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Synthesis, Thermodynamic Properties, and Gas-Liquid Chromatographic Evaluation of a High-Melting Liquid Crystal Series

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The synthesis, phase transition temperatures and thermodynamic data (enthalpies and entropies) are reported for the methoxy through *n*-octyloxy (and *n*-decyloxy) homologues of the liquid crystal series represented by N,N′-bis[*p*-alkoxybenzylidene]-α,α′-bi-*p*-toluidine. The trends in transition temperatures are more or less analogous to previously-studied liquid crystal series. Nematic-isotropic enthalpy values are appreciably higher than average values for other series. Entropy values show the usual odd-even effect, but in contrast to observed trend for other series, they decrease with increasing terminal substituent chain length. Di-Schiff's bases with various terminal substituents that showed interesting linear correlation between nematic-isotropic transition temperatures and the anisotropy of polarizability of the substituent were also synthesized. A simple gas-liquid chromatographic method for the investigation of the selectivity of nematic stationary phases and its dependence on the degree of molecular order in the nematic state is also presented.

INTRODUCTION

In the past, much effort was devoted to the synthesis of room temperature liquid crystals due to their potential application in various electro-optical devices. In contrast, high-melting liquid crystals attracted little attention. The use of liquid crystals in gas-liquid chromatography (GLC) was reviewed by Kelker and Von Schivizhoffen[1] and more recently by Schroeder.[2] The pioneering research in this field dealt primarily with the evaluation of nematogenic phases for the separation of isomeric disubstituted benzenes[1,2] and

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the investigation of solution thermodynamic aspects responsible for the unique selectivity of these phases.[3–6] We reported the application of a commercially-available high-melting nematic liquid crystal for the gas-liquid chromatographic separation of geometric isomers of 3-5 ring polycyclic aromatic hydrocarbons (PAH), including the base-line separation of benzo[a]pyrene from benzo[e]pyrene.[7] This led to the use of the liquid crystal for unique GLC separations of underivatized steroid epimers,[8] polychlorinated biphenyls,[9] methoxy benzanthracenes,[10] methyl naphthalenes,[11] drug isomers,[12] azaheterocyclic compounds,[13] and PAH from combustion effluents.[14] Following our initial report, we synthesized three new high-melting liquid crystals that exhibited substantially enhanced analytical stability and applications versatility. We reported their use for the separation of 3–5 ring[15] and 4–6 ring[16] PAH isomers, and bile acid isomers;[17] and have shown their value in GLC-mass spectrometric analysis of PAH,[16] and for the analysis of benzo[a]pyrene in cigarette smoke.[18] In principle, the capability of liquid crystal phases to separate solutes on the basis of molecular shape is applicable to many GLC problems. However, the narrow temperature range of the most useful liquid crystals (generally nematic) and/or the volatility of some of the liquid crystals used pose restrictive practical limitations.

This paper reports: (a) the synthesis, transition temperatures, enthalpies (ΔH) and entropies (ΔS) of transition for nine members of the series represented by *N*,*N*′-bis[*p*-alkoxybenzylidene]-α,α′-bi-*p*-toluidine ranging from the methoxy to the *n*-decyloxy derivative, (b) the synthesis and transition temperatures determination of several other di-Schiff's bases that showed an interesting correlation between the nematic-isotropic transition temperature T(N-I) and the anisotropy of polarizability ($\Delta\alpha$) of terminal substituents; and (c) GLC studies, using eight of the above liquid crystals in their nematic temperature range as stationary phases. The principle objective of this study is to better understand the effect of molecular structural changes on liquid crystalline properties. Considering the need for stable low-volatility liquid crystal stationary phases of wide useful nematic range, a clearer understanding will allow more accurate prediction of the types of compounds likely to exhibit the best properties for this particular application.

EXPERIMENTAL

Materials

The liquid crystals reported in this study were prepared as illustrated for the compound N,N′-bis[*p*-ethoxybenzylidene]-α,α′-bi-*p*-toluidine (BEBT): a 2:1 molar ratio mixture of *p*-ethoxybenzaldehyde and α,α′-bi-*p*-toluidine respectively was refluxed in absolute ethanol for several days. The pale yellow product was collected by filtration of the hot suspension and thoroughly washed with hot ethanol to remove residual starting materials. *p*-Ethoxybenzaldehyde was purified before use by extraction with 5% sodium carbonate and distillation. All compounds were synthesized in a similar manner using the appropriate starting aldehyde and diamine. Structures for the products were deduced from the method of preparation and satisfactory elemental analysis. Spectroscopic structural verifications (IR, NMR and MS) were made on selected compounds. All data were consistent with that of highly pure di-Schiff's base products. The designations of the mesophases were made on the basis of well-established mesophase transition temperatures vs. terminal substituent correlations that have been documented for homologous series of other liquid crystalline materials,[20] and confirmed by optical microscopy (Bausch and Lomb Stereozoom 7 microscope coupled to a Mettler PF52 heating stage and FP5 temperature control unit). The specific types of the smectic phases exhibited by several of these liquid crystals were not explicitly characterized.

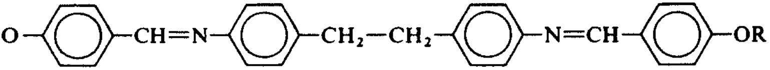
Differential scanning calorimetry

A Perkin–Elmer Model DSC-2 was used for the calorimetric determination. The temperature axis was calibrated with the melting points of pure indium (m.p. 156.60°C), tine (m.p. 231.88°C) and lead (m.p. 327.47°C). The enthalpies of transitions were determined by comparing the chart peak areas per milligram of sample with that of a known weight of indium (ΔH 28.43 Joules/gram). A heating rate of 10°/min. was used for all determinations and the instrument sensitivity settings were adjusted to maximize the areas under the small peaks. Under these conditions, multiple ΔH measurements on aliquots of individual liquid crystals were reproducible to within ±5%, which is believed to be the accuracy of these determinations. Transition temperatures were reproducible to within ±1°C. The purity of these compounds was not determined; however all compounds were purified by washing with hot ethanol to constant mesophase-to-isotropic transition temperatures. The sharp DSC transition peaks (for example, see Figure 5 of Ref. 15) are indicative of highly pure products. To compare our results with literature values we similarly determined the temperature and enthalpy of the nematic-to-isotropic transition for a 99.7% pure *p*-azoxyanisole sample (kindly provided by Dr. D. Martire, Georgetown University). Our calorimetric results [T(N-I) = 136°C; ΔH = 0.72 kJ/mole] were in good agreement with literature values.[20]

The previously reported values for the T(N-I) of BMBT[7] was found to be in error. The results of this study are given in Table I.

TABLE I

Thermodynamic constants for the compounds RO-⟨⟩-CH=N-⟨⟩-CH$_2$-CH$_2$-⟨⟩-N=CH-⟨⟩-OR



		Transitions[a]														
		Solid–Nematic (C-N)			Solid–Smectic (C-S)			Smectic I Smectic II (S_I-S_{II})			Smectic–Nematic (S-N)			Nematic–Isotropic (N-I)		
Compound	R	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS
BMBT[b]	CH_3-	181	43.5	96.0										337	7.2	11.7
BEBT	CH_3CH_2-	173	38.6	86.5										341	9.4	15.3
BPrBT	$CH_3(CH_2)_2$-				169	25.9	58.5				176	11.7	26.1	311	6.2	10.5
BBBT[b]	$CH_3(CH_2)_3$-				159	24.7	57.2				188	12.2	26.5	303	8.5	14.7
BPeBT	$CH_3(CH_2)_4$-				134	22.2	54.4	201	6.1	12.8	208	1.9	4.0	283	5.5	9.8
BHxBT[b]	$CH_3(CH_2)_5$-				127	26.5	66.2	203	5.2	11.0	299	1.8	3.6	274	7.3	13.4
BHeBT	$CH_3(CH_2)_6$-				119	33.1	84.5	203	4.2	8.7	238	2.7	5.2	262	5.2	9.6
BOBT	$CH_3(CH_2)_7$-				118	33.6	85.9	202	4.3	9.1	244	3.6	7.0	255	6.5	12.3
BDBT[c]	$CH_3(CH_2)_9$-				119	43.9	112	197	3.0	6.4						

[a] T = Temperature in °C; ΔH = Enthalpy in kJ/mole; ΔS = Entropy in J/mole-°K.

[b] Compounds previously reported.[7,15,16]

[c] Smectic-Isotropic data: T—241°C; ΔH—17.1 kJ/mole; ΔS—33.3 J/mole-°K.

Gas-Liquid chromatography

A Hewlett-Packard 7610 gas chromatograph equipped with a flame ionization detector was employed for this study. Helium carrier gas flow was regulated by a calibrated Brooks 5840 mass flow controller, and flow rates were accurately measured with a soap-bubble meter. The packing materials were prepared by the solvent slurry method as described in more detail in previous publications.[7,15,16,18] Column temperatures reported were accurately measured by a thermocouple. Certain experimental precautions outlined by Chow and Martire[3] were taken to ensure that α values obtained were independent of specific column parameters. For example, small solute sample sizes were delivered to ensure that the GLC results were independent of sample size. It was also established that α values were independent of carrier gas flow rate. The flow rates (10 to 30 ml/min.) were chosen to give convenient retention times. Highly inert HP Chromosorb W was used as solid support to minimize solute adsorption on support active sites. Solute adsorption could, however, occur at the carrier gas-liquid crystal interface and, hence, the GLC results could depend on stationary phase surface-to-volume ratio.[3] Only one stationary phase weight percent (5 wt. % liquid crystal on 100/120 mesh HP Chromosorb W) was used for all determinations and, therefore, the significance of contribution to solute retention from liquid surface effects was not evaluated.

RESULTS AND DISCUSSIONS

Differential scanning calorimetry

Table I lists the N,N'-bis[*p*-alkoxybenzylidene]-α,α'-bi-*p*-toluidines, together with their respective melting points and mesomorphic transition temperatures. The C_1 and C_2 homologues are pure nematogens. C_3 and C_4 show smectic and nematic phases, C_5–C_8 exhibits two smectic types and a nematic region and C_{10} is a pure smectogen.

Transition temperatures vs. chain length plots for the above homologous series are shown in Figure 1. It was observed that the solid-mesomorphic transition temperatures fall gradually as the homologous series is ascended, levelling-off at C_7. Crystal-mesomorphic transition temperatures were expected to rise slowly with increasing carbon number beyond C_{10}. As with other liquid crystal series, the crystal-mesomorphic transition temperatures show no regular trend because of the diversity of crystal structures embraced by mesophase-forming compounds. The S_I-S_{II} transition temperatures appear to be independent of terminal alkoxy chain length unlike the falling odd-even alternations previously observed for smectic-smectic type transitions.[21] the S-N and N-I transition temperature trends are typical of the

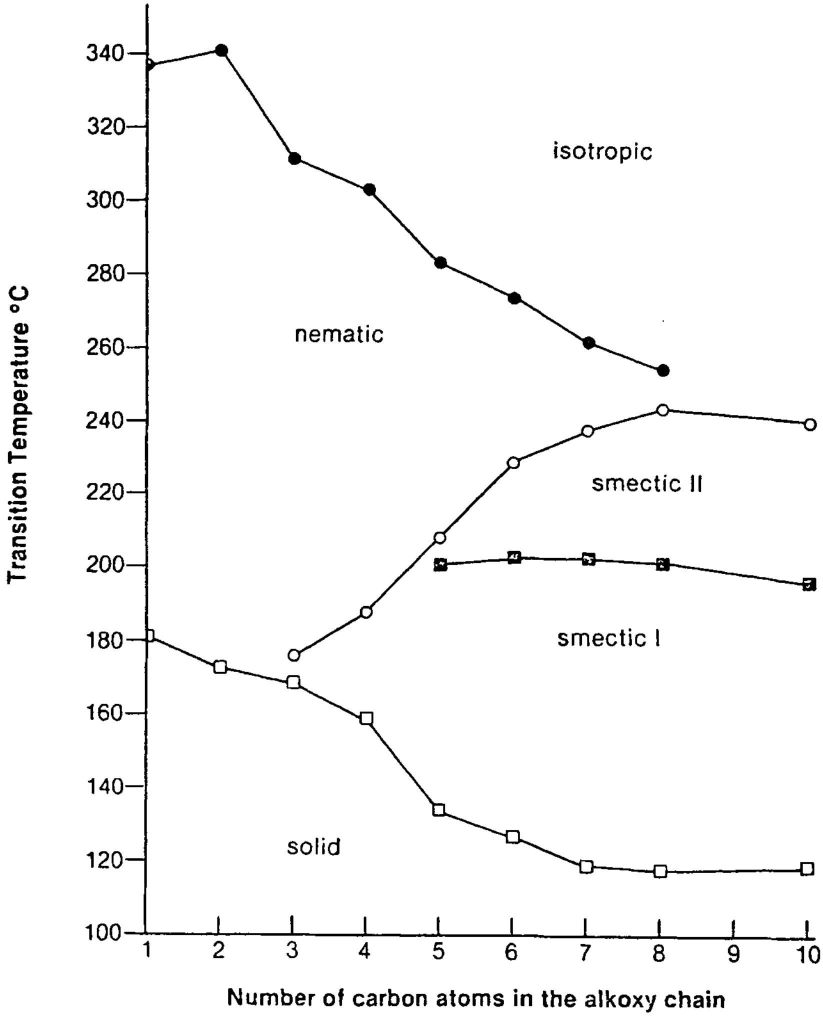


FIGURE 1 Plot of liquid crystal transition temperatures vs. *n*-alkoxy chain length for N,N′-bis[*p*-alkoxybenzylidene]-α,α′-bi-*p*-toluidines.

majority of over 70 homologous series examined by Gray.[21] All S-N points lie on a single curve that rises to a maximum before merging with the falling N-I curve. The usual odd-even alterations in the plot of the N-I transition temperatures are apparent for the lower members of the series and becomes less marked as the series is ascended. This behavior has been discussed in detail elsewhere.[19,21]

While transition temperatures do indicate important trends, it is believed[20,22] that transition enthalpy (ΔH) and entropy (ΔS) values provide better insight into the nature of the mesophase stabilizing intermolecular forces. In Dewar's view,[22] the mesophase disappearance temperature is simply a proportionality variable that forces the equality between the two more fundamental quantities ΔH and ΔS. Considering the scarcity of thermodynamic data on high-melting liquid crystals and having on-hand highly pure and stable materials, a differential scanning calorimetry study was undertaken, and the resulting ΔH and ΔS values are reported in Table I. A plot of ΔS(N-I) versus the number of carbons in the alkoxy chain is shown in Figure 2. ΔS (S_I-S_{II}) and ΔS (S_{II}-N) are also plotted for magnitude comparison purposes. Perhaps the most striking features of the plot are that ΔS values for compounds with even carbon number are appreciably higher than those with odd carbons; and that the points fit two falling curves with ΔS values decreasing more or less linearly with increasing chain length. Other liquid crystal series show evidence for odd-even alternations, but in contrast to our findings ΔS(N-I) values increase with increasing carbon number. It is to be noted that most of the liquid crystal series for which this general trend was observed are low-melting (T(N-I) < 200°C) with ΔH(N-I) values ranging between 0.4 ~ 4 kJ/mole. In contrast, ΔH(N-I) for the members of the homologous series reported here (Table I) are considerably higher, indicating stronger intermolecular interactions in the nematic state.

Table II lists several newly synthesized liquid crystals of three different central linkages and various terminal substituents. All but three of these

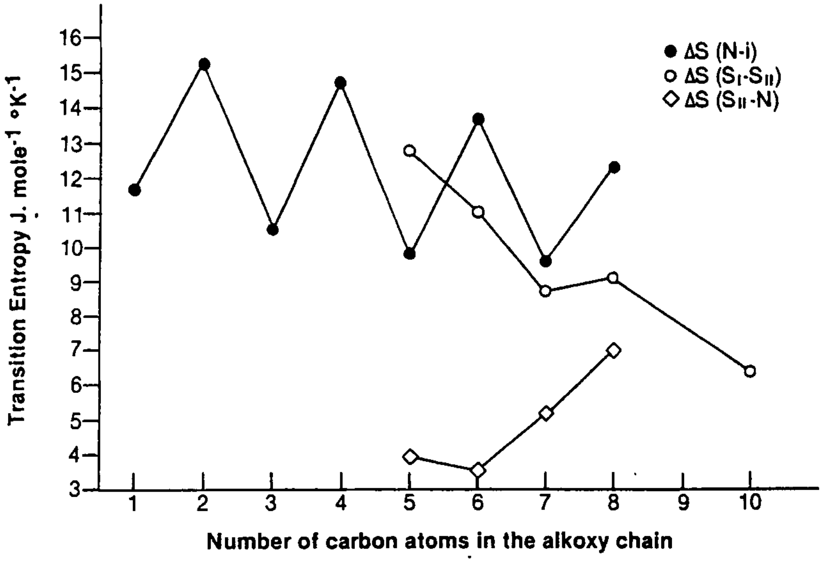
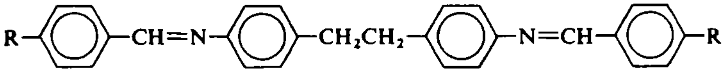
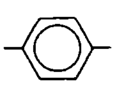
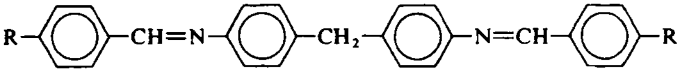
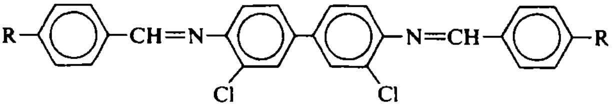


FIGURE 2 Plot of liquid crystal transition entropies vs. *n*-alkoxy-chain length for N,N′-bis[*p*-alkoxybenzylidene]-α,α′-bi-*p*-toluidines.

TABLE II

Transition temperatures (°C) of compounds of the type

		Transitions		
Compound	R	Solid-Nematic	Nematic-Isotropic	Solid-Isotropic
(1)				
I	H-			172
II	CH_3-	197	287	
III[a]	CH_3O-	181	337	
IV	Cl-	232	318	
V	CN-	227	367	
VI	$(CH_3)_2N$-	266	315	
VII[a]		257	403	
VIII	NO_2-	212	330 (decomp.)	
(2)				
IX	CH_3O-			184
	$CH_3(CH_2)_3O$-			163
(3)				
Cl-1[a]	CH_3O-	157	372	
CL-4[b]	$CH_3(CH_2)_3O$-	103	313	
CL-6	$CH_3(CH_2)_5O$-	97	277	

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[a] Compounds previously reported.[7,2,16].

[b] CL-4 thermodynamic data: ΔH(C-N) 26.87 kJ/mole; ΔH(N-I) 2.43 kJ/mole.

compounds exhibit nematic properties. In contrast to other liquid crystal forming structures, the parent compound for the N,N-bis[*p*-alkylbenzylidene]-α,α′-bi-*p*-toluidines (Compound I) does not exhibit mesomorphism. Liquid crystalline tendencies only appear upon substitution of the para hydrogens. Apparently a minimum molecular length is a critical requirement. It is also noted that a -CH_2- central linkage does not promote liquid crystal properties for compounds with up to four carbons in the terminal alkoxy substituents. The results of a recent study,[23] however indicate that stable mesophases are attainable with bent -CH_2 central linkage provided that the terminal chain is sufficiently long.

The effect of the chemical nature of terminal substituents on nematic thermal stability show trends similar to those previously reported for other

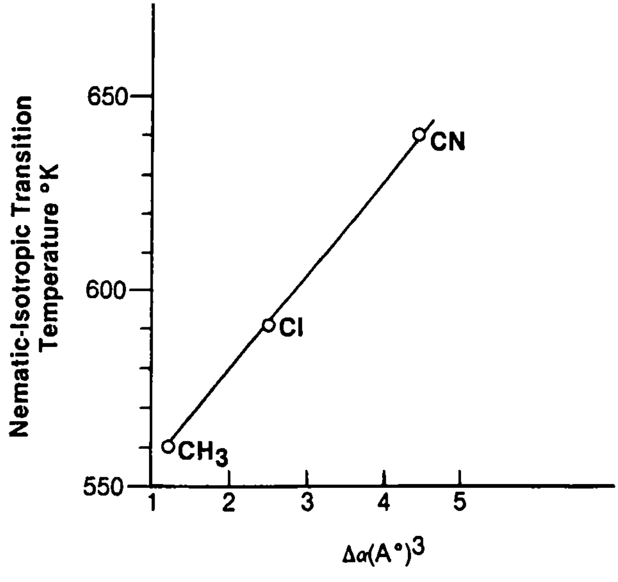

FIGURE 3 Dependence of T(N-I) on terminal substituent Δα.

liquid crystals.[19] As shown in Table II, the order of substituent efficiency in promoting the nematic state is Ph → CN → CH_3O → Cl → $(CH_3)_2N$ → CH_3. The rationale for this behavior is discussed elsewhere.[19]

It is well known that T(N-I) is enhanced the higher the anisotropy of the polarizability (Δα) of the terminal substituent-aromatic bond (C_{ar}-X). Recently, Van der Veen[24] examined this effect in a rather novel approach. Basing his derivations on the Majer-Saupe theory for the nematic state, and assuming the validity of the additivity of bond polarizabilities, he showed that T(N-I) is linearly dependent on Δα. We tested Van der Veen relationship with three compounds from Table II for which substituent Δα values were available,[24] and obtained corroborative evidence for his findings. A plot of T(N-I) vs. Δα (Figure 3) shows excellent linear correlation. Moreover, using the slope and intercept of the plot shown in Figure 2 and T(N-I) for Compound III, we obtained a value of Δα = 3.25 ($A°_3$) for C_{ar}-OCH_3 (a direct measurement of this value is not available). Using this value and data from Van der Veen least squares plot (Curve B, Figure I of Ref. 24), we predicted a value of 228°C for the T(N-I) of the methoxy derivative of the phenyl-*p*-benzoyloxybenzoate series. This is in reasonably good agreement with the experimentally measured value of 223°C.[25] However, the agreement between the predicted and measured values of the T(N-I) of the methoxy derivative of the Schiff's bases series (Curve A, Figure 1 of Ref. 24) was not as good. Griffin[26] examined Van der Veen's relationship for four different liquid crystal series and concluded that this simple relationship is not strictly valid when the molecule into which the terminal substituent is introduced has appreciable conjugative interactions with the terminal substituent. He argued that such interactions invalidate the additivity of molecular polarizabilities.

Gas-Liquid chromatography

A GLC study using compounds reported in Tables I and II as stationary phases was undertaken in an effort to characterize their unique selectivity towards rod-like solute molecules and its relationship to order in the nematic state. GLC is a particularly attractive method for investigating the molecular order in nematic liquid crystals because the solute probe molecules are at infinite dilution and therefore do not disrupt the long range order of the mesophase. According to mechanisms discussed by Martire, *et al.*[4] the logarithm of the separation factor ($\ln \alpha_{1-2}$) which is equal to $\Delta_{1-2}(\bar{G}_e^\infty)/RT$ (the difference in the partial free energy at infinite dilution of two solutes 1 and 2 having similar vapor pressures per unit thermal energy) serves as an index of the relative selectivity of the nematogenic solvent. The more ordered the nematic phase, the more selective it is towards rod-like solutes. The degree of order in the nematic state is given by the order parameter (S) which is a measure of the fraction of molecules aligned with their long axis parallel to the preferred orientation of the mesophase (the optical director). The more ordered the nematic phase, the higher the value of S. According to the Maier-Saupe theory[27] (the most widely quoted theory of the nematic state), S is predicted to be a universal function of reduced temperature $\tilde{T}$ defined as (T/T(N-I)). $S(\tilde{T})$ vs. ($\tilde{T}$) for all nematics fall on a single universal curve decreasing with increasing temperature and vanishing at T(N-I). This prediction is in general qualitative, but not quantitative, agreement with the experiment.[28]

A simple and convenient means of testing this corresponding states principle is by investigating the dependence of GLC-obtained $\Delta_{1-2}(\bar{G}_e^\infty)/RT$ values for two solutes with similar vapor pressure on different liquid crystal stationary phases as a function of $\tilde{T}$. One would intuitively expect $\Delta_{1-2}(\bar{G}_e^\infty)/RT$ vs. $\tilde{T}$ to be a universal curve corresponding qualitatively to the universal $S(\tilde{T})$ vs. $\tilde{T}$ curve predicted by the Maier–Saupe theory. The solutes chosen for this study were the isomers chrysene/triphenylene (C/T). Values of α were determined as the ratio of the corrected retention time of chrysene to that of triphenylene. The selection of these solutes was based upon two particular considerations. First, both are rigid isomers with appreciable difference in their length-to-breadth ratios, thus resulting in large α values. Second, they elute simultaneously on isotropic GLC stationary phases[7] including Compound IX of Table II indicating identical vapor pressures at

TABLE III

$\alpha(C/T)$ as a function of temperature in the nematic region of eight liquid crystal stationary phases

Temperature (°C)	$\alpha(C/T) \pm 0.03$							
	BMBT	BEBT	BPrBT	BBBT	BPeBT	BHxBT	CL-4	CL-6
200	2.22			1.87				
220	2.03	2.03		1.72				
230	1.94	1.97		1.66				
235					1.49	1.47		
240	1.86			1.59			1.33	1.23
245					1.43	1.41		
250	1.79	1.79	1.59	1.55				1.19
255					1.38	1.34		
260							1.24	1.09
265					1.33	1.28		
270		1.66	1.48					
280							1.12	
290			1.39					

the temperatures of the experiment. Table III gives $\alpha(C/T)$ at different temperatures in the nematic range of seven liquid crystals that belong to two homologous series with different central linkage. The values are plotted as 100 $\Delta_{C-T}(\bar{G}_e^{\infty})/RT$ vs. 100/T°K and shown in Figure 4. All lines were drawn according to least square analysis with correlation coefficients >0.99. Plots of 100 $\Delta_{C-T}(\bar{G}_e^{\infty})/RT$ vs. 100 $\tilde{T}$ are shown in Figure 5. Not all points fall on a single curve; instead two separate curves could be drawn, one for each homologous series. On the basis of these findings, it could be concluded that, only for liquid crystals with closely related chemical structures (homologues) does the mesophase selectivity improve the higher the nematic-to-isotropic transition temperature. Optimum selectivity is ultimately achieved at the lowest temperature to which the nematic phase could be cooled in agreement with Kelker's observation.[1] When two liquid crystals with different chemical composition are compared at the same $\tilde{T}$, the one with the higher T(N-I) is not necessarily the more efficient (compare, for example, α value on BBBT and CL-4). Higher T(N-I) may be a consequence of increased molecular polarizability and/or molecular dipolarity that does not necessarily result in a more ordered nematic state.[19,21] It is known that lateral substitution into the rigid aromatic core decreases the molecular length-to-breadth ratio resulting in decreased molecular order.[12,21] This perhaps explains the low ΔS(N-I) value (see Table II) and inferior selectivity (see Figure 4) of Compound CL-4. It seems reasonable to assume that when comparing liquid crystals of different chemical composition, the compound with the higher

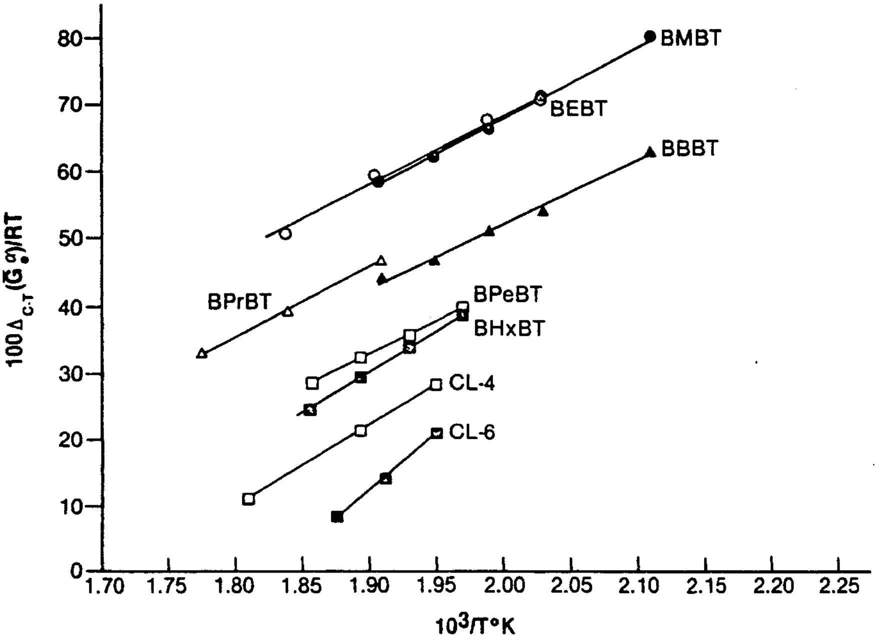

FIGURE 4 $\Delta_{C\text{-}T}(\bar{G}_e^\infty)/RT$ vs. reciprocal temperature in the nematic region of eight liquid crystal stationary phases.

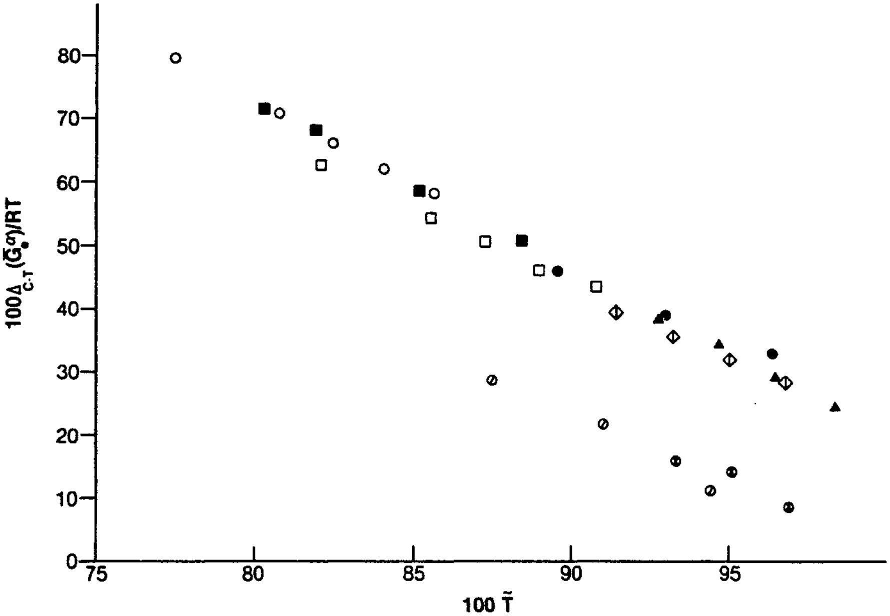

FIGURE 5 A corresponding states plot of the dependence of $\Delta_{C\text{-}T}(\bar{G}_e^\infty)/RT$ on reduced temperature for five N,N′-bis[*p*-alkoxybenzylidene)-α,α′-bi-*p*-toluidines and two 4,4′-bis[*p*-alkoxybenzylideneamino]3,3′-dichlorobiphenyl stationary phases

ΔS(N-I) value is the more efficient nematic solvent. More extensive investigations with liquid crystals of diverse chemical composition are needed in order to fully understand this interesting approach.

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References

1. H. Kelker and E. Von-Schivizhoffen, *Advances in Chromatography*, Vol. 6 (J. C. Giddings and R. A. Keller, Eds.), (Marcel Dekker, New York, N.Y., 1968), p. 247.
2. J. P. Schroeder, *Liquid Crystals and Plastic Crystals* (G. W. Gray and P. A. Winsor, Eds.), (Ellis Horwood Ltd., Chichester, England, 1974), Vol. 1, p. 356.
3. L. C. Chow and D. E. Martire, *J. Phys. Chem.*, **73**, 1127 (1969).
4. W. Zielinski, Jr., D. H. Freeman, D. E. Martire, and L. C. Chow, *Anal. Chem.*, **42**, 176 (1970).
5. L. C. Chow and D. E. Martire, *J. Phys. Chem.*, **75**, 2005 (1971).
6. L. C. Chow and D. E. Martire, *Mol. Cryst. Liq. Cryst.*, **14**, 293 (1971).
7. G. M. Janini, K. Johnston, and W. L. Zielinski, Jr., *Anal. Chem.*, **47**, 670 (1975).
8. W. L. Zielinski, Jr., K. Johnston, and G. M. Muschik, *Anal. Chem.*, **48**, 907 (1976).
9. Anon. Analabs Tech. Bull., North Haven, Connecticut (1975).
10. J. C. Wiley, Jr., C. S. Menon, D. L. Fisher, and J. E. Engel, *Tetrahedron Lett.*, **33**, 2811 (1975).
11. S. Wasik and S. Chesler, *J. Chromatog.*, **122**, 451 (1976).
12. M. Hall and D. N. B. Mallen, *J. Chromatog.*, **118**, 268 (1976).
13. M. Pailer and V. Hlozek, *J. Chromatog.*, **128**, 163 (1976).
14. P. E. Strup, R. D. Giammer, T. B. Stanford, and P. W. Jones, in *Carcinogenesis—A Comprehensive Survey*, (R. Freudenthal and P. W. Jones, Eds.), Vol. 1, p. 241–251, (Raven Press, New York, 1976).
15. G. M. Janini, G. M. Muschik, and W. L. Zielinski, Jr., *Anal. Chem.*, **48**, 809 (1976).
16. G. M. Janini, G. M. Muschik, J. A. Schroer, and W. L. Zielinski, Jr., *Anal. Chem.*, **48**, 1879 (1976).
17. G. M. Janini, G. M. Muschik, W. Manning, and W. L. Zielinski, Jr., Pittsburgh Conf. on Anal. Chem. and Applied Spectros., Cleveland, Ohio (1977).
18. G. M. Janini, B. Shaikh, and W. L. Zielinski, Jr., *J. Chromatog.*, **132**, 136 (1977).
19. G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London, 1962.
20. N. Barrall II and J. Johnson, *Liquid Crystals and Plastic Crystals* (G. W. Gray and P. A. Winsor, Eds.), (Ellis Harwood Ltd., Chichester, England, 1974), Vol. 2, p. 255.
21. G. W. Gray, *Molecular Geometry and the Properties of Nonamphiphilic Liquid Crystals* (G. H. Brown, Ed.), (Academic Press, New York, N.Y., 1976), Vol. 2, p. 1.
22. M. J. S. Dewar, A. Griffin, and R. M. Riddle, *Liquid Crystals and Ordered Fluids* (J. S. Johnson and R. S. Porter, Eds.), (Plenum Press, New York, N.Y., 1973), p. 733.
23. A. C. Griffin, S. F. Thames, and M. S. Bonner, *Mol. Cryst. Liq. Cryst.*, **34** (letters), 135 (1977).
24. J. Van der Veen, *Journal de Physique*, Colloque CI, Supplement 3, **36**, CI-375 (1975).
25. J. P. Van Meter and B. H. Klanderman, *Mol. Cryst. Liq. Cryst.*, **22**, 271 (1973).
26. A. C. Griffin, *Mol. Cryst. Liq. Cryst.*, **34** (letters), 111 (1976).
27. W. Maier and A. Saupe, *Z. Naturforschg.*, **14a**, 882 (1959); **15a**, 287 (1960).
28. R. L. Humphries, P. G. James, and G. R. Luckhurst, *J. Chem. Soc. Faraday Trans. II*, **68**, 1031 (1972).