

# Thermodynamics of Solution of Nonmesomorphic Solutes at Infinite Dilution in the Isotropic and Nematic Phases of *p*-Cyanophenyl *p*-*n*-Alkylbenzoates

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Infinite-dilution activity coefficients ( $\gamma_2^\infty$ ) and partial molar excess enthalpies and entropies obtained using gas–liquid chromatography are reported for 10 solutes, varying in molecular size, shape and flexibility, in the isotropic and the nematic phases of the ethyl, propyl, butyl, pentyl, hexyl, and heptyl members of the *p*-cyanophenyl *p*-*n*-alkylbenzoate homologous series of liquid crystals. General trends in the six solvents are identified. The results, which corroborate earlier results, demonstrate the effects that the solute structure and the length of the flexible alkyl tail on the solvent molecule have on the solution process.

## Introduction

Gas–liquid chromatography (GLC) is now established (Vogel et al., 1983) as a reliable technique for obtaining thermodynamic data for volatile solutes at “infinite dilution” in nonvolatile solvents. The speed and ease with which data may be obtained for a wide variety of solutes make GLC the method of choice in Henry’s law region. The validity of the GLC technique has also been established (Chow and Martire, 1969; Schnur and Martire, 1971; Peterson et al., 1972) for the determination of thermodynamic properties of nonmesomorphic solutes in the mesophase(s) and isotropic phase of liquid crystals. Such measurements provide information on the effect that solute structure (size, shape, flexibility, polarizability, and polarity) has on the solution process. Gas chromatographic separations that use liquid crystals as stationary phases (Janini et al., 1975; Zielenski et al., 1976) rely on differences in structure among the components of the mixture. Furthermore, these results may be combined with the entropy change at the mesophase-to-isotropic transition of the relevant pure liquid crystal to provide information (Oweimreen et al., 1979) on the ability of the solute to disrupt the long-range orientational order in the mesophase, which in turn is needed to test statistical theories of binary mixtures (Martire et al., 1976; Oweimreen and Martire, 1980) and to assess the effect of potential additives or impurities on mesophase stability.

The *p*-cyanophenyl *p*-*n*-alkylbenzoates were obtained from F. Hoffmann-La Roche and Co. (Switzerland). They are chemically stable with a manufacturer quoted purity in excess of 99.5% and a water content below 0.03%. The use of internal standards showed that bleeding and decomposition of these liquid crystal stationary phases from GLC columns were negligible during the period of operation. The liquid crystal solvents used in this study are *p*-cyanophenyl *p*-ethylbenzoate, *p*-cyanophenyl *p*-*n*-propylbenzoate, *p*-cyanophenyl *p*-*n*-butylbenzoate, *p*-cyanophenyl *p*-*n*-pentylbenzoate, *p*-cyanophenyl *p*-*n*-hexylbenzoate, and *p*-cyanophenyl *p*-*n*-heptylbenzoate. The solutes used are hexane, heptane, octane, nonane, 3-methylpentane, 2,4-dimethylhexane, hex-1-ene, cyclohexane, 1-*cis*-4-hexadiene, and benzene. By systematically studying various categories of solutes with members of homologous series of liquid crystalline solvents, the effects of both the solute structure

and the length of the *n*-alkyl tail on the solvent molecule on the solution process may be examined. This study follows previous similar studies (Oweimreen, 1981, 1982; Ghodbane et al., 1991) on the *p*-(*n*-alkyl)-*p*'-cyanophenyl (RCB) and the *p*-(*n*-alkyloxy)-*p*'-cyanophenyl (ROCB) homologous series (Oweimreen and Shihab, 1994) of liquid crystals.

In this paper thermodynamic measurements are reported, at infinite dilution, for the above mentioned solute + solvent systems. The activity coefficients of solutes in nematic *p*-cyanophenyl *p*-*n*-alkylbenzoates extrapolated to (or interpolated at) 40 °C show an odd–even effect. Also the activity coefficients of solutes in isotropic *p*-cyanophenyl *p*-*n*-alkylbenzoates extrapolated to (or interpolated at) 60 °C show an odd–even effect. This odd–even effect persisted when the above mentioned extrapolations (or interpolations) were made to (or at) 50 °C. The general trends obtained were similar to those encountered with the RCB (Oweimreen, 1982) and ROCB (Oweimreen and Shihab, 1994) homologous series of liquid crystals. Differences in the extents (or near suppression in the case of the ROCBs) of the odd–even effect may be attributable to structural differences between the different liquid crystalline homologous series and/or to the use of *p*-cyanophenyl *p*-*n*-alkylbenzoate homologues of shorter alkyl tails.

## Experimental Section

The high purity of the *p*-cyanophenyl *p*-*n*-alkylbenzoates used was evident from their sharp phase transitions (Martire et al., 1976; Oweimreen and Martire, 1980) at the temperatures given in Table 1 obtained using a Perkin-Elmer differential scanning calorimeter (DSC). The DSC runs show that the nematic phases of the ethyl, propyl, butyl, and pentyl members of the series are monotropic (i.e., they first appear after their isotropic phases are cooled) and persist down to 36 °C (except for the propyl homologue, which solidifies at 43.6 °C); the low-temperature limit of the DSC unit used. The DSC runs also showed that once the nematic phase appears, and as long as solidification does not occur, reproducible and close nematic-to-isotropic and isotropic-to-nematic transition temperatures were obtainable over repeated heating and cooling cycles respectively.

Recently (Zhou et al., 1994) there has been justified concern as to whether the physical properties of liquid crystals coated on surfaces are the same as those of the

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**Table 1. List of Solvents**

solvent	molar mass	melting point/°C		$T_{IN}$ (or $T_{NI}$ )/°C	
		manufacturer values	this study <sup>a</sup>	manufacturer values <sup>b</sup>	this study <sup>a</sup>
<i>p</i> -cyanophenyl <i>p</i> -ethylbenzoate	237.28	75.1	74.8 (76.1)	42.6	42.8
<i>p</i> -cyanophenyl <i>p</i> - <i>n</i> -propylbenzoate	251.31	101.6	101.4 (100.9)	53.2	53.8 (53.9)
<i>p</i> -cyanophenyl <i>p</i> - <i>n</i> -butylbenzoate	265.33	66.5	66.2 (65.9)	42.3	42.6 (42.6)
<i>p</i> -cyanophenyl <i>p</i> - <i>n</i> -pentylbenzoate	279.36	60.0	59.5 (62.6)	56.5	57.5 (57.3)
<i>p</i> -cyanophenyl <i>p</i> - <i>n</i> -hexylbenzoate	293.39	44.5	44.3 (43.9)	48.0	47.9 (47.8)
<i>p</i> -cyanophenyl <i>p</i> - <i>n</i> -heptylbenzoate	307.42	43.5	43.5 (43.0)	56.5	56.6 (56.6)

<sup>a</sup> Measured by differential scanning calorimetry. The values in parentheses are for the solvents coated on Chromosorb W. <sup>b</sup> Measured using a polarizing microscope.

**Table 2. List of Solutes**

solute	molar mass	bp/°C	$V_c^a \times 10^{22}/\text{cm}^3$	$d^b/(\text{J}\cdot\text{g}^{-1})$	$e^b/(\text{J}\cdot\text{g}^{-1}\cdot\text{deg}^{-1})$
hexane	86.18	68.74	6.11	92.06	0.1751
heptane	100.21	98.43	7.08	91.93	0.1659
octane	114.23	125.66	8.07	90.50	0.1479
nonane	128.26	150.80	8.72	89.29	0.1102
3-methylpentane	86.18	63.28	6.09	88.23	0.1636
2,4-dimethylhexane	114.23	109.10	7.66	85.14	0.1293
hex-1-ene	84.16	63.49	6.07	91.48	0.1705
cyclohexane	84.16	80.74	5.14	98.33	0.1602
1- <i>cis</i> -4-hexadiene	82.15	65.00		97.45	0.1773
benzene	78.11	80.11	4.3	107.85	0.1711

<sup>a</sup> Critical molecular volume, calculated using critical volumes ( $\text{cm}^3/\text{g}$ ) given in Dreisbach's (1955, 1959) compilations. <sup>b</sup> Dreisbach's (1955, 1959) compilations give the parameters  $d$  and  $e$  for calculating  $\Delta_{\text{vap}}H$  (J/g) at  $T$  (°C) from  $\Delta_{\text{vap}}H = 4.1844(d - eT)$ .

bulk. There is evidence (Apfel et al., 1985) that, depending on the nature of the substrate and the amount of material deposited, the physical properties of liquid crystals may be identical to those of the bulk or they may be altered substantially. In some instances (Mullin and Guyot-Sionnest, 1989; Nazarora et al., 1992) the mesogenic properties disappear due to strong interactions with the substrate and degradation of alignment at the interface. These findings led us to carry out DSC measurements on the packings used in our GLC columns. The results, given in parentheses in Table 1, show that the phase behavior and transition temperatures are the same whether the *p*-cyanophenyl *p*-*n*-alkylbenzoates are in bulk or are coated on Chromosorb W at loadings about 12%, except for the ethyl homologue that, when coated on Chromosorb W, does not show a sharp isotropic-to-nematic transition temperature. The results of the DSC measurements were used to decide on the temperature ranges (Table 3) for the GLC measurements in the nematic and isotropic phases of the *p*-cyanophenyl *p*-*n*-alkylbenzoates.

The liquid crystals used were coated on a Johns-Manville 60–80 mesh acid-washed and DMCS-treated Chromosorb W. Details of the preparation of the columns are given elsewhere (Oweimreen et al., 1979). Copper columns 1.2 m long with an outside diameter of 0.25 in. were used. The mass percentage of the liquid phase in each packing (i.e., the liquid-phase loading) was about 12% and was determined by careful ashing (Oweimreen and Shihab, 1994) of three samples of about 1 g of packing and of three samples of about 1 g of the bare support to correct for organic matter present in the support. The loadings of all columns used in this study were accurate to within  $\pm 0.04\%$ . Preliminary measurements on the least and most retained solutes at a representative temperature in each of the nematic and isotropic phases of each of the liquid crystalline stationary phases gave identical solute-specific retention volumes at loadings above and below 12%.

The solutes (Table 2), obtained from Fluka, were highly pure and were used as supplied. All the solutes were sufficiently volatile at the experimental temperatures and,

except for the critical constants of 1-*cis*-4-hexadiene, their physical properties either were available (Dreisbach, 1955, 1959) or could be computed (McGlashen and Potter, 1962; Guggenheim and Wormald, 1965).

A Perkin-Elmer Auto-System gas chromatograph, modified (Oweimreen, 1981) for accurate measurement of pressure at the column inlet, was used. The temperature inside the oven of the gas chromatograph was constantly monitored during all runs using a chromel-alumel thermocouple, and the observed control of the column temperature was within  $\pm 0.03$  °C. The procedure followed to obtain accurate retention volumes is described elsewhere (Oweimreen et al., 1979). Adequate care was taken to ensure the attainment of the infinite dilution condition (Martire and Riedl, 1968; Oweimreen et al., 1979). Interfacial effects (Liao and Martire, 1972; Oweimreen et al., 1979) were absent.

## Results

Solute-specific retention volumes,  $V_g^\circ$  (Liao and Martire, 1972; Oweimreen et al., 1979) were obtained at four temperatures in the nematic (except for *p*-cyanophenyl *p*-ethylbenzoate, which when coated on Chromosorb W did not give a sharp isotropic-to-nematic transition temperature by DSC and gave spurious GLC results) and isotropic phases of the six liquid crystalline solvents studied. The  $V_g^\circ$  values were obtained from the average of at least three separate measurements and agreed to within  $\pm 0.07\%$ . The nematic phases of the ethyl, propyl, butyl, and pentyl homologues of the *p*-cyanophenyl *p*-*n*-alkylbenzoates are monotropic; i.e., these homologues melt to give rise to isotropic fluids that supercool to temperatures well below their melting points undergoing an isotropic-to-nematic transition along the way. Except for the propyl homologue that solidified at 43.6 °C, solidification was not observed for the other isomers after cooling down to 36 °C. The hexyl and heptyl homologues melt to give nematic fluids, which on further heating undergo a nematic-to-isotropic phase transition. Like their ethyl, butyl, and pentyl homologues, the nematic phases of the hexyl and heptyl homologues supercool down to 36 °C without solidifying. Because of the nature of the liquid crystalline stationary phases the GLC columns were first heated above their melting points and then cooled to the temperatures used for the measurements in their isotropic and nematic phases. The lowest temperature used in each of the isotropic phases was more than 2.5 °C (1.0 °C in the case of the propyl homologue) above its isotropic-to-nematic transition temperature. The highest temperature used in each of the nematic phases was more than 4.5 °C below its isotropic-to-nematic transition temperature. Measurements were not made in the immediate neighborhood of the isotropic-to-nematic transition temperature to avoid possible pre- or post transitional effects inherent in the liquid crystals or the induction of a phase transition by the solute band (Martire et al., 1976; Oweimreen and Martire, 1980).

**Table 3. Infinite-Dilution Solute Activity Coefficients,  $\gamma_2^\infty$ , for Each Solute at Four Temperatures in Each of the Five Nematic and Six Isotropic Phases of the Six Liquid Crystals**

solute	$\gamma_2^\infty$							
	nematic phase					isotropic phase		
	<i>p</i> -Cyanophenyl <i>p</i> -Ethylbenzoate							
<i>t</i> <sup>o</sup> C =					52.95	55.95	58.98	62.00
hexane					6.50	6.47	6.44	6.40
heptane					8.27	7.87	7.48	7.13
octane					9.58	9.13	8.80	8.47
nonane					9.96	9.93	9.90	9.89
3-methylpentane					6.83	6.47	6.22	5.99
2,4-dimethylhexane					10.03	9.60	9.17	8.78
hex-1-ene					4.76	4.52	4.30	4.09
cyclohexane					4.88	4.72	4.50	4.31
1- <i>cis</i> -4-hexadiene					3.30	3.21	3.10	3.01
benzene					1.47	1.42	1.37	1.34
	<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Propylbenzoate							
<i>t</i> <sup>o</sup> C =	38.02	41.08	43.99	46.88	54.91	57.94	60.94	63.91
hexane	9.42	8.91	8.43	7.96	6.82	6.48	6.16	5.87
heptane	10.79	10.26	9.83	9.40	7.83	7.46	7.07	6.61
octane	12.40	11.84	11.38	10.98	8.83	8.35	7.98	7.59
nonane	14.37	13.69	12.90	12.33	10.03	9.53	9.03	8.59
3-methylpentane	9.58	9.07	8.63	8.28	6.98	6.62	6.25	5.95
2,4-dimethylhexane	14.50	13.79	13.34	12.81	9.46	9.01	8.54	7.98
hex-1-ene	6.24	6.17	6.12	6.05	5.02	4.74	4.48	4.28
cyclohexane	6.66	6.39	6.18	6.04	4.63	4.44	4.20	3.99
1- <i>cis</i> -4-hexadiene	4.63	4.38	4.18	3.94	3.31	3.20	3.11	3.02
benzene	1.91	1.87	1.84	1.80	1.58	1.51	1.46	1.40
	<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Butylbenzoate							
<i>t</i> <sup>o</sup> C =	30.03	32.02	34.00	35.98	48.98	51.98	55.01	58.00
hexane	7.21	6.98	6.71	6.49	5.13	4.93	4.73	4.56
heptane	8.31	8.04	7.80	7.54	5.86	5.64	5.43	5.28
octane	9.54	9.30	8.96	8.70	6.66	6.41	6.17	6.01
nonane	11.02	10.71	10.54	10.30	7.58	7.29	6.99	6.79
3-methylpentane	7.26	7.06	6.88	6.68	5.18	4.95	4.72	4.51
2,4-dimethylhexane	11.05	10.58	10.14	9.73	7.34	6.95	6.53	6.23
hex-1-ene	4.92	4.81	4.63	4.53	3.59	3.47	3.36	3.27
cyclohexane	5.22	5.04	4.87	4.72	3.58	3.45	3.32	3.20
1- <i>cis</i> -4-hexadiene	3.65	3.54	3.43	3.33	2.62	2.55	2.50	2.41
benzene	1.60	1.56	1.52	1.50	1.26	1.23	1.20	1.18
	<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Pentylbenzoate							
<i>t</i> <sup>o</sup> C =	40.87	43.88	46.90	49.97	59.97	63.00	65.97	69.09
hexane	6.92	6.61	6.24	5.92	4.25	4.16	4.07	4.02
heptane	7.98	7.65	7.33	7.03	4.96	4.80	4.71	4.58
octane	9.06	8.72	8.32	7.98	5.55	5.35	5.18	5.01
nonane	10.37	9.91	9.34	8.95	6.12	5.95	5.76	5.59
3-methylpentane	7.15	6.79	6.47	6.21	4.29	4.13	3.98	3.83
2,4-dimethylhexane	10.58	9.98	9.40	8.81	5.83	5.64	5.50	5.34
hex-1-ene	5.02	4.82	4.54	4.35	3.20	3.14	3.09	3.02
cyclohexane	5.08	4.88	4.64	4.44	3.06	2.94	2.84	2.72
1- <i>cis</i> -4-hexadiene	3.83	3.67	3.52	3.37	2.41	2.34	2.30	2.26
benzene	1.73	1.69	1.64	1.59	1.20	1.19	1.17	1.14
	<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Hexylbenzoate							
<i>t</i> <sup>o</sup> C =	34.97	37.80	40.84	43.44	52.80	56.00	58.98	61.98
hexane	4.61	4.44	4.22	4.14	3.80	3.70	3.62	3.56
heptane	5.28	5.07	4.79	4.64	4.33	4.19	4.06	3.99
octane	5.85	5.65	5.33	5.14	4.78	4.65	4.54	4.43
nonane	6.52	6.20	6.04	5.79	5.30	5.14	5.01	4.87
3-methylpentane	4.70	4.51	4.29	4.11	3.75	3.61	3.51	3.40
2,4-dimethylhexane	6.83	6.41	5.98	5.74	5.02	4.84	4.66	4.50
hex-1-ene	3.37	3.21	3.08	2.96	2.81	2.73	2.69	2.65
cyclohexane	3.44	3.26	3.10	2.94	2.72	2.63	2.55	2.49
1- <i>cis</i> -4-hexadiene	2.59	2.48	2.39	2.34	2.15	2.08	2.04	1.99
benzene	1.26	1.22	1.17	1.14	1.10	1.09	1.07	1.06
	<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Heptylbenzoate							
<i>t</i> <sup>o</sup> C =	45.06	47.06	49.06	51.11	60.12	63.08	66.10	69.12
hexane	4.21	4.10	4.01	3.90	3.18	3.10	2.99	2.88
heptane	4.81	4.67	4.52	4.36	3.51	3.47	3.39	3.34
octane	5.37	5.22	5.06	4.92	3.93	3.84	3.71	3.57
nonane	5.96	5.81	5.62	5.42	4.18	4.15	4.12	4.09
3-methylpentane	4.37	4.22	4.05	3.92	3.08	3.01	2.93	2.87
2,4-dimethylhexane	6.07	5.86	5.62	5.36	4.13	3.97	3.89	3.77
hex-1-ene	3.25	3.15	3.03	2.93	2.38	2.33	2.29	2.26
cyclohexane	3.21	3.09	2.99	2.88	2.22	2.18	2.13	2.09
1- <i>cis</i> -4-hexadiene	2.58	2.51	2.42	2.34	1.83	1.81	1.79	1.75
benzene	1.27	1.24	1.21	1.18	0.99	0.98	0.97	0.96

**Table 4. Infinite-Dilution Solute Partial Molar Excess Enthalpies,  $H^E$ , and Entropies,  $S^E$ , in Nematic  $p$ -Cyanophenyl  $p$ - $n$ -Alkylbenzoates<sup>a</sup>**

solvent	$H^E$ /(kJ·mol <sup>-1</sup> )	$S^E$ /(J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\gamma_N^*$	$-\Delta_{\text{soln}}H_N^*/$ (kJ·mol <sup>-1</sup> )	$-\Delta_{\text{soln}}S_N^*/$ (kJ·mol <sup>-1</sup> ·K <sup>-1</sup> )	solvent	$H^E$ /(kJ·mol <sup>-1</sup> )	$S^E$ /(J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\gamma_N^*$	$-\Delta_{\text{soln}}H_N^*/$ (kJ·mol <sup>-1</sup> )	$-\Delta_{\text{soln}}S_N^*/$ (kJ·mol <sup>-1</sup> ·K <sup>-1</sup> )
<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Propylbenzoate											
hexane	15.7 ± 0.4	31.9 ± 1.4	7.5	14.3	61.00	2,4-dimethylhexane	11.4 ± 0.5	14.6 ± 1.6	12.3	26.2	101.8
heptane	12.8 ± 0.2	21.5 ± 0.6	9.0	22.2	87.1	hex-1-ene	2.9 ± 0.1	-5.9 ± 0.3	6.0	26.3	96.3
octane	11.4 ± 0.3	15.5 ± 1.0	10.5	28.4	107.4	cyclohexane	9.2 ± 0.6	13.9 ± 2.0	5.8	22.6	84.5
nonane	14.6 ± 0.6	24.6 ± 1.8	11.7	30.4	114.5	1- <i>cis</i> -4-hexadiene	14.7 ± 0.5	34.6 ± 1.5	3.7	15.7	59.7
3-methylpentane	13.7 ± 0.4	25.2 ± 1.3	7.9	15.2	64.2	benzene	5.3 ± 0.2	11.6 ± 0.5	1.8	27.2	88.8
<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Butylbenzoate											
hexane	14.0 ± 0.4	29.6 ± 1.3	5.1	16.1	63.3	2,4-dimethylhexane	16.7 ± 0.1	35.2 ± 0.2	7.3	20.9	81.2
heptane	12.7 ± 0.3	24.2 ± 0.9	6.1	22.4	84.3	hex-1-ene	11.3 ± 0.9	23.9 ± 3.0	3.7	18.0	66.5
octane	12.3 ± 0.6	21.6 ± 1.9	7.1	27.5	101.3	cyclohexane	13.3 ± 0.1	30.1 ± 0.3	3.8	18.5	68.3
nonane	8.5 ± 0.6	8.2 ± 1.9	8.9	36.4	131.0	1- <i>cis</i> -4-hexadiene	12.2 ± 0.3	29.5 ± 0.9	2.7	18.3	64.7
3-methylpentane	11.0 ± 0.2	19.7 ± 0.6	5.6	17.9	69.7	benzene	8.7 ± 0.5	24.6 ± 1.8	1.3	23.8	75.8
<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Pentylbenzoate											
hexane	14.6 ± 0.5	30.4 ± 1.7	5.9	15.4	62.6	2,4-dimethylhexane	16.9 ± 0.3	34.2 ± 1.0	8.8	20.7	82.2
heptane	11.7 ± 0.1	20.0 ± 0.3	7.0	23.3	88.5	hex-1-ene	13.6 ± 0.7	29.9 ± 2.3	4.3	15.7	60.5
octane	11.9 ± 0.3	19.5 ± 0.9	8.0	27.8	103.4	cyclohexane	12.6 ± 0.3	26.6 ± 0.9	4.4	19.2	71.8
nonane	13.9 ± 0.7	24.8 ± 2.0	8.9	31.1	114.3	1- <i>cis</i> -4-hexadiene	11.8 ± 0.1	26.4 ± 0.5	3.4	18.7	67.8
3-methylpentane	13.2 ± 0.4	25.7 ± 1.4	6.2	15.7	63.7	benzene	7.8 ± 0.3	20.2 ± 1.0	1.6	24.7	80.2
<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Hexylbenzoate											
hexane	10.8 ± 1.0	22.4 ± 3.3	3.8	19.2	70.5	2,4-dimethylhexane	17.1 ± 0.9	39.4 ± 3.0	5.0	20.4	77.0
heptane	12.9 ± 0.6	27.9 ± 1.9	4.2	22.2	80.6	hex-1-ene	12.5 ± 0.4	30.6 ± 1.2	2.7	16.7	59.8
octane	12.8 ± 0.8	26.9 ± 2.5	4.7	26.9	96.0	cyclohexane	15.1 ± 0.4	38.8 ± 1.3	2.6	16.7	59.6
nonane	11.1 ± 1.1	20.4 ± 3.4	5.3	33.9	118.7	1- <i>cis</i> -4-hexadiene	10.1 ± 0.8	24.7 ± 2.5	2.1	20.4	69.5
3-methylpentane	13.1 ± 0.3	29.5 ± 0.8	3.7	15.8	59.8	benzene	10.2 ± 0.2	31.0 ± 0.6	1.0	22.3	69.4
<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Heptylbenzoate											
hexane	10.8 ± 0.3	22.0 ± 1.0	4.0	19.2	71.0	2,4-dimethylhexane	17.6 ± 0.9	40.3 ± 2.7	5.5	20.0	76.1
heptane	13.9 ± 0.6	30.7 ± 1.7	4.4	21.1	77.8	hex-1-ene	15.0 ± 0.6	37.4 ± 1.9	3.0	14.2	53.0
octane	12.6 ± 0.2	25.6 ± 0.5	5.0	27.1	97.3	cyclohexane	15.5 ± 0.2	38.9 ± 0.7	2.9	16.3	59.5
nonane	13.6 ± 0.9	27.9 ± 2.7	5.5	31.3	111.2	1- <i>cis</i> -4-hexadiene	14.4 ± 0.6	37.3 ± 1.8	2.4	16.1	56.9
3-methylpentane	15.7 ± 0.3	37.0 ± 1.0	4.0	13.2	52.4	benzene	10.0 ± 0.6	29.4 ± 1.8	1.2	22.4	71.0

<sup>a</sup> The infinite-dilution solute activity coefficients,  $\gamma_N^*$ , and partial molar enthalpies,  $\Delta_{\text{soln}}H_N^*$ , and entropies,  $\Delta_{\text{soln}}S_N^*$ , of solution are from extrapolations (or interpolations) of linear least-squares fits of  $\ln \gamma_2^\infty$  against  $1/T$  in the nematic phase to (or at) 50 °C.

The infinite-dilution solute activity coefficients,  $\gamma_2^\infty$ , were calculated from the corresponding  $V_g^\circ$  values using

$$\ln \gamma_2^\infty = \ln(273.2R/M_1P_2^\circ V_g^\circ) - B_{22}P_2^\circ/RT \quad (1)$$

where  $M_1$  is the solvent molar mass and  $P_2^\circ$  and  $B_{22}$  are, respectively, the saturated vapor pressure and second virial coefficient of the pure solute at the experimental temperature  $T$ . The calculation is considered fully by Oweimreen et al. (1979). A propagation of error analysis showed that the  $\gamma_2^\infty$  values obtained by us are correct to within  $\pm 1.2\%$ . The  $\gamma_2^\infty$  values obtained are listed in Table 3. In addition  $\gamma_2^\infty$  values obtained at 50 °C from extrapolations (or interpolations) of linear least-squares fits of  $\ln \gamma_2^\infty$  against  $1/T$  in the nematic ( $\gamma_N^*$ ) and isotropic ( $\gamma_I^*$ ) phases of the six liquid crystals studied are given in Tables 4 and 5, respectively. Since from thermodynamics

$$\ln \gamma_2^\infty = G^E/RT = H^E/RT - S^E/R \quad (2)$$

infinite-dilution solute partial molar excess enthalpies,  $H^E$ , and entropies,  $S^E$ , were obtained, respectively, from the slopes and intercepts of linear least-squares fits of  $\ln \gamma_2^\infty$  as a function of  $T^{-1}$  and are reported along with their standard deviations in Tables 4 and 5. Representative plots of  $\ln \gamma_2^\infty$  as a function of  $T^{-1}$  are given in Figure 1.  $H^E$  and  $S^E$  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. If we consider the hypothetical transfer of solute from an ideal gaseous mixture to the actual solution (again, both being at the same temperature, pressure, and composition), the corresponding quantities become  $\Delta_{\text{soln}}H^\circ$  and  $\Delta_{\text{soln}}S^\circ$ , the infinite dilution solute partial molar enthalpy and entropy of solution, respectively (Chow and Martire, 1971; Meyer, 1973).  $\Delta_{\text{soln}}H^\circ$  is related to  $H^E$

through

$$\Delta_{\text{soln}}H^\circ = H^E - \Delta_{\text{vap}}H \quad (3)$$

where  $\Delta_{\text{vap}}H$  is the molar enthalpy of vaporization of the pure solute. The relation and parameters needed for  $\Delta_{\text{vap}}H$  computation are available in Dreisbach's (1955, 1959) compilation. Whereas  $H^E$  contains a contribution due to solute-solute interactions,  $\Delta_{\text{soln}}H^\circ$  reflects only solvent-solute and solute-solvent interaction terms (Chow and Martire, 1971; Meyer, 1973). Hence, in a given solvent (or a given liquid crystalline phase),  $\Delta_{\text{soln}}H^\circ$  should be primarily a measure of relative solute-solvent interaction strengths. Similarly, the infinite dilution partial molar entropy of solution,  $\Delta_{\text{soln}}S^\circ$ , for such a process is related to  $S^E$  by (Chow and Martire, 1971; Meyer, 1973).

$$\Delta_{\text{soln}}S^\circ = S^E - \Delta_{\text{vap}}H/T \quad (4)$$

Incorporated in Tables 4 and 5 are  $\Delta_{\text{soln}}H^\circ$  and  $\Delta_{\text{soln}}S^\circ$  at 50 °C in the nematic ( $\Delta_{\text{soln}}H_N^*$  and  $\Delta_{\text{soln}}S_N^*$ ) and isotropic ( $\Delta_{\text{soln}}H_I^*$  and  $\Delta_{\text{soln}}S_I^*$ ) phases of the six liquid crystals studied. Since  $\Delta_{\text{vap}}H$  is known to within a few joules per mole (Dreisbach, 1955, 1959), the standard deviations of  $\Delta_{\text{soln}}H^\circ$  and  $\Delta_{\text{soln}}S^\circ$  are essentially those for  $H^E$  and  $S^E$ .

## Discussion

The results (Tables 3–5) are examined in the light of an infinite-dilution solution model proposed by Chow and Martire (1971) and later refined by Martire (1974). They generally corroborate earlier studies on members of the RCB (Oweimreen, 1982) and ROCB (Oweimreen and Shihab, 1994) series of liquid crystals. The infinite-dilution activity coefficients for all the solutes in the nematic and isotropic phases of all the six  $p$ -cyanophenyl  $p$ - $n$ -alkylbenzoate liquid crystals studied exhibit positive deviations

**Table 5. Infinite-Dilution Solute Partial Molar Excess Enthalpies,  $H^E$ , and Entropies,  $S^E$ , in Isotropic *p*-Cyanophenyl *p*-*n*-Alkylbenzoate<sup>a</sup>**

solute	$H^E$ /(kJ·mol <sup>-1</sup> )	$S^E$ /(J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\gamma_1^*$	$-\Delta_{\text{soln}}H_1^*$ /(kJ·mol <sup>-1</sup> )	$-\Delta_{\text{soln}}S_1^*$ /(kJ·mol <sup>-1</sup> ·K <sup>-1</sup> )	solute	$H^E$ /(kJ·mol <sup>-1</sup> )	$S^E$ /(J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\gamma_1^*$	$-\Delta_{\text{soln}}H_1^*$ /(kJ·mol <sup>-1</sup> )	$-\Delta_{\text{soln}}S_1^*$ /(kJ·mol <sup>-1</sup> ·K <sup>-1</sup> )
<i>p</i> -Cyanophenyl <i>p</i> -Ethylbenzoate											
hexane	1.5 ± 0.0	-10.9 ± 0.1	6.5	28.5	103.9	2,4-dimethylhexane	13.4 ± 0.2	21.8 ± 0.5	10.5	24.2	94.5
heptane	14.8 ± 0.1	27.9 ± 0.2	8.7	20.2	80.6	hex-1-ene	15.3 ± 0.1	34.0 ± 0.3	5.0	13.9	56.4
octane	12.2 ± 0.5	18.7 ± 1.6	9.4	27.5	104.3	cyclohexane	12.8 ± 0.7	25.9 ± 2.1	5.1	19.1	72.5
nonane	0.7 ± 0.1	-16.9 ± 0.2	10.0	44.2	156.9	1- <i>cis</i> -4-hexadiene	9.4 ± 0.3	18.8 ± 0.8	3.4	21.0	75.5
3-methylpentane	13.2 ± 0.8	24.4 ± 2.3	7.1	15.7	64.9	benzene	10.0 ± 0.7	27.5 ± 2.0	1.5	22.4	72.9
<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Propylbenzoate											
hexane	15.3 ± 0.1	30.7 ± 0.3	7.4	14.7	62.3	2,4-dimethylhexane	17.3 ± 1.0	33.9 ± 3.1	10.5	20.4	82.5
heptane	17.2 ± 0.1	35.4 ± 3.0	8.7	17.8	73.2	hex-1-ene	16.3 ± 0.4	63.2 ± 1.3	5.5	13.0	54.2
octane	15.3 ± 0.3	28.5 ± 1.0	9.6	24.4	94.4	cyclohexane	15.2 ± 0.8	33.6 ± 2.3	5.0	16.6	64.8
nonane	15.9 ± 0.1	29.3 ± 0.4	11.0	29.1	109.9	1- <i>cis</i> -4-hexadiene	9.5 ± 0.3	19.0 ± 0.8	3.5	20.9	75.2
3-methylpentane	16.5 ± 0.3	34.2 ± 1.0	7.7	12.3	55.1	benzene	11.6 ± 0.6	31.5 ± 1.7	1.7	20.9	68.9
<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Butylbenzoate											
hexane	11.5 ± 0.2	20.1 ± 0.5	5.1	18.5	70.9	2,4-dimethylhexane	16.3 ± 0.6	34.0 ± 1.0	7.2	21.3	82.4
heptane	10.4 ± 0.4	17.6 ± 1.4	5.8	24.7	91.0	hex-1-ene	9.2 ± 0.4	18.0 ± 1.2	3.5	20.0	72.5
octane	10.2 ± 0.5	15.9 ± 1.4	6.6	29.5	107.0	cyclohexane	11.2 ± 0.1	24.2 ± 0.3	3.5	20.6	74.3
nonane	11.0 ± 0.5	17.4 ± 1.6	7.4	33.9	121.8	1- <i>cis</i> -4-hexadiene	8.0 ± 0.5	16.8 ± 1.4	2.6	22.5	77.5
3-methylpentane	13.5 ± 0.0	28.3 ± 0.1	5.1	15.3	61.0	benzene	6.1 ± 0.6	17.2 ± 1.8	1.2	26.3	83.3
<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Pentylbenzoate											
hexane	6.0 ± 0.5	5.9 ± 1.4	4.5	24.1	87.0	2,4-dimethylhexane	9.0 ± 0.2	12.5 ± 0.6	6.4	28.6	103.9
heptane	8.0 ± 0.5	10.8 ± 1.6	5.4	27.0	97.7	hex-1-ene	6.0 ± 0.1	8.3 ± 0.3	3.4	23.2	82.1
octane	10.6 ± 0.1	17.5 ± 0.4	6.6	29.2	105.5	cyclohexane	12.0 ± 0.1	26.8 ± 0.3	3.5	19.8	71.7
nonane	9.5 ± 0.2	13.4 ± 0.6	6.8	35.5	125.8	1- <i>cis</i> -4-hexadiene	6.3 ± 0.4	11.7 ± 1.2	2.6	24.1	82.5
3-methylpentane	11.8 ± 0.1	23.2 ± 0.3	4.9	17.1	66.2	benzene	5.4 ± 0.3	14.6 ± 1.0	1.3	27.1	85.9
<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Hexylbenzoate											
hexane	6.4 ± 0.2	8.6 ± 0.6	3.8	23.6	84.3	2,4-dimethylhexane	10.9 ± 0.1	20.1 ± 0.3	5.2	26.7	96.3
heptane	8.1 ± 0.6	12.6 ± 1.9	4.4	27.0	95.9	hex-1-ene	6.0 ± 0.6	9.7 ± 1.7	2.9	23.3	80.7
octane	7.5 ± 0.1	10.0 ± 0.4	4.9	32.2	113.0	cyclohexane	9.1 ± 0.3	19.6 ± 0.9	2.8	22.7	78.8
nonane	8.3 ± 0.1	11.6 ± 0.2	5.4	36.7	127.6	1- <i>cis</i> -4-hexadiene	7.5 ± 0.4	16.7 ± 1.1	2.2	23.0	77.6
3-methylpentane	9.5 ± 0.1	18.1 ± 0.4	3.8	19.4	71.3	benzene	3.4 ± 0.0	9.7 ± 0.1	1.1	29.0	90.7
<i>p</i> -Cyanophenyl <i>p</i> - <i>n</i> -Heptylbenzoate											
hexane	10.5 ± 0.5	21.8 ± 1.5	3.6	19.6	71.2	2,4-dimethylhexane	9.2 ± 0.8	15.8 ± 2.5	4.6	28.4	100.5
heptane	5.3 ± 0.1	5.5 ± 0.3	3.7	29.8	103.1	hex-1-ene	5.4 ± 0.3	9.1 ± 1.1	2.5	23.8	81.3
octane	10.1 ± 0.8	18.8 ± 2.3	4.4	29.7	104.1	cyclohexane	6.4 ± 0.3	12.4 ± 1.0	2.4	25.5	86.0
nonane	2.4 ± 0.1	-4.8 ± 0.2	4.3	42.6	143.9	1- <i>cis</i> -4-hexadiene	4.8 ± 0.4	9.5 ± 1.2	1.9	25.6	84.8
3-methylpentane	7.4 ± 0.2	12.9 ± 0.7	3.4	21.4	76.4	benzene	3.0 ± 0.2	9.2 ± 0.6	1.0	29.4	91.2

<sup>a</sup> The infinite-dilution solute activity coefficients,  $\gamma_1^*$ , and partial molar enthalpies,  $\Delta_{\text{soln}}H_1^*$ , and entropies,  $\Delta_{\text{soln}}S_1^*$ , of solution are from extrapolations (or interpolations) of linear least-squares fits of  $\ln \gamma_2^\infty$  against  $1/T$  in the isotropic phase to (or at) 50 °C.

from Raoult's law ( $\gamma_2^\infty > 1$ ). For whatever reason, in 4 (out of 110) solute–solvent systems, small solute partial molar excess enthalpies and negative solute partial molar excess entropies were obtained. For the remaining solute–solvent systems, the solute partial molar excess enthalpies and excess entropies are positive. These results corroborate earlier finds (Oweimreen, 1982; Oweimreen and Shihab, 1994) that nonmesomorphic solutes are incompatible with both the nematic and isotropic phases of liquid crystals. Since when coated on Chromosorb W the *p*-cyanophenyl *p*-ethylbenzoate did not give a sharp isotropic-to-nematic transition and its "nematic" phase GLC results were spurious only the results in the nematic and isotropic phases of the remaining five *p*-cyanophenyl *p*-*n*-alkylbenzoates may be contrasted. Excluding the systems of the solutes studied (except 1-*cis*-4-hexadiene) in *p*-cyanophenyl *p*-*n*-propylbenzoate and nonane and 3-methylpentane in *p*-cyanophenyl *p*-*n*-butylbenzoate, all the solutes in the remaining solute-liquid crystalline solvent systems studied followed the general trends

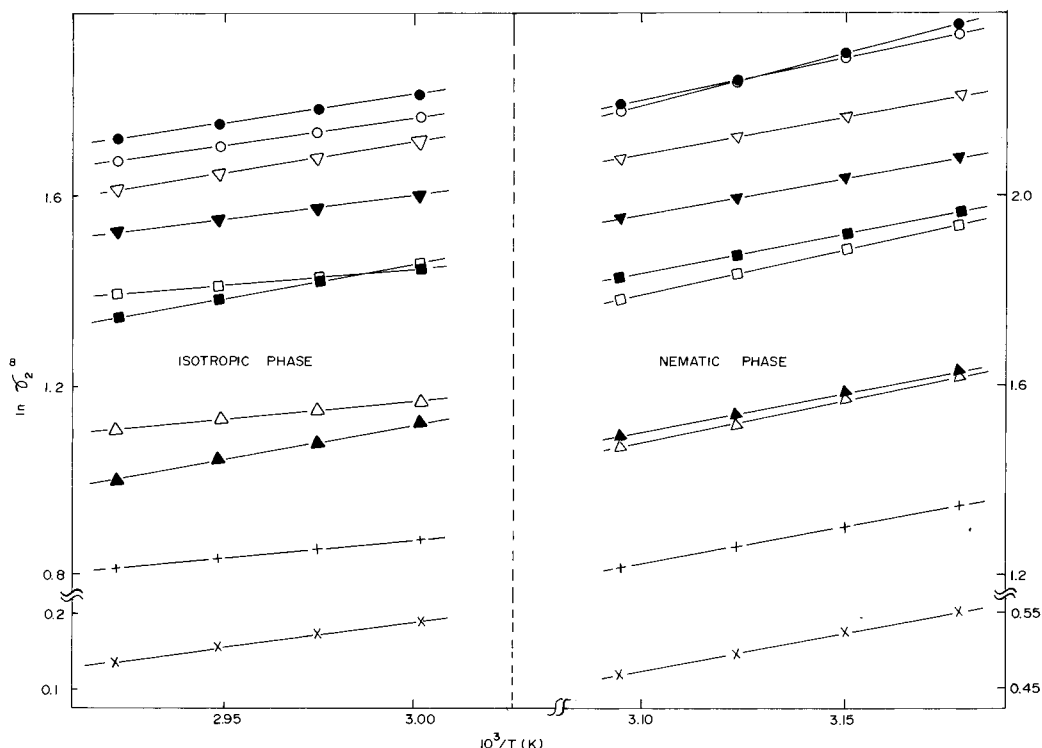
$$(\Delta_{\text{soln}}H^E)_I < (\Delta_{\text{soln}}H^E)_N \quad \text{and} \quad (H^E)_I < (H^E)_N \quad (\text{a})$$

$$(\Delta_{\text{soln}}S^E)_I < (\Delta_{\text{soln}}S^E)_N \quad \text{and} \quad (S^E)_I < (S^E)_N \quad (\text{b})$$

$$(\gamma_2^\infty)_I < (\gamma_2^\infty)_N \quad (\text{c})$$

which were also exhibited by similar systems of nonmesomorphic solutes in the RCB (Oweimreen, 1982) and ROCB (Oweimreen and Shihab, 1994) series of liquid crystalline solvents, where the subscripts I and N refer to the isotropic

and nematic phases, respectively. Trends a and b were attributed (Oweimreen and Shihab, 1994) to effectively weaker solute–solvent interactions in the nematic phase. Together these trends indicate that the lower solute excess Gibbs energy in the isotropic phase (trend c) is enthalpic in origin. It is noteworthy that all the solvents that gave rise to trends a and b have alkyl or alkyloxy tails with four or more atoms. For the above mentioned excluded solute–solvent systems, trends a and b are reversed while trend c is unchanged. Since the solutes are the same in all the solute–solvent systems studied, the reversal of trends a and b can only be attributed to the shortness of the alkyl tail(s) of the liquid crystal solvent molecule(s). Unfortunately this proposition could not be tested on *p*-cyanophenyl *p*-ethylbenzoate; the homologue with the shortest tail. Nevertheless the effect of the length of the alkyl tail of the *p*-cyanophenyl *p*-*n*-alkylbenzoates is demonstrated by the nonane and 3-methylpentane solutes, which give rise to trends a and b in the pentyl, hexyl, and heptyl homologues and to the reversal of trends a and b in the butyl and propyl homologues. That in *p*-cyanophenyl *p*-*n*-butylbenzoate only the nonane and 3-methylpentane (out of the 10 solutes studied, of which 6 are alkanes) result in the reversal of trends a and b reflects the complex interplay between enthalpy and entropy effects in these systems, particularly when the solvent has a borderline alkyl tail length. Such complex interplay is also demonstrated by the proximity of the  $(H^E)_I$  and  $(H^E)_N$  values (and  $(S^E)_I$  and  $(S^E)_N$  values) for the other solutes, particularly 2,2-dimethylhexane, in *p*-cyanophenyl *p*-*n*-butylbenzoate. 1-*cis*-4-Hexadiene (and possibly hexane considering the proximity of its  $(H^E)_I$  and



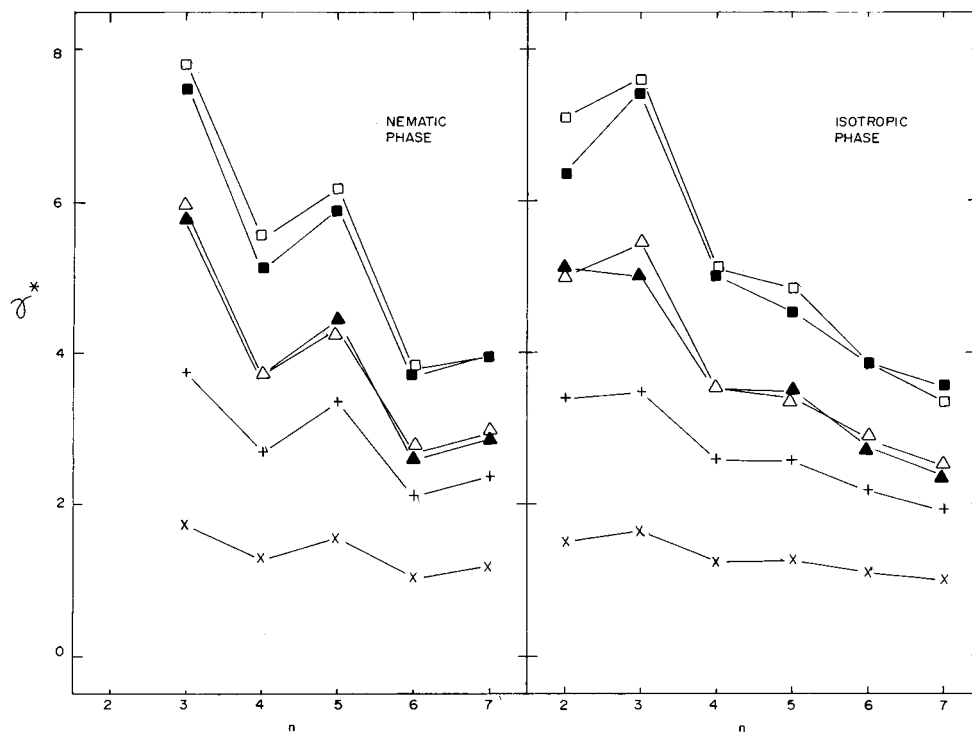
**Figure 1.**  $\ln \gamma_2^\infty$  against  $10^3/T$  for hexane (■), heptane (▼), octane (▽), nonane (●), 3-methylpentane (□), 2,4-dimethylhexane (○), hex-1-ene (△), cyclohexane (▲), 1-*cis*-4-hexadiene (+) and benzene (×) in the nematic and isotropic phases of *p*-cyanophenyl *p*-*n*-pentylbenzoate. The isotropic-to-nematic transition temperature is indicated by the dashed vertical line.

$(H^E)_N$  and  $(S^E)_I$  and  $(S^E)_N$  values) in *p*-cyanophenyl *p*-*n*-propylbenzoate exhibited trends a and b in all the solvents studied. For solution systems where trends a and b are reversed, trend c can only be entropic in origin.

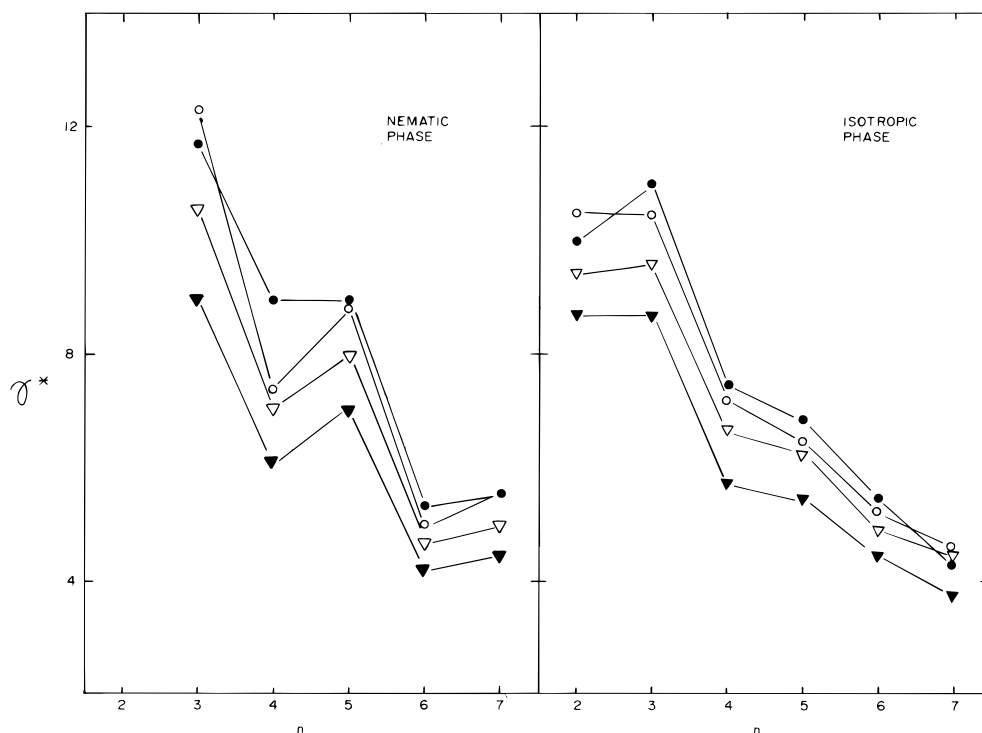
Next we examine the effect of solute structure. Since increased rigidity in the solute molecule leads to weaker solute-solvent interactions (less negative  $\Delta_{\text{soln}}H^\circ$  and  $\Delta_{\text{soln}}S^\circ$  values) and tends to increase  $\gamma_2^\infty$  while increased polarizability of the solute molecule has the opposite effect, the trend hexane > hexene > cyclohexane > hexadiene > benzene obtained in this study and in previous studies (Oweimreen, 1982; Oweimreen and Shihab, 1994) for the  $\gamma_2^\infty$  values of molecules containing six carbon atoms in nematic and isotropic phases of liquid crystalline solvents is attributed to the predominance of the polarizability effect. The increased compatibility of cyclohexane (with a polarizability comparable to that of hexane and a rigidity less than that of benzene) with the liquid crystalline phases relative to hexane was attributed (Oweimreen and Shihab, 1994) to its smaller size. As the chain length of an unbranched alkane solute increases (i) its molecular polarizability increases resulting in stronger solute-solvent interactions (through dispersion forces) and more negative  $\Delta_{\text{soln}}H^\circ$  and  $\Delta_{\text{soln}}S^\circ$  values, (ii) the solute-to-solvent size ratio increases and the combinatorial entropy contribution leads to more negative  $\Delta_{\text{soln}}H^\circ$  and  $\Delta_{\text{soln}}S^\circ$  values, and (iii) its losses of rotational and conformational freedom upon solvation increase, leading to more negative  $\Delta_{\text{soln}}S^\circ$  values. The trend of increase in  $\gamma_2^\infty$  with increase in the chain length of the unbranched alkane solutes indicates that the enthalpy of solution increases (i.e., becomes more negative) less rapidly with increasing chain length than do the combined entropy of solution effects. Relative to its unbranched alkane isomer the branched alkane (i) loses less rotational and conformational freedom upon solvation and has a less negative  $\Delta_{\text{soln}}S^\circ$  and (ii) has a smaller effective solute-solvent interaction energy leading to less negative  $\Delta_{\text{soln}}H^\circ$  and  $\Delta_{\text{soln}}S^\circ$  values. Less negative  $\Delta_{\text{soln}}H^\circ$  and

$\Delta_{\text{soln}}S^\circ$  tend, respectively, to increase and decrease the  $\gamma_2^\infty$  value of the branched alkane relative to that of its unbranched isomer. The interplay between the opposing enthalpy and entropy effects is complex particularly as the number of carbon atoms in the branched alkane increases and as the location and extent of branching varies. The available data (Oweimreen et al., 1979; Oweimreen, 1981; Oweimreen and Shihab, 1994) indicate that, for the same number of carbon atoms in the solute molecule, the branched alkane has, in general, a higher  $\gamma_2^\infty$  value than the unbranched alkane isomer. Exceptions to this rule where the  $\gamma_2^\infty$  values are comparable and/or reversed (Oweimreen, 1981) are encountered among branched alkane solutes with centrally located branches. The observed general trend nonane > 2,2-dimethylpentane > octane > heptane > 3-methylpentane > hexane in the  $\gamma_2^\infty$  values in the nematic and isotropic phases of all the *p*-cyanophenyl *p*-*n*-alkylbenzoate liquid crystalline solvents studied is thus explained. Figures 2 and 3 illustrate the above mentioned trends in  $\gamma_2^\infty$  for all solutes in the nematic and isotropic phases of the *p*-cyanophenyl *p*-*n*-alkylbenzoates studied.

To examine the effect on the solution process of solvents of different structures with different isotropic-to-nematic transition temperatures and different temperature ranges for their nematic and isotropic phases, the data for both phases of the *p*-cyanophenyl *p*-*n*-alkylbenzoates were extrapolated to (or interpolated at) a common temperature. A temperature of 50 °C was chosen because of its proximity to the average value for the isotropic-to-nematic transition temperature of the six liquid crystals studied. The symbols  $\gamma_N^*$ ,  $\Delta_{\text{soln}}H_N^*$  and  $\Delta_{\text{soln}}S_N^*$  refer to the results from extrapolations (or interpolations) of linear least-squares fits of  $\ln \gamma_2^\infty$  against  $1/T$  in the nematic phase to (or at) 50 °C. These results are given in Table 4.  $\gamma_I^*$ ,  $\Delta_{\text{soln}}H_I^*$ , and  $\Delta_{\text{soln}}S_I^*$  are similarly defined for the isotropic phase and are given in Table 5. The trends outlined below for the solvents and outlined in the preceding paragraph for the



**Figure 2.** Solute activity coefficients from extrapolations to (or interpolations at) 50 °C in the nematic and isotropic phases against the number of carbon atoms,  $n$ , in the alkyl chain of the *p*-cyanophenyl *p*-*n*-alkylbenzoate. The solutes are hexane (■), 3-methylpentane (□), hex-1-ene (△), cyclohexane (▲), 1-*cis*-4-hexadiene (+) and benzene (×).



**Figure 3.** Solute activity coefficients from extrapolations to (or interpolations at) 50 °C in the nematic and isotropic phases against the number of carbon atoms,  $n$ , in the alkyl chain of the *p*-cyanophenyl *p*-*n*-alkylbenzoate. The solutes are nonane (●), 2,4-dimethylhexane (○), octane (▽) and heptane (▼).

solutes and illustrated in Figures 2 and 3 are independent (between 40 °C and 60 °C) of the temperature to which (or at which) the extrapolation (or interpolation) is made.

Generally,  $\gamma_N^*$  and  $\gamma_I^*$  decrease as the number of carbon atoms,  $n$ , in the alkyl tail of the solvent molecule increases from 2 to 7. Along this trend  $\gamma_N^*$  and  $\gamma_I^*$  exhibit an odd-even effect. This holds for all the solutes and liquid crystal solvents studied. The decrease of  $\gamma^*$  with  $n$  is attributable (Oweimreen, 1982) to the increase of the polarizability of

the solvent molecule and in turn the increase in the solute-solvent interaction strength with increasing  $n$ . The accompanying odd-even effect is attributable (Oweimreen, 1982) to the anisotropy of the polarizability of the solvent molecules. Such anisotropy is demonstrated by the odd-even effect of the isotropic-to-nematic transition temperatures (Gray et al., 1974) of the liquid crystals (Table 1). As  $n$  increases, the extent of the anisotropy of the polarizability decreases and the extent of the odd-even effect

diminishes. This is seen clearly in this study and in the variation of  $\gamma^*$  with  $n$  for similar solutes in the nematic RCBs (Oweimreen, 1982). The odd-even effect was either nonexistent or highly subdued in isotropic RCBs (Oweimreen, 1982) and in the nematic and isotropic phases of the ROCBs (Oweimreen and Shihab, 1994).

The results for the *p*-cyanophenyl *p*-*n*-alkylbenzoates generally agree with those for the RCB (Oweimreen, 1982) and ROCB (Oweimreen and Shihab, 1994) series of liquid crystals except for the above mentioned reversal of trends a and b in the propyl homologue (and for some solutes in the butyl homologue) and in exhibiting a more marked odd-even effect for the variations of  $\gamma_N^*$  and  $\gamma_I^*$  with  $n$ , the number of carbon atoms in their alkyl tails. These differences may be attributable to the wider range of alkyl tail lengths covered in this study, which includes shorter alkyl tails, and/or to the ester linkage between the central phenyl groups of the *p*-cyanophenyl *p*-*n*-alkylbenzoates that is absent in the alkyl- or (alkyloxy)cyanobiphenyls.

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