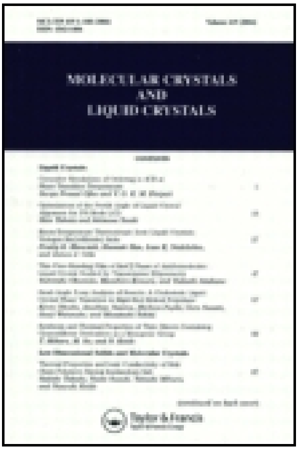

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Thermodynamics of Solutions of Various Nonmesomorphic Solutes in the Nematic and Isotropic Phases of 7CB†

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Thermodynamic results from gas-liquid chromatography, (GLC) are reported for thirty two nonmesomorphic solutes, at infinite dilution, in the nematic and isotropic phases of *p*-*n*-heptyl-*p*'-cyanobiphenyl (7CB). The solutes fall into five categories: normal alkanes, branched alkanes, alkenes, hexadienes and aromatics. The results are examined within the framework of statistical thermodynamic models. The observed trends are interpreted on the basis of solute structure (e.g. shape, size, flexibility, polarity and polarizability). The results conclusively show that the presence of one or more double bonds in the solute structure increases its compatibility with the nematic and isotropic phases of the liquid crystalline solvent. This effect is more drastic when the double bonds are conjugated. Other implications of this study include shape selective GLC separation of geometric isomers and an examination of the effect of solute structure on the stability of the nematic phase at finite solute concentrations.

INTRODUCTION

Gas-liquid chromatography (GLC) provides, rapidly, reliable thermodynamic data for volatile solutes "at infinite dilution" in nonvolatile solvents.[1] It has been successfully used to investigate mixtures of nonmesomorphic solutes dissolved in the mesophase(s) and isotropic phase of several liquid crystals.[3–16] These studies aimed at examining the effect of solute structure (size, shape, flexibility, polarity and polarizability) on the solution process in ordered and disordered assemblies of rodlike molecules. Many trends have been identified and qualitatively analyzed. Further progress requires additional systematic

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studies (thermodynamic, spectroscopic, structural, etc) which, in turn, should aid in the development of a more quantitative theory. Currently an infinite dilution solution model, originally due to Chow and Martire[6] and recently refined by Martire,[17] offers a plausible framework within which free energies, enthalpies and entropies of solution in liquid crystalline solvents may be examined.

In this study, thermodynamic data from GLC are reported for 32 nonmesomorphic solutes in both the nematic and isotropic phases of *p*-*n*-heptyl-*p*′-cyanobiphenyl (7CB). This study complements previous work[2] on *p*-*n*-pentyl-*p*′-cyanobiphenyl (5CB) and forms part of a systematic study on the members of the *p*-*n*-alkyl-*p*′-cyanobiphenyl homologous series. The solutes used in this work fall into five categories: (a) normal alkanes (C_5 to C_9), (b) several branched alkanes (hexanes, heptanes and 2,2,4-trimethylpentane), (c) several alkenes (trans-2-pentene, hexenes and heptenes), (d) several conjugated and unconjugated hexadienes, and (e) the aromatic molecules: benzene, toluene and the xylenes. The data, interpreted in the light of the above mentioned model, are compared to previous results. The analytical implications of these measurements and their use in estimating the effect of volatile solute impurities on mesophase stability,[2] are briefly discussed.

In addition to complementing earlier work, this study examines the effect that one or more double bonds in the solute structure has on the solution process. Differences between solute structures with conjugated and unconjugated double bonds are also examined.

EXPERIMENTAL SECTION

Chemicals. The stationary liquid phase or solvent 7CB was obtained in sealed containers from BDH Chemicals. The nematic-to-isotropic transition temperature of this liquid crystal, measured visually in a well-stirred and thermally regulated water bath, was 42.60° C. The bath temperature was controlled and measured to better than ±0.05° C using a Sargent Welch heater and circulator in conjunction with a Sargent Welch thermonitor, Model ST. From the sharpness of the phase transition[18,19] (a two-phase region existed over less than 0.10° C) and the agreement of the transition temperature with that observed in other studies,[20,21] the 7CB sample was assessed to be highly pure and was used without further purification. Coles and Strazielle[21] reported a nematic-to-isotropic transition enthalpy of 0.15 $\text{kcal}\cdot\text{mol}^{-1}$ for 7CB. Guided by the earlier study on 5CB,[2] it was assumed that there was no variation in the properties between the bulk sample of 7CB and the support coated samples.

7CB was coated on a Johns-Manville 60–80 mesh, acid washed, and DMCS-treated Chromosorb W. The column used to obtain the thermody-

TABLE I
List of solutes

Solute Number	Compound	Solute Number	Compound
1	*n*-pentane[b]	17	1-heptene
2	*n*-hexane[b]	18	trans-2-pentene
3	*n*-heptane[b]	19	trans-2-hexene
4	*n*-octane[b]	20	trans-3-hexene
5	*n*-nonane[b]	21	trans-2-heptene
6	2-methylpentane	22	1,5-hexadiene
7	3-methylpentane	23	*c*2,*t*4-hexadiene
8	2,2-dimethylbutane	24	*t*2,*t*4-hexadiene
9	2,3-dimethylbutane	25	1,3-hexadiene[a]
10	2-methylhexane[b]	26	1,4-hexadiene[a]
11	3-methylhexane[b]	27	2,3-hexadiene[a]
12	2,2-dimethylpentane[b]	28	benzene[b]
13	2,3-dimethylpentane[b]	29	toluene[b]
14	3,3-dimethylpentane	30	*o*-xylene[b]
15	2,2,4-trimethylpentane	31	*m*-xylene[b]
16	1-hexene	32	*p*-xylene[b]

[a] Available as a mixture of isomers.
[b] Solutes previously studies with 5CB[2].

namic data contained 11.43 ± 0.01% 7CB. Details of the column preparation are given elsewhere.[2,10,26]

The solutes, listed in Table 1, were all sufficiently volatile at the experimental temperatures and, except for the critical constants of the hexadienes, their physical properties were available[22] or could be accurately computed.[22-25] All the solutes, obtained from Fluka chemicals, were highly pure and were used as supplied.

Apparatus and Procedure. A Perkin Elmer Model 3920 gas chromatograph, equipped with a hot-wire thermal conductivity detector (with W-Re elements), was used as a dual-column instrument in this investigation. Temperature control better than ±0.05° C was achieved by circulating water at a constant temperature (using a Lauda K-4/R constant temperature circulator) through a copper coil in the cavity housing the columns. An impeller circulating air within this cavity ensured temperature uniformity throughout the column. The carrier gas (high purity helium) was further purified by passing it consecutively through packings of silica gel and 5 Å molecular seive supplied by Analabs Inc. Carrier gas pressure was controlled using the regulator supplied with the instrument and measured at the column inlet, to within ±0.5 torr, using a mercury manometer. The procedure followed to obtain accurate solute retention volumes is described elsewhere.[1,2,6,26] Adequate care was taken to ensure the attainment of the "infinite dilution condition."[2,26,29] Interfacial effects[2,4,8,27,29] were absent. Use of internal standards indicated negligible bleeding or decomposition of the liquid phase during the period of this study.

RESULTS

The primary data and thermodynamic quantities determined from it,[52] are too large for inclusion within this text. Therefore, only the results (representative in some cases) relevant to the discussion and analyses which follow are given.

Solute specific retention volumes (V_g^0)[1,6,26] were obtained at four well-spaced temperatures in the nematic and isotropic phases of 7CB. The nematic region temperatures were 32.25, 33.70, 36.20, and 38.90° C. The isotropic region temperatures were 44.65, 46.65, 48.65, and 50.80° C. The temperature region in the vicinity of T_{NI} was not studied to avoid pre- or post-transitional effects inherent in the pure nematogen and to preclude the possibility of the solute band inducing a phase transition as it passed through the column.[18,19]

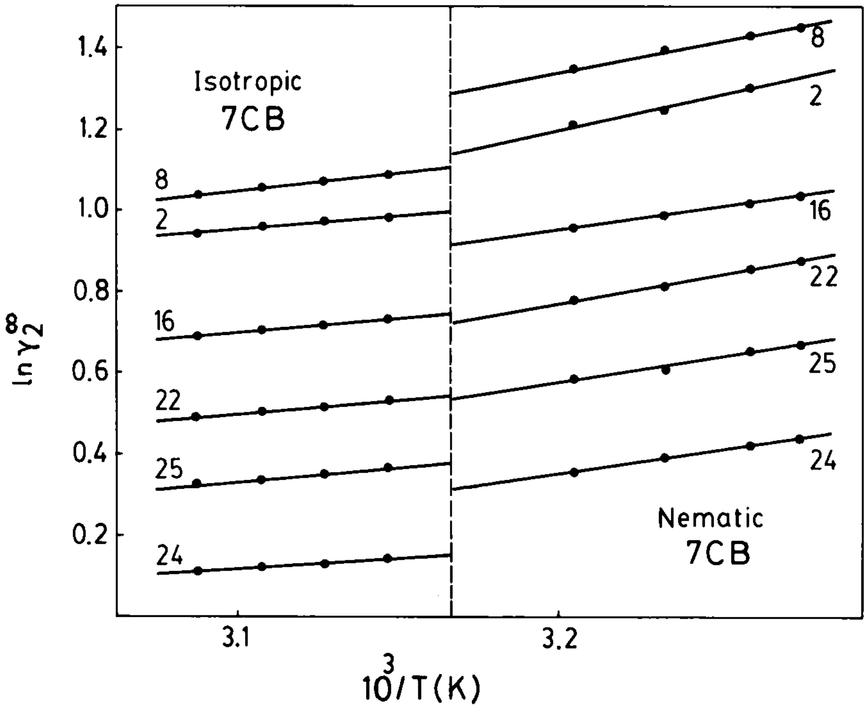

FIGURE 1 Plots of ln γ_2^∞ (infinite dilution solute activity coefficient) vs. $10^3 T^{-1}$ (T in Kelvin) for representative solutes with six carbon atoms in 7CB. Solutes numbered according to Table I. Dashed vertical line indicates T_{NI}^{-1}.

The V_g^0 results[52] represent the average of three separate measurements for each point. The slopes and intercepts from linear least-squares analysis of ln V_g^0 as a function of T^{-1} were also obtained.[52] (All correlation coefficients were found to be in excess of 0.994).

The infinite dilution solute activity coefficients (γ_2^∞) were calculated[2,6] and are reported at representative temperatures in the nematic and isotropic phases of 7CB in Tables II and III. The relative standard deviation in γ_2^∞ is estimated to be approximately 1%.

The infinite dilution solute partial molar excess enthalpies ($\bar{H}^e$) and entropies ($\bar{S}^e$) were obtained[2] from the slopes and intercepts, respectively, of linear least squares fits of ln γ_2^∞ as a function of T^{-1}. Typical plots of ln γ_2^∞ vs. T^{-1} are shown in Figure 1. $\bar{H}^e$ and $\bar{S}^e$ values and their standard deviations are given in Tables II and III.

$\bar{H}^e$ and $\bar{S}^e$ represent molar values for the hypothetical transfer of solute from an ideal solution to the actual solution both being at the same temperature, pressure and composition. They are simply related[2,6,31] to $\Delta\bar{H}$ and $\Delta\bar{S}$, the partial molar enthalpies and entropies of solution respectively, which describe solute transfer from an ideal gaseous mixture to the actual solution (again both being at the same temperature, pressure and composition). Unlike $\bar{H}^e$ $\Delta\bar{H}$ does not contain a solute-solute interaction term and provides a *relative* measure of solute-solvent interaction strengths. $\Delta\bar{H}$ and $\Delta\bar{S}$ values at representative temperatures are given in Tables II and III.

BACKGROUND

The various trends observed on systems similar to those considered in this study have been discussed in an earlier paper.[2] For the sake of consistency we present here the salient features of that discussion.

The main sources of deviation from ideal solution behavior are: combinational, structural (rotational and conformational), and energetic.[6,17] Nematogenic solvents possess orientational order which is long-ranged (thousands of angstroms) in the nematic phase and short-ranged (tens of angstroms) in the isotropic phase.[32] This orientational order, believed to result from anisotropic repulsive interactions,[18,33] imposes rotational and conformational restrictions on dissolved nonnematogenic solutes. In such systems the structural contribution to deviations from ideal solution behavior depends on the orientational order and is coupled to the energetic contribution.[6,17]

The combinational contribution, for a given solute/solvent mixture, is the same in the nematic and isotropic liquid phases. For the systems at hand (solutes smaller in size than the solvent) this contribution leads to positive excess entropies and negative deviations from Raoult's law, both of which become more pronounced as the solvent-to-solute size ratio increases.

TABLE II
Thermodynamic data for solutes in nematic 7CB[a]

Solute No.[b]	γ_2^∞ at 36.20°C	H^e	S^e	$-\Delta\overline{H}$ at 36.20°C	$-\Delta\overline{S}$ at 36.20°C
1	3.21	2.09 ± 0.15	4.43 ± 0.49	4.07	15.48
2	3.48	3.41 ± 0.25	8.55 ± 0.80	3.97	15.33
3	3.78	2.99 ± 0.25	7.02 ± 0.82	5.62	20.81
4	4.07	3.19 ± 0.13	7.53 ± 0.43	6.53	23.91
5	4.39	3.03 ± 0.36	6.88 ± 1.17	7.91	28.48
6	3.78	2.89 ± 0.21	6.69 ± 0.69	4.11	15.92
7	3.54	2.98 ± 0.18	7.12 ± 0.58	4.11	15.81
8	4.03	2.95 ± 0.13	6.77 ± 0.42	3.52	14.14
9	3.64	2.94 ± 0.19	6.95 ± 0.62	3.87	15.08
10	4.11	2.86 ± 0.16	6.46 ± 0.51	5.32	20.01
11	3.94	3.05 ± 0.18	7.15 ± 0.57	5.19	19.50
12	4.47	3.22 ± 0.26	7.46 ± 0.84	4.39	17.14
13	3.84	3.28 ± 0.25	7.95 ± 0.80	4.78	18.10
14	3.85	3.33 ± 0.20	8.09 ± 0.66	4.44	17.03
15	4.91	3.45 ± 0.22	8.00 ± 0.72	4.85	18.83
16	2.70	2.24 ± 0.07	5.27 ± 0.23	4.94	17.93
17	2.92	2.61 ± 0.13	6.30 ± 0.42	5.77	20.80
18	2.52	2.02 ± 0.09	4.68 ± 0.30	4.22	15.47
19	2.81	2.07 ± 0.12	6.69 ± 0.38	4.65	17.09
20	3.04	2.66 ± 0.27	6.40 ± 0.87	4.66	17.28
21	3.07	2.65 ± 0.19	6.34 ± 0.62	5.88	21.23
22[c]	2.24	2.80 ± 0.24	7.43 ± 0.79	4.46	16.03
23[c]	1.48	2.36 ± 0.15	6.86 ± 0.48	5.71	19.25
24[c]	1.42	1.81 ± 0.26	5.12 ± 0.84	6.27	20.98
25[c,d]	1.84	2.43 ± 0.22	6.62 ± 0.72	5.37	18.58
26[c,d]	2.32	2.92 ± 0.10	7.75 ± 0.32	4.56	16.43
27[c,d]	1.45	2.05 ± 0.18	5.87 ± 0.57	6.03	20.24
28	1.07	1.89 ± 0.19	5.97 ± 0.62	6.05	19.69
29	1.09	2.06 ± 0.29	6.46 ± 0.93	6.88	22.43
30	1.11	1.68 ± 0.07	5.22 ± 0.23	8.58	27.96
31	1.21	2.77 ± 0.31	8.59 ± 1.01	7.31	24.00
32	1.09	1.80 ± 0.44	5.67 ± 1.41	8.21	26.70

[a] Enthalpies are in kcal/mol and entropies are in cal/mol deg.
[b] Solutes numbered according to Table I.
[c] Solutes with activity coefficients uncorrected for the non-ideality of the vapor phase.
[d] Solutes available as a mixture of isomers.

For rigid, rodlike solutes, the longer the molecule is the greater is its orientational order,[34] the more negative is its excess entropy and the more positive is its deviation from Raoult's law. This trend applies to semiflexible chain-like solutes (such as *n*-alkanes) that acquire some orientational order in the nematogenic solvent.[35] Conformational restrictions on such molecules reinforce the above trends, which are more pronounced with more ordered and more rigid solvents. These effects, mainly entropic, are negligible for rigid unaligned molecules.[18]

The energetic contribution provides the bulk of the observed $\overline{H}^{e}$[6,17,35] and

TABLE III
Thermodynamic data for solutes in isotropic 7CB[a]

Solute Number	γ_2^∞ at 48.65°C	$\bar{H}^e$	$\bar{S}^e$	$-\Delta\bar{H}$ at 48.65°C	$-\Delta\bar{S}$ at 48.65°C
1	2.44	1.83 ± 0.27	3.93 ± 0.84	4.16	14.68
2	2.61	1.21 ± 0.03	1.86 ± 0.09	5.99	20.51
3	2.80	1.70 ± 0.24	3.22 ± 0.76	6.71	22.89
4	3.00	1.20 ± 0.19	1.52 ± 0.60	8.32	28.04
5	3.24	1.36 ± 0.10	1.88 ± 0.32	9.41	31.57
6	2.77	1.92 ± 0.33	3.94 ± 1.04	4.89	17.23
7	2.59	0.96 ± 0.18	1.09 ± 0.56	5.95	20.40
8	2.88	1.70 ± 0.05	3.18 ± 0.15	4.60	16.40
9	2.64	1.79 ± 0.20	3.65 ± 0.61	4.85	17.00
10	2.98	1.52 ± 0.07	2.57 ± 0.22	6.46	23.26
11	2.83	1.44 ± 0.16	2.39 ± 0.49	6.61	22.62
12	3.14	1.93 ± 0.20	3.74 ± 0.62	5.49	19.34
13	2.72	1.40 ± 0.06	2.37 ± 0.20	6.47	22.10
14	2.71	1.76 ± 0.20	3.50 ± 0.62	5.84	20.12
15	3.41	1.71 ± 0.14	2.88 ± 0.45	6.41	22.36
16	2.02	1.39 ± 0.03	2.93 ± 0.08	5.61	18.82
17	2.19	1.10 ± 0.11	1.86 ± 0.34	7.09	23.59
18	1.90	1.23 ± 0.12	2.54 ± 0.36	4.85	16.33
19	2.09	1.27 ± 0.12	2.48 ± 0.38	5.91	19.83
20	2.24	1.40 ± 0.11	2.74 ± 0.33	5.74	19.46
21	2.26	1.21 ± 0.21	2.12 ± 0.65	7.13	23.79
22[c]	1.66	1.36 ± 0.03	3.22 ± 0.10	5.72	18.78
23[c]	1.13	1.06 ± 0.05	3.06 ± 0.15	6.83	21.46
24[c]	1.14	0.92 ± 0.10	2.58 ± 0.30	6.97	21.94
25[c,d]	1.40	1.73 ± 0.18	4.71 ± 0.55	5.88	18.95
26[c,d]	1.68	1.41 ± 0.04	3.34 ± 0.14	5.89	19.34
27[c,d]	1.31	0.78 ± 0.05	2.16 ± 0.16	7.11	22.35
28	0.85	0.85 ± 0.02	2.96 ± 0.08	6.92	21.19
29	0.87	0.75 ± 0.14	2.60 ± 0.44	8.03	24.69
30	0.88	0.62 ± 0.09	2.20 ± 0.28	9.51	29.31
31	0.94	0.76 ± 0.17	2.50 ± 0.54	9.20	28.45
32	0.89	0.62 ± 0.13	2.18 ± 0.39	9.26	28.55

[a] Enthalpies are in kcal/mol and entropies are in cal/mol deg.
[b] Solutes numbered according to Table I.
[c] Solutes with activity coefficients uncorrected for the non-ideality of the vapor phase.
[d] Solutes available as a mixture of isomers.

depends on the orientational order present in the system.[36] According to lattice models and a recent extension of the Maier–Saupe theory,[34] the energetic contribution leads to more positive excess quantities and more positive deviations from Raoult's law in the nematic phase relative to the isotropic phase. These differences are greater for globular solutes which are less ordered relative to the nematic phase.

DISCUSSION

Comparison with Previous Results. Aromatic solutes in isotropic 7CB showed negative deviations ($\gamma_2^\infty < 1$) from Raoult's law. Otherwise, the trends within the same phase and between the nematic and isotropic phases of 7CB are like those previously encountered with MBBA and 5CB.[2]

Solutes common to this work and the earlier study[2] on MBBA and 5CB are; *n*-alkanes (solutes 1–5), branched heptanes (solutes 10–13) and the aromatics (solutes 28–32). For all these solutes the differences between two phases of a solvent are generally more pronounced than the differences between a given phase of the three solvents. Only for aromatic solutes in the isotropic phase are the $\bar{H}^e$ and $\bar{S}^e$ values of 7CB and 5CB somewhat closer together and different from those of MBBA (See Tables IV and V). On the whole it seems that for these liquid crystals (of comparable nematic-to-isotropic transition temperatures and length-to-breadth ratios) the solvent orientational order overrides the solvent chemical nature in determining the relative solution properties of a given nonmesomorphic solute.

Relative to solutions in MBBA, solutions in 7CB and 5CB were similar with comparable $\Delta\bar{H}$ and $\Delta\bar{S}$ values. This statement holds in both the nematic and isotropic phases and for all the solutes studied in these three liquid crystals. Thus earlier comparisons[2] between 5CB and MBBA apply equally well for 7CB and MBBA solutions.

Although for 7CB and 5CB the $\Delta\bar{H}$ and $\Delta\bar{S}$ values are comparable, the γ_2^∞

TABLE IV

$\bar{H}^e$ values for aromatic solutes in the isotropic phases of 5CB[a], 7CB and MBBA[a]

Solute Number[b]	5CB	7CB	MBBA
28	0.86 ± 0.05	0.85 ± 0.02	0.44 ± 0.01
29	0.62 ± 0.04	0.76 ± 0.14	0.10 ± 0.02
30	0.84 ± 0.22	0.62 ± 0.09	0.32 ± 0.03
31	0.72 ± 0.13	0.76 ± 0.17	0.25 ± 0.07
32	0.66 ± 0.14	0.62 ± 0.18	0.08 ± 0.01

[a] Ref. 2.

[b] Solutes numbered according to Table I.

TABLE V

$\bar{S}^e$ values for aromatic solutes in the isotropic phases of 5CB[a], 7CB and MBBA[a]

Solute Number[b]	5CB	7CB	MBBA
28	2.70 ± 0.17	2.69 ± 0.08	1.07 ± 0.03
29	1.87 ± 0.13	2.60 ± 0.44	−0.08 ± 0.05
30	2.50 ± 0.68	2.28 ± 0.28	0.55 ± 0.09
31	2.27 ± 0.41	2.50 ± 0.54	0.20 ± 0.20
32	1.95 ± 0.44	2.10 ± 0.39	−0.28 ± 0.03

[a] Ref. 2.

[b] Solutes numbered according to Table I.

values for 7CB are invariably smaller than those for 5CB. This is not unreasonable since the 7CB values are at a higher temperature. The γ_2^∞ trends in both the nematic and isotropic phases are as follows:

For alkane solutes,

$$(\gamma_2^\infty)_{7CB} < (\gamma_2^\infty)_{MBBA} < (\gamma^\infty{}_2)_{5CB}$$

and for aromatic solutes,

$$(\gamma_2^\infty)_{7CB} < (\gamma_2^\infty)_{5CB} < (\gamma_2^\infty)_{MBBA}$$

In all following discussions, we adopt the following terminology with respect to $\Delta\bar{H}$ nd $\Delta\bar{S}$: *larger* will refer to *more negative* values, while *smaller* will refer to *less negative* ones.

For *n*-alkanes (solutes 1-5), isomeric hexanes (solutes 2 and 6–9), isomeric heptanes (solutes 3 and 10–14), isomeric octanes (solutes 4 and 15) and the aromatics (solutes 28–32), the discernable γ_2^∞, $\Delta\bar{H}$ and $\Delta\bar{S}$ trends in the nematic and isotropic phases of 7CB are very similar to those previously encountered with MBBA and 5CB solvents.[2]

The absence of a general trend in the γ_2^∞ values of isomeric alkanes is due to a complex interplay between smaller $\Delta\bar{H}$ (tending to increase γ_2^∞) and smaller $\Delta\bar{S}$ (tending to decrease γ_2^∞) values resulting from increased branching.[2] To understand how these counteracting enthalpy and entropy effects affect the γ_2^∞ values of isomeric alkanes, more information on the structure of solution, the molecular conformations, etc., is needed. In the absence of such information we content ourselves with an overall description of the variation of γ_2^∞ amongst isomeric alkanes.

The available data (See Tables VI and VII) indicates that, for the same number of carbon atoms in the solute molecule, the branched alkane has, in general, a higher γ_2^∞ value than the *n*-alkane. Exceptions to this rule where γ_2^∞ values are comparable and/or the above trend is reversed, are encountered among solutes with centrally located branches. The variation of γ_2^∞ with the extent in branching is more pronounced in the nematic phase. At least for hexanes and heptanes, the more centrally located the branches are the closer is the γ_2^∞ value to that of the straight chain isomer. Contrasted with 2-methylhexane (solute 10), 3-methylhexane (solute 11) has a lower γ_2^∞, i.e. *solute compatibility with the solvent increases as the branching is more centrally located.* A similar trend is observed when 3,3-dimethylpentane and 2,2-dimethylpentane are compared.

Alkenes (*Solute 16–21*). The same trends between the nematic and isotropic phases (i.e. smaller γ_2^∞ values and larger $\Delta\bar{H}$ and $\Delta\bar{S}$ values in the isotropic phase) are encountered here. For alkene solutes with the double bond in the same position, the trend with increasing chain length is, understandably, the same as that encountered with *n*-alkane solutes. Thus in both phases of 7CB,

TABLE VI

Values of γ_2^∞ for alkanes in the nematic phases of 5CB[2], MBBA[2] and 7CB at $T/T_{NI} = 0.979731$[a]

Solute	5CB	MBBA	7CB
n-pentane	4.58	—	3.21
2,2-dimethylbutane	—	—	4.03
2-methylpentane	—	—	3.78
2,3-dimethylbutane	—	—	3.64
3-methylpentane	—	—	3.54
n-hexane	5.05	4.24	3.48
2,4-dimethylpentane	6.75	—	—
2,2-dimethylpentane	6.69	5.57	4.47
2-methylhexane	6.11	5.09	4.11
2,2,3-trimethylbutane	5.96	5.06	—
3-methylhexane	5.87	4.87	3.94
3,3-dimethylpentane	—	4.85	3.85
2,3-dimethylpentane	5.64	4.75	3.84
n-heptane	5.51	4.63	3.78
2,2,4-trimethylpentane	—	—	4.91
n-octane	5.98	5.13	4.07
3,3-diethylpentane	5.97	5.24	—
n-nonane	6.40	5.52	4.39

[a] This reduced temperature corresponds to 28.75° C for 5CB, 38.55° C for MBBA and 36.2° C for 7CB.

γ_2^∞, $\Delta\bar{H}$ and $\Delta\bar{S}$ are larger for longer chains. Comparing an alkene with its alkane counterpart (i.e. an alkane with the same number of carbon atoms) is less straightforward. The introduction of a double bond into a straight chain structure of carbon atoms increases its rigidity and polarizability. Alkenes are therefore somewhat less easily aligned than their alkane counterparts and upon solvation, lose fewer degrees of conformational freedom and this tends to make their $\Delta\bar{S}$ values smaller. Because alkenes are less aligned they are, on the average, at larger intermolecular distances from their host molecules. This results in smaller solute-solvent interaction and therefore smaller $\Delta\bar{H}$ values. To sum up, the increased rigidity of alkenes relative to alkanes tends to make their $\Delta\bar{H}$ and $\Delta\bar{S}$ values smaller. On the other hand the increase in polarizability leads to stronger solute-solvent interactions and larger $\Delta\bar{H}$ and $\Delta\bar{S}$ values. The interplay between these opposing effects is complex and difficult to determine in the absence of knowledge of solution structure. In addition the rigidity effect depends on the position of the double bond, with the more centrally located double bond resulting in a more rigid structure. Also the smaller conformational entropy losses of alkenes relative to alkanes may be made up for by an increase in the rotational freedom of the molecule as a whole.

TABLE VII
Values of γ_2^∞ for alkanes in the isotropic phases of 5CB[2], MBBA[2] and 7CB at $T/T_{NI} = 1.019161$[a]

Solute	5CB	MBBA	7CB
n-pentane	3.40	—	2.44
2,2-dimethylbutane	—	—	2.88
2-methylpentane	—	—	2.77
2,3-dimethylbutane	—	—	2.64
3-methylpentane	—	—	2.59
n-hexane	3.67	3.45	2.61
2,4-dimethylpentane	4.66	—	—
2,2-dimethylpentane	4.57	4.31	3.14
2-methylhexane	4.35	4.01	2.98
2,2,3-trimethylbutane	4.09	3.92	—
3-methylhexane	4.10	3.82	2.83
3,3-dimethylpentane	—	3.78	2.71
2,3-dimethylpentane	3.94	3.71	2.72
n-heptane	3.99	3.72	2.80
2,2,4-trimethylpentane	—	—	3.41
n-octane	4.32	4.13	3.00
3,3-diethylpentane	3.99	3.91	—
n-nonane	4.69	4.46	3.24

[a] This reduced temperature corresponds to 41.40°C for 5CB, 51.10°C for MBBA and 48.65°C for 7CB.

In nematic 7CB alkenes have larger $\Delta\bar{H}$ and comparable or larger $\Delta\bar{S}$ values relative to their alkane counterparts. Lower γ_2^∞ values for alkenes reflect the predominance of the enthalpy effect. No definite $\Delta\bar{H}$ and $\Delta\bar{S}$ trends exist in isotropic 7CB where again the γ_2^∞ values for alkenes are smaller than those for the alkane counterparts. In general alkenes are more compatible with both phases of 7CB (i.e. have lower γ_2^∞ values) than their alkane counterparts. Amongst themselves the ***compatibility of alkenes with both phases of 7CB increases (i.e. γ_2^∞ decreases) as the double bond moves towards the end carbon atoms.***

Hexadienes (*Solutes 22-27*). Again the same general trends between the nematic and isotropic phases (i.e. smaller γ_2^∞'s and larger $\Delta\bar{H}$ and $\Delta\bar{S}$ values in the isotropic phase) are encountered here. Judging by their lower γ_2^∞ values the hexadienes are more compatible with both phases of 7CB than their hexene counterparts. For 1,5-hexadiene (solute 22) and 1,4-hexadiene (solute 26) in nematic 7CB this increased compatibility seems to result from more favorable (smaller) $\Delta\bar{S}$ values, which are possibly due to their greater ease of alignment. Nevertheless the more general trend (for the remaining hexadienes in the nematic phase and all the hexadienes in the isotropic phase) is larger $\Delta\bar{H}$

values due to stronger solute-solvent interactions resulting from the greater molecular polarizability of the hexadienes. That the enthalpy effect, resulting from conjugation of the double bonds, predominates over the entropy effect, resulting from increased solute rigidity, is seen in the results for 1,4-hexadiene (solute 26) and 1,3-hexadiene (solute 25) in both phases (See Figure 1). The smaller γ_2^∞ values for 1,3-hexadiene indicate the predominance of its more favorable (larger) $\Delta\bar{H}$ over its less favorable (larger) $\Delta\bar{S}$. Even larger $\Delta\bar{H}$ and $\Delta\bar{S}$ values are encountered in both phases when the conjugation is in the center of the six-carbon-structure as in the case of the 2,4-hexadienes (solutes 24, 25 and 27). Again the favorable enthalpy predominates resulting in smaller γ_2^∞ for these solutes (See Figure 1). Differences can even be discerned between the isomers *t*2,*t*4-hexadiene (solute 24) and *c*2,*t*4-hexadiene (solute 23) in nematic 7CB. The more rodlike *t*2,*t*4-hexadiene is slightly more compatible with nematic 7CB via its favorable enthalpy, that is due to a more negative interchange energy, which in turn is a result of its greater orientational order. In the isotropic phase their γ_2^∞ values are much closer to each other and the above trend is reversed (See Figure 2).

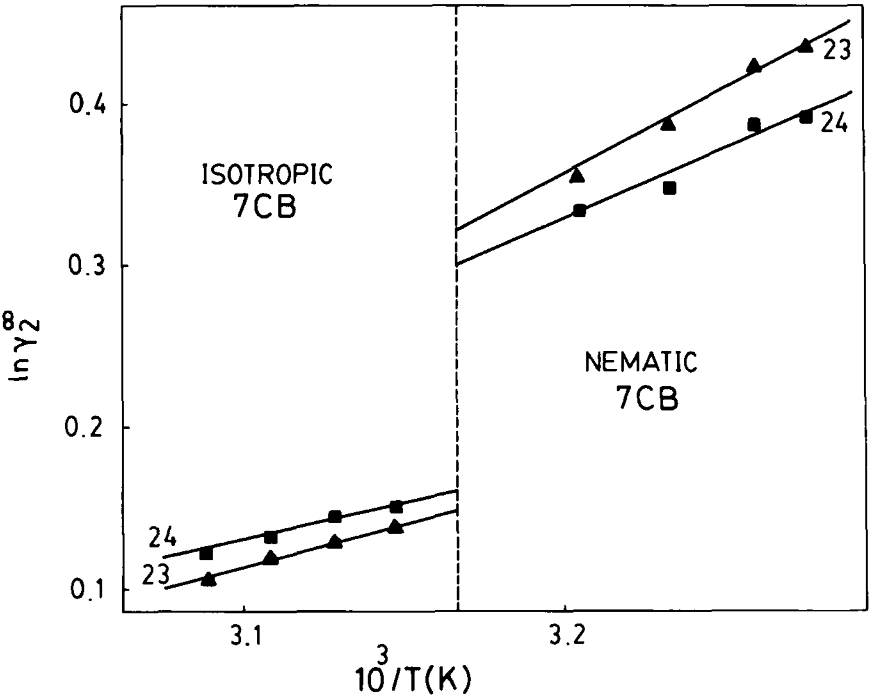

FIGURE 2 Plots of ln γ_2^∞ (infinite dilution solute activity coefficient) vs. 10^3T^{-1} (T in Kelvin) for *t*2,*t*4-hexadiene (solute 24) and *c*2,*t*4-hexadiene (solute 23). Dashed vertical line indicates T_{NI}^{-1}.

Aromatics (*Solutes 28-32*). For both phases, the trends in $\Delta\bar{H}$ and $\Delta\bar{S}$ are *o*-oxylene > *p*-xylene > *m*-xylene > toluene > benzene, while γ_2^∞ follows the trend *m*-xylene > *p*-xylene ≈ *o*-xylene > toluene ≈ benzene. Contrary to earlier studies[2] on 5CB and MBBA solvents, here the trends in the isotropic phase are well defined and the positions of the *o*- and *p*-xylenes are reversed. The $\Delta\bar{H}$ trend may be rationalized on the basis of molecular shape, molecular size and dispersion forces. The larger xylene molecules (with greater molecular polarizability) should have stronger solute-solvent interactions, and therefore larger $\Delta\bar{H}$ values, than the smaller toluene molecule. The same argument applies for toluene and benzene. The $\Delta\bar{H}$ values for *o*- and *p*-xylene are rather close in this study and even closer in the earlier measurements[2] with 5CB and MBBA solvents. Because of its rodlike structure, one expects *p*-xylene to be most ordered in solution and to experience the strongest effective solute-solvent (dispersion) interactions. That $\Delta\bar{H}$ for *o*-xylene is close to (in earlier studies) or slightly greater than (in this study) the $\Delta\bar{H}$ for *p*-xylene, is possibly due to a role played by dipolar interactions, which are non-existant in the symmetric *p*-xylene structure. *m*-xylene seems to be least ordered in solution. The trend in $\Delta\bar{S}$ follows both the trend in $\Delta\bar{H}$ (stronger interactions should result in greater translational entropy losses) and the trend expected from the combinational term ($\bar{S}^c$ increases and $\Delta\bar{S}$ decreases with decreasing solute size). The trend in γ_2^∞ indicates that the enthalpy trend predominates. The larger $\Delta\bar{H}$ and $\Delta\bar{S}$ values and smaller γ_2^∞ values for *p*-xylene relative to *m*-xylene found in this study have been encountered before.[2]

Finally comparing collectively the γ_2^∞ values for the various classes of solutes, the following trend: alkanes > alkenes > unconjugated dienes > conjugated dienes > aromatics, holds in both phases of 7CB. This trend is indicated in Figure 1 for representative solutes with six carbon atoms. It is attributed, in general, to the increase in $\Delta\bar{H}$ as the number of double bonds in the structure increases and, in part, to increasingly unfavorable conformational contributions in the direction of structures with fewer double bonds. Also, as has been indicated earlier, *the more centrally located the conjugated double bonds are the smaller is the* γ_2^∞ *value.*

ANALYTICAL CONSIDERATIONS

In gas chromatographic separations, the separation factor $\alpha_{x,y}$ for two components x and y in a mixture is given by

$$\alpha_{x,y} = S_{x,y} \cdot F_{x,y} \tag{1}$$

where $S_{x,y} = \gamma_x^\infty / \gamma_y^\infty$ is the selectivity and $F_{x,y} = f_x^0 / f_y^0$ is the ratio of fugacities (or approximately vapor pressures).

To effect separations of mixtures whose components have similar boiling points ($F_{x,y} \approx 1.0$), an $S_{x,y}$ factor greater than unity is needed. Such is the case in separations of meta- and para-disubstituted benzenes using nematic liquid phases[5,6,37] where the more rodlike para isomer achieves the lower γ_2^∞ via its more favorable enthalpy.

Because no general trend exists for the γ_2^∞ values of branched alkanes, the elution order of a complex mixture of alkane isomers cannot be predicted. Nevertheless, it has been shown[2] that separations of certain pairs of "close boiling" alkane isomers are enhanced in nematic liquid phases. This conclusion is confirmed by the results of this study on 7CB. From the isomeric hexanes, the pair 2-methylpentane (x), $bp = 60.3°C$, and 3-methylpentane (y), $bp = 63.3°C$ have $F_{x,y} = 1.11$ at 32.35°C. In nematic 7CB, $S_{x,y} = 1.06$ and $\alpha_{x,y} = 1.18$. From the isomeric heptanes, the pair 2-methylhexane (x), $bp = 90.1°C$, and 3-methylhexane (y), $bp = 91.9°C$ have $F_{x,y} = 1.07$ at 32.25°C. In nematic 7CB, $S_{x,y} = 1.04$ and $\alpha_{x,y} = 1.11$. Therefore, a relatively difficult "boiling-point" separation requiring high column efficiency now becomes a relatively routine one, owing to the healthy $S_{x,y}$ factor. It must be noted that sometimes, the selectivity factor for a pair of solutes is less than unity, resulting in a more difficult separation than one based purely on the fugacity ratio. For example, for the pair 2,3-dimethylbutane (x), $bp = 58.0°C$, and 2-methylpentane (y), $bp = 60.3°C$ $F_{x,y} = 1.10$ at 32.25°C. In nematic 7CB, $S_{x,y} = 0.97$ and $\alpha_{x,y} = 1.06$.

Next we consider the pair of solutes *t*2,*t*4-hexadiene (y) and *c*2,*t*4-hexadiene (x), with identical boiling points and Antoine equation parameters,[22] and therefore having an $F_{x,y} = 1.00$ at all temperatures. As discussed earlier, the more rodlike *t*2,*t*4-isomer has the lower γ_2^∞ value, via its more favorable enthalpy. For this pair of solutes, in nematic 7CB at 32.35°C, $S_{x,y} = \alpha_{x,y} = 1.05$. In fact if such a separation is achieved, it would have been done *solely* on the basis of the selectivity factor. Such separation would be even more difficult in isotropic 7CB at 48.65°C in which case $S_{x,y} = \alpha_{x,y} = 1.01$. Figure 2 illustrates how the γ_2^∞ values for the *t*2,*t*4- and *c*2,*t*4-hexadiene isomers are reversed and closer in value in the isotropic phase relative to the nematic phase.

The use of nematic liquid crystals as stationary phases in gas chromatographic separations has become increasingly popular in recent years.[38-45]

PHASE DIAGRAMS

With few exceptions,[46,48] nonmesomorphic solute impurities depress the nematic-to-isotropic transition temperature (T_{NI}) in liquid crystals[50] and lead to the formation of a two phase region.[18,49,50] The general phase behavior at low

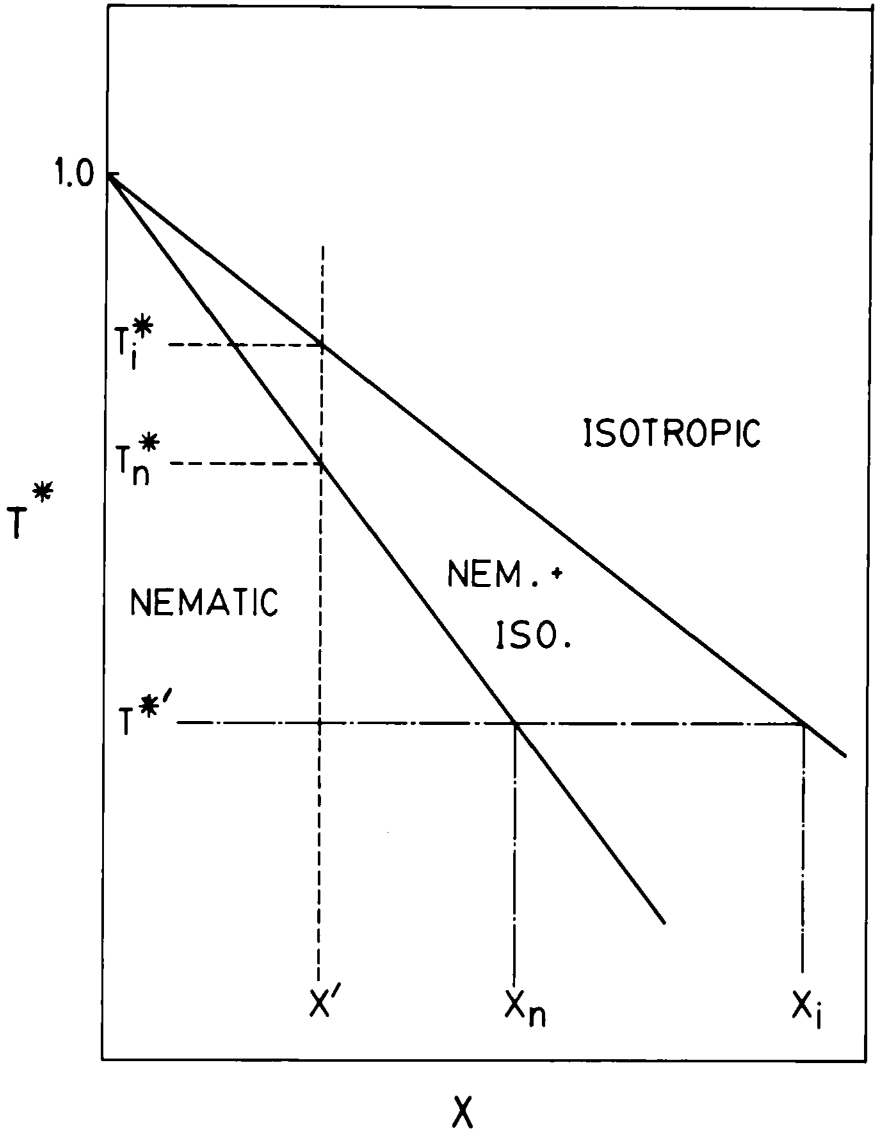

FIGURE 3 Typical reduced temperature (T^*)—solute mole fraction (x) phase diagram for binary mixture at low solute mole fraction.

solute mole fraction ($x < \sim 0.1$) is illustrated in Figure 3, where $T^*(= T/T_{NI})$ is a reduced temperature.

Direct determinations of these phase diagrams[18,19] show that both phase boundary lines are virtually linear in the region of low solute mole fractions.

If, β_n and β_i, the *negatives* of the nematic and isotropic phase boundary lines respectively, and given by

$$\beta_n = -(dT^*/dx)_n \tag{2a}$$

$$\beta_i = -(dT^* \ dx)_i \tag{2b}$$

are known, one can (a) construct the phase diagram, (b) determine the extent of the two phase region, and (c) evaluate the ability of the solute to disrupt the long-range order in the nematic phase. Moreover, from thermodynamics, it has been shown[18,33] that the *negatives* of the *limiting slopes* ($x \to 0$, $T \to T_{NI}$ or $T^* \to 1$) are given by

$$\beta_n^\infty = \left(\frac{\gamma_n^\infty}{\gamma_i^\infty} - 1\right) \cdot \frac{R}{\Delta S_{NI}} \tag{3a}$$

$$\beta_i = \left(1 - \frac{\gamma_i^\infty}{\gamma_n^\infty}\right) \cdot \frac{R}{\Delta S_{NI}} \tag{3b}$$

where $R/\Delta S_{NI}$ refers to the pure nematogenic solvent, and γ_n^∞ and γ_i^∞ are the infinite dilution solute activity coefficients in the nematic and isotropic phase, respectively, each extrapolated to T_{NI}. The *solution* property ($\gamma_\eta^\infty / \gamma_i^\infty$) is obtained from GLC. The solvent property ΔS_{NI} (= $\Delta H_{NI}/T_{NI}$) is measured calorimetrically (DSC).

Accordingly, β_n^∞ and β_i^∞ (which have been shown[2] to approximate well to β_n and β_i respectively) can be directly obtained through a combination of GLC and DSC measurements. This finding provides an experimental approach for (a) testing statistical theories of binary nematic mixtures,[19,37] and (b) assessing the effect of potential impurities (introduced possibly during the synthesis and separation of the nematogen), or of additives (used in liquid crystalline displays), on nematic phase stabilty. It is more rapid that the tedious direct determination of β_n and β_i using the "visual method"[18,19] especially (as in this work) when various series of solutes are studied. This method is limited by the requirement that the solute be sufficiently volatile[51] and the accuracy of DSC measurement.

We note from Eq. (3) that, while both the ($\gamma_n^\infty/\gamma_i^\infty$) ratio and ΔS_{NI} determine the magnitude of β, it is the former that determines the sign of β. All the solute examined in this study, have positive β values ($\gamma_n^\infty/\gamma_i^\infty > 1$) and depress the nematic-to-isotropic transition temperature T_{NI}. Clearly the stabilty of the nematic phase does not depend on the individual γ_n^∞ and γ_i^∞ values (which reflect solute compatibility with the nematic and isotropic phases respectively) but on their *ratio* (which reflects the *relative preference* of the solute for the two phases). This is why the $\gamma_n^\infty/\gamma_i^\infty$ trends (and of course the β_n^∞ and β_i^∞ trends) indicated in Table VIII for the various solute groups are different from the individual γ_2^∞ trends, discussed previously and indicated, in part, in Figure 2

TABLE VIII

Values of $(\gamma^{\infty}_{n}/\gamma^{\infty}_{i})$ at T_{NI}, $\beta^{\infty a}_{n}$ and $\beta^{\infty a}_{i}$ for various solute groups in 7CB.

Solutes	$(\gamma^{\infty}_{n}/\gamma^{\infty}_{i})$	β^{∞}_{n}	β^{∞}_{i}
n-alkanes[b]	1.12 ± 0.01	0.53	0.48
branched alkanes	1.16 ± 0.01	0.70	0.61
alkenes	1.16 ± 0.01	0.70	0.61
hexadienes	1.14 ± 0.01	0.61	0.54
aromatics	1.12 ± 0.02	0.53	0.48

[a] Standard deviation not given for β values since they have not been reported[21] for the ΔH_{NI} value.

[b] The $(\gamma^{\infty}_{n}/\gamma^{\infty}_{i})$ for *n*-pentane (1.164) was suspect so it has not been included in the averaged result for *n*-alkanes.

for various representative solutes. From Eq. (2) and (3) it can be shown that

$$\frac{x_i}{x_m} = \frac{\beta_n}{\beta_i} = \frac{\gamma^{\infty}_{n}}{\gamma^{\infty}_{i}} \tag{4}$$

where x_i and x_n are the values of the solute mole fraction at the isotropic and nematic phase boundary lines at a fixed T^* value. Thus the *extent* of the two phase regions also depends solely on $\gamma^{\infty}_{n}/\gamma^{\infty}_{i}$.

The smaller the values of ΔS_{NI} the larger is β^{∞}. Hence, nematic solvents exhibiting more weakly first order nematic-to-isotropic transitions are more easily pertubed by solute impurities. The values of β^{∞}_{n} and β^{∞}_{i} given in Table VIII were calculated using the value of ΔH_{NI} reported by Coles and Strazielle.[21] The role played by the solvent structure will be considered in a future study when more measurements are done on other members of the *p*-*n*-alkyl-*p'*-cyanobiphenyl series are completed, and when more DSC measurements are made.

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52. Tables containing the primary data and the thermodynamic quantities obtained therefrom may be obtained directly from the author.