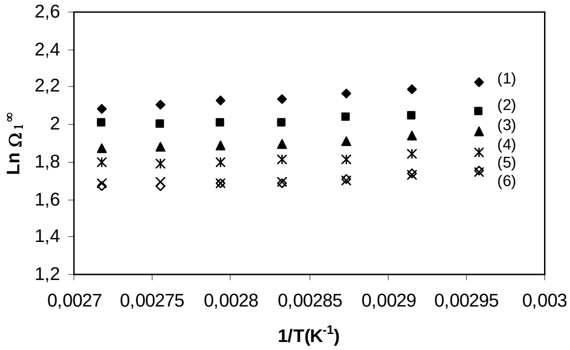


Fig. 5. The logarithm of the weight fraction activity coefficients, Ln Ω_1^∞ *of the P(1), Hx(2), MA(3), cP(4) and cHx(5) and EA(6) in MBHPIMP as a function of temperature.*

Table 4. The partial molar heat of sorption, $\Delta\overline{H}_{1,sorp}$ *(kcal/mol), the partial molar heat of mixing,* $\Delta\overline{H}_1^\infty$ *(kcal/mol), molar heat of vaporization,* ΔH_v *(kcal/mol) obtained by Eq. 8 and molar heat of vaporization,* ΔH_v *[18] (kcal/mol).*

Solvents	$-\Delta\overline{H}_{1,sorp}$	$\Delta\overline{H}_1^\infty$	ΔH_v	$\Delta H_{v(lit)}$
MA	6.3	0.7	7.0	7.2
EA	7.2	0.5	7.7	7.7
P	4.7	1.1	5.8	6.2
Hx	6.3	0.6	6.9	6.9
c-P	5.8	0.5	6.3	6.5
c-Hx	6.6	0.7	7.3	7.2

4. Conclusions

We have synthesized and characterized new salicylaldimine compound MBHPIMP and also investigated the mesomorphic properties of these materials. Phase transition temperatures of MBHPIMP were determined by PM, DSC, and IGC. The transition temperatures of MBHPIMP obtained by IGC are in good agreement with the ones obtained by DSC and PM. The values of the parameters suggest that all solvents are poor for MBHPIMP but solvent quality increases with temperature. According to the values of X_{eff} and $\Delta\overline{H}_1^\infty$, the solubility of liquid crystal in studied solvents are endothermic.

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