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A Series of Di-Schiff Base Liquid Crystals. Studies with Gas-Liquid Chromatography and Differential Scanning Calorimetry†

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A di-Schiff base liquid crystal series with terminal alkyl substituents was synthesized. Phase transition temperatures and nematic-isotropic thermodynamic properties are reported for the methyl through *n*-hexyl, and *n*-octyl members. All are mesomorphic except the unsubstituted hydrogen homologue. The nematic-isotropic transition temperatures and entropies show the usual alternations characteristic of a high-melting series. Relative retention data for the isomeric rigid solute probes phenanthrene and anthracene, in the nematic region of five liquid crystal stationary phases was correlated with the degree of order in the mesophase. The mechanism of gas-liquid chromatographic shape-dependent selectivity of nematic stationary phases towards isomeric polycyclic aromatic hydrocarbons is examined in light of current solution thermodynamic theory.

INTRODUCTION

The use of liquid crystals as stationary phases in gas-liquid chromatography (GLC) is rapidly gaining acceptances as demonstrated by the volume of literature on this subject.¹⁻¹² It has been recognized for some time that liquid crystals can be used as GLC stationary phases to provide shape-selective separation of rigid solute isomers. Many of the ear-

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lier studies employed relatively low molar mass liquid crystals for the separation of isomeric di-, and poly-substituted benzene isomers.¹ Our first experience with liquid crystals in GLC was to use the nematogen *N,N'*-bis(*p*-methoxybenzylidene) α,α' -bi-*p*-toluidine to separate three to five ring polycyclic aromatic hydrocarbons.¹³ This compound was then used to separate polycyclic aromatic environmental pollutants and other classes of compounds.² More recently, other liquid crystal stationary phases have been developed and their use in GLC reported.^{2,3}

We have concentrated on the development of high molar mass liquid crystals that combine the desired characteristics of shape-selectivity, wide working temperature range, and thermal stability at elevated temperatures. Recently, we reported the synthesis, characterization and GLC application of a series of eight liquid crystals that exhibit these characteristics.¹⁴ This study contributed to a better understanding of the effect of molecular structure change on mesomorphic properties, especially in relation to shape-selectivity towards rigid isomers. A relationship between selectivity of nematic stationary phase and the degree of order in the nematic melt was described. The present work was undertaken to test the validity of this relationship for other series of liquid crystals and to investigate the mechanism of GLC separations of polycyclic aromatic hydrocarbon isomers using nematic liquid phases. The liquid crystals used are of the general formula *N,N'*bis(*p*-alkylbenzylidene)- α,α' -bi-*p*-toluidine.

EXPERIMENTAL

The liquid crystals were synthesized by refluxing a 2:1 molar ratio mixture of *p*-alkylbenzaldehyde and α,α' -bi-*p*-toluidine in absolute ethanol for 5 days. The products were collected by filtration while hot and washed with several volumes of hot ethanol and dried under vacuum. Structures were deduced from the method of preparation and satisfactory elemental analysis. Spectroscopic structural verifications (IR, NMR and MS) were performed on all compounds, and all data were consistent with the structures. The designations of the mesophases were confirmed by optical microscopy using a Bauch and Lomb Sterozoom 7 microscope coupled to a Mettler PF52 heating stage and FP5 temperature control unit. The types of the smectic phases exhibited by several of these liquid crystals were not explicitly characterized.

A Perkin-Elmer model DSC-2 was used for the calorimetric determinations. The temperature axis was calibrated with the melting points

of pure indium (mp 156.7°C), tin (mp 231.9°C), and lead (mp 327.5°C). The enthalpies of transition were determined by comparing the chart peak areas per milligram of sample with that of a known mass of indium. A rate of 10°/min was used for both heating and cooling. The instrument sensitivity settings were adjusted to maximize the area under the small nematic-isotropic transition peaks. Under these conditions multiple enthalpy measurements on aliquots of individual liquid crystals were reproducible to within $\pm 1^\circ\text{C}$.

Gas-liquid chromatography was carried out on a Hewlett-Packard 7610 instrument equipped with a flame-ionization detector. Chromatograms were generated on a 1 mV f.s. chart recorder using an electrometer setting of 4×10^2 . Retention data was obtained from a multi-input on-line data system and carrier helium flow was monitored by a calibrated Brooks 5840 dual GC mass flow controller. The column oven temperatures were independently calibrated with a digital thermometer. The column packing (5% liquid crystal on 100/120 mesh HP Chromosorb W) was prepared by the solvent slurry technique using chloroform. Columns (2 mm I.D. borosilicate glass) were conditioned at 250°C for 2 h prior to initial use.

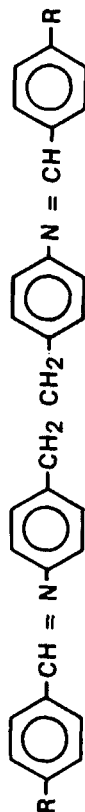
Chemicals were obtained from standard commercial sources and solvents were glass-distilled (Burdick and Jackson).

RESULTS AND DISCUSSION

Table I lists the di-Schiff base mesogens prepared for this study together with their respective mesomorphic transition temperatures and the thermodynamic properties of the nematic-isotropic transition. The thermodynamic properties of melting and smectic transitions are not reported as we were unable to characterize them. Transition temperatures versus chain length for the above homologous series are shown in Figure 1. A plot of the entropies of the nematic-isotropic transition versus chain length is shown in Figure 2.

All members are mesomorphic in nature except the parent compound ($R=H$) which melted at 173.3°C. Compounds CI and CII are purely nematic but the rest exhibit polymesomorphism with the appearance of the smectic mesophase with the propyl derivative (compound CIII). The nematic-isotropic transition temperature curve falls as the series is ascended, a known characteristic of high-melting series. The usual odd-even effect is clearly demonstrated in both nematic-isotropic transition temperatures and entropies. The smectic-nematic

TABLE I



Mesomorphic transition temperatures and thermodynamic properties for the nematic-isotropic transition for the series.

Compound	R	Solid-Nematic T^a T^b	Solid-Smectic T^a T^b	Smectic-Smectic T^a T^b	Smectic-Nematic T^a T^b	Nematic-Isotropic T^a T^b	ΔH	ΔS
CI	CH_3	199.5 (175)				294 (286.5)	6.28	11.08
CII	CH_2CH_2	170.5 (136.5)				276 (268.5)	5.35	9.78
CIII	$\text{CH}_2(\text{CH}_2)_2$		108 (104)	122	160 (151)	282.4 (274.5)	6.75	12.17
CIV	$\text{CH}_2(\text{CH}_2)_3$		56 (64)	84	179 (171)	260.7 (256)	5.35	9.96
CV	$\text{CH}_2(\text{CH}_2)_4$		55 (58.8)	77	192 (183)	256.4 (249)	6.54	12.37
CVI	$\text{CH}_2(\text{CH}_2)_5$		56 (42)	64	194 (185.5)	240 (231)	5.21	10.16
CVIII	$\text{CH}_2(\text{CH}_2)_6$		49 (32)	57	194 (186)	225 (218)	6.24	12.50

^aTemperature in °C recorded on heating of a virgin sample

^bTemperature in °C recorded in cooling (bracketed). ΔH = Enthalpy in kJ mol⁻¹; ΔS = Entropy in Jmol⁻¹ K⁻¹

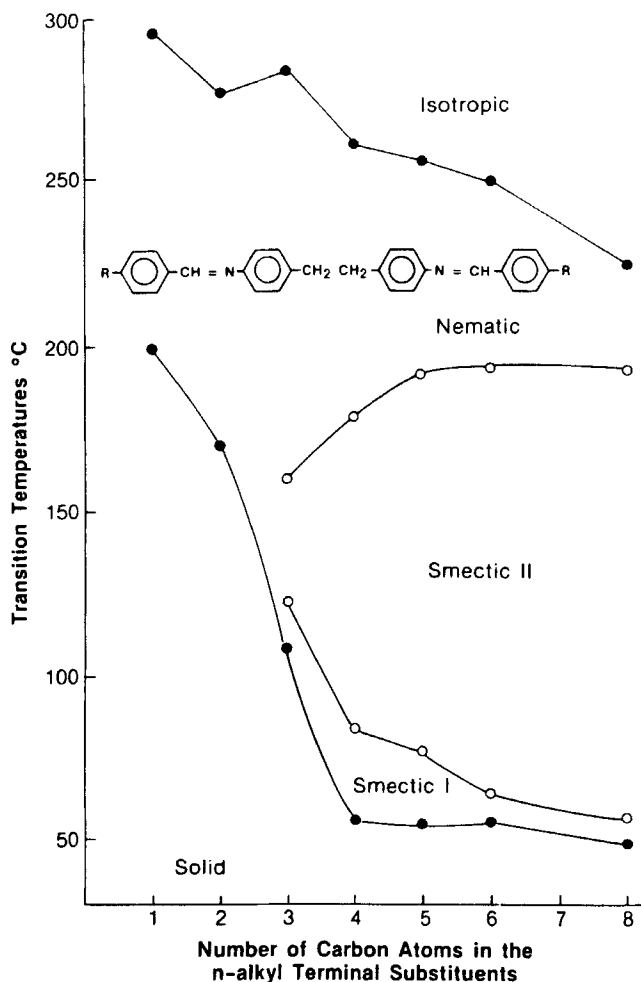


FIGURE 1 Plot of liquid crystal transition temperatures versus alkyl carbon number for the series N,N' -bis(*p*-alkylbenzylidene)- α,α' -bi-*p*-toluidine.

transition temperature curve rise steeply and level off at the pentyl homolog. The entropy values for compounds with odd carbon numbers are higher than those with even numbers, and the points fit two slightly rising curves. Other liquid crystal series show evidence for odd-even alterations and increasing entropy values with increasing carbon number.¹⁵ A noted exception is the trend of decreasing entropy values with increasing carbon number reported earlier¹⁴ for an alkoxy series analogous to our di-Schiff base series.

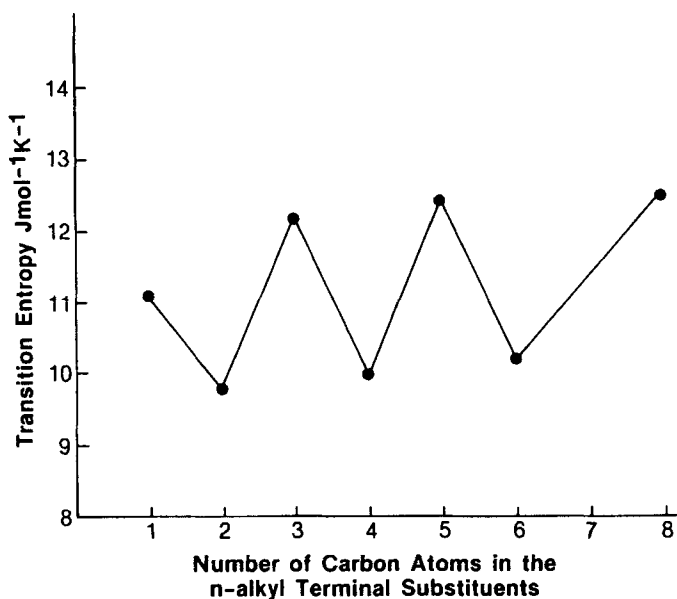


FIGURE 2 Nematic-isotropic transition entropies versus alkyl carbon number for the series *N,N'*-bis(*p*-alkylbenzylidene)- α,α' -bi-*p*-toluidine.

Supercooling is observed for all the mesomorphic transitions. The upper smectic phase supercools to temperatures close to the solid-smectic transition and only one DSC peak is observed (Table I). We found that the liquid crystal transition temperatures recorded on cooling are independent of the cooling rate. In one DSC experiment, a sample of compound CII was heated through the nematic-isotropic transition, cooled to 140°C, and left isothermally for 6 hours. When cooling was continued the nematic-solid transition appeared as expected at 136.5°C. This is not surprising since some liquid crystals can be maintained in the supercooled state for extended periods of time.¹⁶

Much attention has been focused on the nematic state in view of its use in analysis (e.g. solvent properties and GLC applications), industrial application (e.g. electro-optical devices), as well as its theoretical importance. The nematic state is characterized by long-range orientational order of the major axes of neighboring molecules. The degree of order is best represented by the order parameter (*S*) which is a measure of the fraction of molecules aligned with their long axes parallel to the optical director.¹⁷ For perfect alignment *S* = 1, while for complete disorder *S* = 0. Perfect alignment is unattainable in the absence of external constraints because of the normal thermal motion of

molecules, and perfect orientational disorder is also not possible because of the persistence of residual short-range order in the isotropic melt. The normal range of S values encountered in the unperturbed nematic mesophase is $0.8 \geq S \geq 0.4$. The upper limit is at the lowest temperature to which the nematic mesophase can be cooled without crystallization or transition to a smectic phase, and the lower limit is found at, or near, the nematic-isotropic transition temperature.

According to the Maier-Saupe theory¹⁷ S is predicted to be a universal function of reduced temperature (\tilde{T} defined as $\tilde{T} = T/(T - I)$), where T is the experimental temperature and $T(I)$ is the nematic-isotropic transition temperature. It follows that $S(\tilde{T})$ versus (\tilde{T}) is a universal curve for all nematogens representing decreasing values of S with increasing temperature and vanishing at $T(I)$. It is to be noted that the Maier-Saupe theory is in good qualitative agreement with experiment results.¹⁸

When used as stationary phases in GLC nematogens show remarkable shape selectivity toward rigid isomers, with the more rod-like isomer retained longer.^{1,2} A direct relationship between selectivity of nematic stationary phase and the degree of order in the nematic melt has long been sought. Kelker¹⁹ observed that selectivity of the mesophase is better the wider the nematic temperature range, being optimum at the lowest temperature. This approach to the problem, although only partially successful, is not fully justified, since the nematic range is limited at the lower end by the solid-nematic transition temperature and this, in turn, does not show regular trends. Exceptions to Kelker's generalization were apparent when Schroeder²⁰ attempted a similar correlation with data on eight nematic stationary phases.

Alternatively, a direct correlation between the relative retention (α) of two close-boiling solute isomers and the order parameter of the nematic phase is an attractive idea. As articulated by Martire, *et al.*,⁴ the logarithm of the relative retention ($\log \alpha_{1-2}$) which is equal to $\Delta_{1-2}(G_1^0)/RT$ (the difference in the partial Gibbs energy at infinite dilution per unit thermal energy for two solutes 1 and 2 having similar vapor pressures) serves as an index for the relative selectivity of the nematic mesophase. The more ordered the nematic mesophase (higher S value) the better the differential solubility towards rigid rod-like isomers. Accordingly, one would expect $\log \alpha_{1-2}$ versus \tilde{T} for two isomeric solute probes on a series of nematic stationary phases to be a universal curve corresponding qualitatively to the universal $S(\tilde{T})$ versus \tilde{T} curve predicted by the Maier-Saupe theory. This approach has been tested in our laboratory¹⁴ using triphenylene and chrysene as solute probes on two homologous nematic liquid phases series with different central moi-

ties. It was thought that further studies along these lines with other liquid crystal series of diverse chemical composition were needed in order to fully characterize this approach.

In this study relative retention data for the two isomers anthracene(A) and phenanthrene(P) were collected at several temperatures in the nematic region of compound CI through CV. Data in the temperature region immediately below (Ca 15°) the nematic-isotropic transition was not included to avoid anomalous results due to pre-transition effects. Values of α (A/P) were determined as the ratio of the corrected retention time of anthracene to phenanthrene. The selection of these two probe solutes was based upon two particular considerations that contribute to large α values, mainly attributed to differences in shape. First, both are rigid with an appreciable difference in their length-to-breadth ratio (The shape factor n defined as the ratio of the longer to the shorter side of a rectangle having a minimum area and enveloping the molecule, is 1.56 for anthracene and 1.45 for phenanthrene).²¹ Secondly, their vapor pressures at the temperatures of the experiment are almost identical as calculated with the Antoine equation from data available in the literature.²²

The α 's reported in Table II represent an average of at least two measurements. Minimum solute sample injections were delivered to ensure that the retention data were independent of sample size. The carrier flow rates (10 to 40 ml/min) were chosen to allow the collection of retention data at all temperatures on each stationary phase without any changes in column parameters. The results are plotted as $100 \log \alpha$ (A/P) vs. $100 \bar{T}$ (Figure 3). Qualitatively, the resulting curve is in accord with the predictions of the corresponding states principle. Moreover, published values of α (A/P) in the nematic region of five other liquid crystals (Table III of Ref. 2) also fall on the same curve. This

TABLE II

Relative retention of anthracene to phenanthrene, α (A/P), in the nematic region of the liquid crystal series *N,N'*-bis(*p*-alkylbenzylidene)- α,α' -bi-*p*-toluidine.

Temperature °C	α (A/P) \pm .02					
	C0	CI	CII	CIII	CIV	CV
190	1.09	—	1.29	1.29	—	—
200	1.09	1.31	1.27	1.28	1.24	1.24
210	1.08	1.29	1.24	1.25	1.22	1.22
220	1.08	1.27	1.22	1.23	1.20	1.19
230	1.08	1.25	1.19	1.21	1.18	1.17

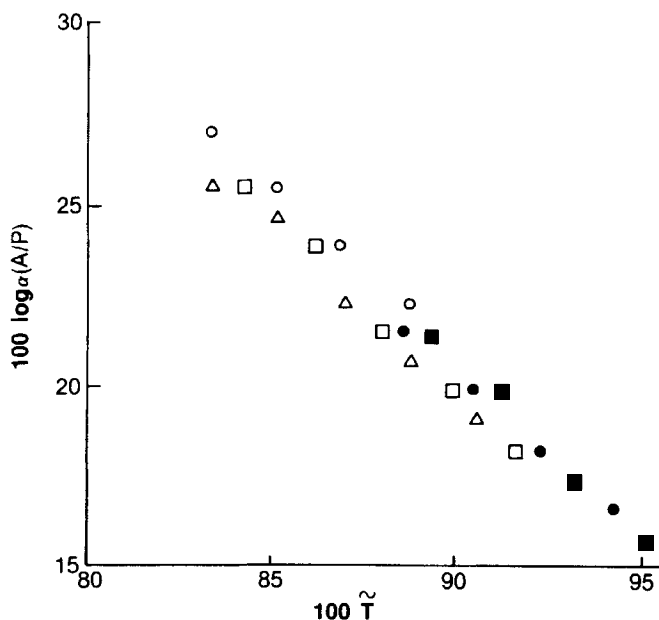


FIGURE 3 Plot of the logarithm of α (A/P) versus reduced temperature in the nematic region of five N,N' -bis(p -alkylbenzylidene)- α,α' -bi- p -toluidine phases. O, CI; □, CII; △, CIII; ●, CIV; and ■, CV.

supports our feeling that this relationship is a general one. It should be pointed out, however, that all 10 nematic phases studied are of the Schiff base type. Nevertheless, since most of the nematic phases used for the separation of polycyclic aromatic hydrocarbons are of the Schiff base type,² the results of this study are of special significance.

Martire *et al.*,⁴ suggested that the mechanism of solution of polycyclic aromatic hydrocarbons in nematic solvents could be studied using the temperature dependence of the relative retention of isomeric solute pairs. The expression relating the relative retention of two solutes (e.g. P/A) to the molar enthalpy ΔH_2^S and entropy ΔS_2^S of solution accompanying the infinite dilute transfer of solute² from the ideal gaseous mixture (solute plus carrier gas) to the real solution is given in Eq. 9 of Ref. 4 as

$$\ln \alpha(A/P) = \frac{-\Delta H_A^S + \Delta H_P^S}{RT} + \frac{\Delta S_A^S - \Delta S_P^S}{R}$$

$$= \frac{\Delta(\Delta H_{P-A}^S)}{RT} - \frac{\Delta(\Delta S_{P-A}^S)}{R}$$

The enthalpy term $\Delta(\Delta H_{P-A}^S)$ represents the difference (phenanthrene-anthracene) in the strength of the solute-solvent intermolecular interactions, while the entropy term $\Delta(\Delta S_{P-A}^S)$ is a reflection of the compatibility of the solute in the nematic area. The relative retention data from Table II are plotted as $\log \alpha$ (A/P) vs reciprocal temperature (Figure 4), and $\Delta(\Delta H_{P-A}^S)$ and $\Delta(\Delta S_{P-A}^S)$ values obtained from the slopes and intercepts of the plots are given in Table III. $\Delta(\Delta H_{P-A}^S)$ as well as $\Delta(\Delta S_{P-A}^S)$ are all positive for the five liquid crystals studied. A positive $\Delta(\Delta H_{P-A}^S)$ results from a more negative ΔH_2 for the more rod-like anthracene isomer indicating stronger solute-solvent interaction for interaction. Since solute-solvent interactions with the nematic solvent (for both anthracene and phenanthrene) are expected to be of the same nature, it can be safely assumed that anthracene-solvent interactions operate at shorter average distances than those of the more globular phenanthrene. Concomitantly, the greater orientational order resulting from the closer approach of the anthracene molecules to the solvent molecules leads to lower translational and rotational entropy upon solution, making $\Delta(\Delta S_{P-A}^S)$ positive (Table III). However, the fa-

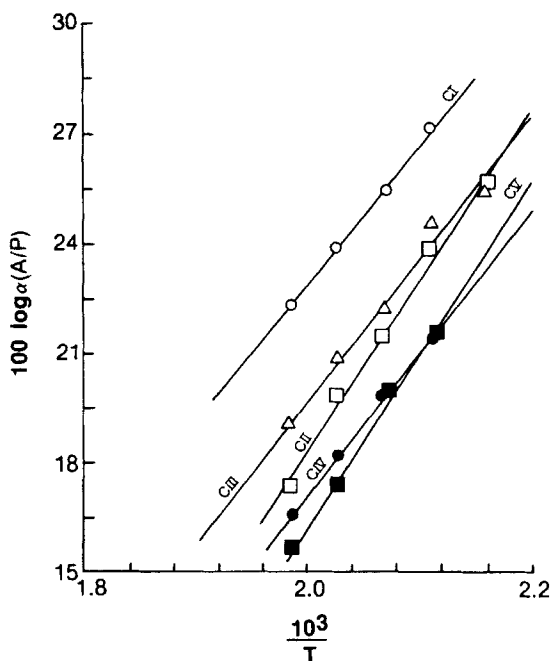


FIGURE 4 $\log \alpha$ (A/P) versus reciprocal temperature in the nematic region of five *N,N'*-bis(*p*-alkylbenzylidene)- α,α' -bi-*p*-toluidine.

TABLE III

Enthalpy and entropy of solution differences between anthracene and phenanthrene in the nematic region of the liquid crystals *N,N'*-bis(*p*-alkylbenzylidene)- α,α' -bi-*p*-toluidine.

Liquid crystal	$\Delta^*(\Delta H_{\text{P-A}}^{\text{S}})$ kJ mol ⁻¹	$\Delta^*(\Delta S_{\text{P-A}}^{\text{S}})$ JK ⁻¹ mol ⁻¹
CI	3.09 ± .05	4.29 ± .11
CII	3.90 ± .21	6.25 ± .43
CIII	3.25 ± .26	4.86 ± .53
CIV	3.27 ± .06	5.12 ± .12
CV	3.94 ± .24	6.53 ± .49

* The differences are the phenanthrene value minus the anthracene value.

vorable enthalpic enhancement of solubility outweigh the unfavorable entropic factor as anthracene is invariably retained longer (Table II). As the temperature is increased the enthalpic advantage is diminished and the relative retention decreases. Thus optimum selectivity of nematic phases for polycyclic aromatic hydrocarbon separation is ultimately achieved at the lowest temperature to which the nematic meso-phase can be cooled without a phase change.

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