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On the Question of Molecular Flexibility in Nematogenic Compounds

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A statistical thermodynamic model is used to interpret the nematic-isotropic transitional entropy increment per methylene group for the dialkoxyazoxybenzene series and the infinite dilution activity coefficients of n-alkane solutes in the nematic phase of two members of this series. Existing evidence and the findings of this study indicate that there is an appreciable population of alkyl chain conformations other than the all trans one, both in the nematic phase and, more so, in the isotropic liquid phase.

INTRODUCTION

In recent years there has been much theoretical and experimental activity directed toward a more detailed understanding of relationships between molecular structure and certain physical properties of nematogenic liquid crystals. Synthetic chemists, experimental physical scientists and theoreticians have interacted in attempts to elucidate these relationships. A common situation is that homologous series are prepared of compounds with different central linkages (often with the goal of obtaining stable room temperature nematics) and, then, experimental and theoretical studies are performed with the hope of interpreting the observed behavior in terms of the nature of the central core and/or the chain length(s) of the pendant alkyl group(s). For example, nematic-isotropic transition temperatures and enthalpies for a homologous series are obtained and interpreted in terms of possible attractive and repulsive interactions present, often with the aid of statistical mechanics. Although a few papers have dealt with the

subject, one question which merits further study is the extent and effect of molecular flexibility in these pendant alkyl groups, in both the nematic and isotropic liquid phases.

Statistical mechanical models of rigid rod-like particles, such as the scaled particle theory [1,2] and the lattice model [3,4] (with [3,4] or without [1,2,4] attractive interactions) are found to yield rather high fractional volume changes for the aligned-isotropic phase transition as the length-to-breadth ratio of the rod increases. In real nematogenic systems the nematic-isotropic fractional volume change is quite small (<1%) and, if anything, decreases slightly as the alkyl chain length of the pendant groups increases.[5] Further, the molar volume contribution of a single methylene group in the nematic phase (16.34 cm^3/mole) is found to be much closer to the isotropic liquid value for n-alkanes (16.4) than to the solid state value (14.5).[5] This recent finding is consistent with earlier suggestions [1-3,6] that appreciable flexibility of the n-alkyl pendant groups exists in both the nematic and isotropic liquid phases. The results of the scaled particle theory, [1,2] for example, appear to be more reasonable if one regards the length-to-breadth ratio as representing a time-averaged value for all possible molecular conformations, i.e., while the addition of methylene groups lengthens the molecule, the length-to-breadth ratio does not change appreciably, because the molecular motion of the pendant groups (due to conformational changes) also effectively broadens the molecule. This picture is consistent with the observation that the nematic order parameters at the nematic-isotropic transition are nearly the same for members of the same homologous series.[7]

A lattice model for long semiflexible molecules devised by Wulf and de Rocco[8] represents the most definitive statistical mechanical study to date on the question of the role of molecular flexibility. Noteworthy was the ability of this model to generate sensible values (< 1%) for the fractional volume change at the aligned-isotropic transition in a system of hard, long molecules. The results of this study strongly suggest that n-alkyl groups in a nematic mesophase are not confined to one conformation, but, rather, are quite flexible. Young, Haller and Aviram,[5] upon examining the transition extropies along several homologous series, came to the same conclusion. (Their observations will be discussed later). Finally, the recent Raman work of Schnur[9] on the dialkoxyazoxybenzene series provides further evidence of the existence of several conformations for the alkoxy chains in both the nematic and isotropic phases, and of progressive chain shortening as one proceeds through the phase sequence solid→nematic→isotropic. In fact, the observed low frequency Raman spectra indicate the presence of only one conformation in the solid phase (the fully extended or zig-zag or trans conformation) and a nematic phase pattern which more closely resembles that of the isotropic liquid than that of the solid state. From these three studies one obtains the general qualitative picture of nematic pendant groups being quite flexible, but not as flexible as in the isotropic liquid. Only the recent X-ray

work of de Vries [10] presents a different picture. His values for the "apparent molecular length" of three 4-alkoxybenzal-4'-ethylanilines (pentyl, hexyl and heptyl), as determined through analysis of the inner diffraction ring, indicate that the alkoxy chains are in the extended conformation in the nematic phase *and in the isotropic phase at the transition point.*

In this paper the statistical thermodynamics of mesophase-isotropic transitions, as it bears on the question of molecular flexibility in nematogenic liquid crystals, will be considered. The conformational contribution to the partition function will be estimated by coupling a model developed over thirty years ago by Pitzer [11] to concepts recently employed by Seelig [12] in investigating the flexibility of hydrocarbon chains in a smectic lipid bilayer. Prior to applying the resulting equations to the problem at hand, the validity of the treatment will be tested by comparison of predicted and observed values for related systems (Seelig's study [12] and the transition entropy per methylene group in n-alkane melting). [13] Also, the reasonableness of this hybrid model will be further demonstrated by analyzing infinite dilution activity coefficients and heats of solution for n-alkane solutes dissolved in nematic liquids. [14, 15]

THE MODEL

Statistical Thermodynamic Relations

The molar entropy (S), Helmholtz function (A) and internal energy (U) are related to each other and to the partition function (Q) through the expressions:

$$S = \frac{U - A}{T} \tag{1}$$

$$U = RT^2 \left(\frac{\partial \ln Q}{\partial T}\right) \tag{2}$$

$$A = -RT \ln Q \ . \tag{3}$$

Q can as usual be written as the product of translational, rotational, vibrational and electronic parts:

$$Q = Q^t Q^r Q^v Q^e \ . \tag{4}$$

In this paper we deal only with changes in the thermodynamic functions (e.g., upon a phase transition or upon transferring solute from an ideal solution to the real solution) and not with their absolute values. Therefore, we need be concerned only with those parts of the total partition function which are affected by the environment. Thus we assume that the Hamiltonian of the system is separable into a part depending only on a set of internal coordinates and mo-

menta, and a part depending only on external coordinates and momenta, the former coordinates being independent of the relative positions of the molecules. This implies that the partition function can be written as the product of an internal part, depending only on temperature, and an external part depending on temperature and volume, i.e.

$$Q(T, V) = Q_{int}(T) \cdot Q_{ext}(T, V) \ . \tag{5}$$

The criterion for a coordinate to be external or internal is whether a change in that coordinate requires a *major* change in the relative arrangement of the molecules or not. Thus, the electronic degrees of freedom, and all stretching and bending vibrations in the molecules are considered as internal degrees of freedom, whereas the translations and rotations of the molecules as a whole are external motions. The rotational motions *within* the molecules (about bonds) would be considered as external motions if they were completely free, but in most practical cases, such as for the n-alkanes, these rotations are hindered. Thus, they can best be represented as twisting vibrations around one of the various possible equilibrium positions (one trans and two gauche positions in the case of n-alkanes) which are superimposed on discrete jumps from one equilibrium position (rotational isomer) to another. The former are considered as internal, the latter as external motions. [16, 17]

Therefore, for the remainder of this paper we will consider only $Q_{ext}(T,V)$ which is now written as the following product

$$Q_e(T, V) = Q^t Q^r Q^s \ , \tag{6}$$

where Q^s, the conformational (or steric [11]) contribution to the partition function, will be discussed in the next section. Implied by the above equation is that the stretching and bending frequencies are independent of conformation. There is good reason to believe that this approximation is valid. [18] Also, it implies that these vibrational modes and the electronic degrees of freedom should be same in, say, a nematic liquid and an isotropic liquid. There is also supporting evidence for this view. [19]

Conformational Partition Function (Q^s)

We employ the essence of the rotational isomeric model [20] to describe the statistically averaged conformational behavior of the molecules. This model is both convenient and well-justified by physical circumstances. Each molecule, or bond, is treated as occurring in one or another of several *discrete* rotational states (conformations). The equilibrium positions of these states are chosen to coincide with the potential minima. In the case of n-alkyl chains, the three conformations of the C-C bonds are the trans conformation and two gauche conformations, the former being energetically more stable than the latter two by an amount E. If we

define a statistical weight factor σ equal to exp (−E/RT), the conformational partition function for a given n-alkane takes the form [11, 18]

$$Q^S = \sum_i g_i \sigma^i = 1 + g_1\sigma + g_2\sigma^2 + \dots , \quad (7)$$

where the total number of conformers, Σg_i, is equal to 3^{n-3} for an n-alkyl chain containing n carbon atoms (or n−1 C–C bonds), and g_i is the number of conformers having statistical weight σ^i. (Conformers with a weighting σ^2, for example, would be energetically less stable than the completely extended or trans conformers by an energy 2E).

One approach to evaluating the various g_i's is via the statistical mechanical matrix technique developed by Flory and coworkers [20] and utilized recently by others. [12, 18] However, for the present purposes, a more tractable approach is the approximate, statistical method proposed by Pitzer [11] for calculating the thermodynamic properites of normal and branch chain alkanes. The predictive and correlative ability of Pitzer's simple method (which, in effect, utilizes the rotational isomeric model without calling it such) is comparable to that of the more elegant matrix technique. [18] (Further evidence of this will be presented in the next section). To evaluate Q^S Pitzer, with the aid of Fisher-Hirschfelder models, assigned an energy, in integer multiples of E, to each of the various conformations. The results for n-pentane through n-octane (Table VI in Ref. 11) are summarized in Table 1.

TABLE 1

Number of conformers g_i with statistical weight σ^i for n-pentane through n-octane[11].

Substance/i	0	1	2	3	4	5	∞
Pentane	1	4	2	0	0	0	2
Hexane	1	6	8	2	0	0	10
Heptane	1	8	18	12	2	0	40
Octane	1	10	32	38	16	2	144

Note that certain conformers were deemed energetically so improbable that their statistical weights were taken as zero (i.e., $i \to \infty$).

Through analysis of the liquid phase Raman spectral intensities as a function of temperature for n-C_5 and n-C_6, a value of about 500 cal was established for the parameter E. [21] This value for the energy of the gauche minima relative to the trans minimum for a given bond in higher n-alkanes ($n \geq 5$) is still acceptable today. [20] It is a sufficiently small energy difference that the fraction of liquid phase n-alkane molecules in the completely extended conformation (a number which becomes progressively smaller as the chain length increases) approaches a

value of about 0.01 for n-C_{11} at 100°C (see Table 2 later). On the other hand, X-ray and Raman evidence [13, 20] indicates that solid state n-paraffin molecules are exclusively in the zig-zag conformation. In fact, the Raman spectra show a discontinuous change at the melting point, with the solid state spectrum containing one sharp band attributable to the zig-zag conformation and additional bands, attributable to rotational isomers within the chain, appearing in the liquid state. [13, 20]

The fraction (P_t) of n-alkyl chains or n-alkane molecules to be found in the completely trans conformation is

$$P_t = (Q^s)^{-1}. \tag{8}$$

Accordingly, in the solid state Q^s must be unity, which implies that the effective E, call it E′, approaches infinity for the crystal (see eq. 7). It is argued [20] that in the crystalline phase, there exist external constraints in addition to the usual internal constraints relating to the geometrical features of the bond structure, and hindrances to rotation about bonds. Thus, the requirements of efficient packing and optimization of the intermolecular energy lead to the predominance of the trans form. However, in the liquid state, where disorder prevails, it can be reasoned that the *intra*molecular potential faithfully represents the average state of affairs confronting a given molecule. Hence, in the absence of constraints imposed by neighboring molecules in an ordered crystalline array, departures from the preferred conformation will be abundant. [20]

Environmental influences on the conformational behavior of long chain alkanes is a subject that has concerned other researchers in the past. [22, 23] The entropy of fusion [22] and the aqueous solubility [23] of n-alkanes have been interpreted in terms of external intermolecular constraints to rotation about C-C bonds in the solid state [22] and aqueous solution, [23] respectively. More recently, Seelig [12] employed a spin label (NO) epr technique to investigate the flexibility of the hydrocarbon chains of a smectic phase with bilayer structure. The experiments revealed a high degree of order of the hydrocarbon chains. To provide a quantitative explanation of the experimental data, the following approximation was introduced. The hydrocarbon chains were treated as if their increased stiffness (due to external constraints) in the bilayer was due to an apparent increase in the energy difference E between the trans and gauche conformations; i.e., E was no longer regarded as a pure intramolecular potential energy difference, but as an empirical factor which comprises contributions from intra- as well as inter-molecular forces. In this paper, Seelig's phenomenological approach will be followed. The environmentally dependent E values will be designated by the parameter E′, where the unperturbed E value will be taken as 500 cal. and where $E' > E$.

TEST OF THE CONFORMATIONAL MODEL

Entropy of Melting of n-Alkanes

After initial odd-even effects for the lower molecular weight n-alkanes, the melting point converges to a limiting temperature (~370°K) as the number of carbon atoms increases. Furthermore, the transition entropy change (ΔS) begins to increase more or less linearly with increasing carbon number, (n), producing a slope ($d\Delta S/dn$) of about 0.98 R e.u. per methylene group.[13, 22] This entropic behavior has been analysed in terms of the onset at melting of increased freedom of rotation around C-C bonds,[13, 22] i.e.,

$$\frac{d\Delta S}{dn} = \frac{dS_{liq.}}{dn} - \frac{dS_{sol.}}{dn}$$

$$= \frac{d}{dn}\left\{RT\left(\frac{\partial \ln Q^s}{\partial T}\right) + R\ln Q^s\right\}_{liquid} - \left[RT\left(\frac{\partial \ln Q^s}{\partial T}\right) + R\ln Q^s\right\}_{solid} \quad . \quad (9)$$

Utilizing eq. 7 and letting the effective E value (E') be infinity for the solid state, we obtain a Q^s_{sol} value of unity; thus,

$$\frac{dS_{sol}}{dn} = 0, \text{ for all T and n.} \quad (10)$$

For the liquid phase, if we let E=0, all 3^{n-3} n-alkane conformations become equally probable and $Q^s_{liq} = 3^{n-3}$ (see Eq. 7); thus,

$$\frac{d\Delta S}{dn} = \frac{dS_{liq}}{dn} = \frac{d\,[R\,(n-3)\ln 3]}{dn} \approx 1.10R \; . \quad (11)$$

This value is somewhat high, suggesting that the liquid E value should be greater than zero, as one would expect.[21] Choosing values of E=500 cal and T=370°K, we have, utilizing Eqs. 7 and 9 and Table 1,

$$\frac{d\Delta S}{dn} = \frac{dS_{liq}}{dn} = \frac{d\left[RT\left(\frac{\partial \ln Q^s}{\partial T}\right) + R\ln Q^s\right]_{liq}}{dn} \quad (12)$$

$$= (0.256 + 0.584)\,R = 0.840\,R \; .$$

It is found empirically that both $\ln Q^s_{liq}$ and $T(\partial \ln Q^s/\partial T)_{liq}$ are linear functions of n. The standard deviations in the slopes of the lines are, respectively, $<\pm 0.001$ and ± 0.003. Better agreement with the experimental value of 0.98 R could be achieved by introducing an additional empirical parameter[22] or by treating E as an adjustable parameter (with $E \approx 300$ cal, excellent agreement would be pro-

duced). Thus, it is clear that, within the framework of the present approach, a satisfactory explanation of the observed entropy increment is possible.

Seelig's Results [12]

A more stringent test of the applicability of Pitzer's formulation for Q^s is provided through analysis of Seelig's results.[12] Utilizing Flory's matrix formalism,[20] Seelig obtained a value of $E' = 1500$ cal. at 20°C for the hydrocarbon chains in the smectic phase of the lipid bilayer and assumed a value of $E = 500$ cal. for the isotropic liquid. With these values, he calculated that the probability of finding a n-C_{10} chain in the all-trans conformation was 0.40 for the liquid crystal and 0.03 for the isotropic liquid, a striking difference in flexibility. He also determined the configurational entropy per methylene group in each of the two phases at 20°C (equivalent to dS/dn), obtaining values of 1.61 and 0.86 e.u. for the isotropic and aniostropic phases, respectively. Further, he found that $d\Delta S/dn$ (equal to 0.75 e.u.) was virtually independent of temperature in the range 10° to 40°C.

Again, utilizing Eq. 7 and Table 1, $\ln Q^s$ and $T(\partial \ln Q^s/\partial T)$ were determined for n-C_5 through n-C_8 in both the anisotropic (primed) condition ($E' = 1500$ cal.) and isotropic (unprimed) condition ($E = 500$ cal.) at 20°C. As before, it is observed that $\ln Q^s$ and $T(\partial \ln Q^s/\partial T)$ are linear functions of n for both conditions. Once more,

$$\frac{dS}{dn} = \frac{d\left[RT\left(\frac{\partial \ln Q^s}{\partial T}\right) + R\ln Q^s\right]_{\text{isotropic}}}{dn} \tag{13}$$

$$= R[0.303 + 0.517] = 1.63 \text{ e.u., and}$$

$$\frac{dS'}{dn} = \frac{d\left[RT\left(\frac{\partial \ln Q^s}{\partial T}\right) + R\ln Q^s\right]_{\text{anisotropic}}}{dn} \tag{14}$$

$$= R[0.303 + 0.133] = 0.87 \text{ e.u., and}$$

$d\Delta S/dn = 0.76$ e.u. (constant in the temperature range 10° to 30°C), all in excellent agreement with Seelig's values. Further, our value of 0.133 for $(d\ln Q^s/dn)_{aniso}$ compares quite favorably with his value of 0.132. Finally, linear extrapolation of $\ln Q^s$ to n-C_{10}, yields values of $Q^s_{aniso} = 2.566$ and $Q^s_{iso} = 40.57$. Through eq. 8, the fraction of n-C_{10} chains in the all-trans conformation is found to be 0.390 for the liquid crystal phase and 0.025 for the isotropic phase. Thus, this remarkable agreement with the results derived using the more sophisticated matrix technique provides further justification for use of Pitzer's

simplified method. It is noteworthy that the results derived from Table 1 represent successful extrapolations to longer chain lengths and demonstrate the valid transferability of statistical weight factors. [18]

MESOPHASE-ISOTROPIC TRANSITIONS AND MOLECULAR FLEXIBILITY

There have been extensive studies of the liquid-crystal transition temperatures in homologous series of nematogenic compounds as a function of the carbon number in the alkyl pendant groups. Inspection of Gray's book [24] reveals that the most common type of phase behavior is that illustrated in Figure 1. For very short chain lengths, one finds only the liquid-crystal phase sequence nematic-isotropic. For the first few members of this series, odd-even effects may occur in the transition temperature. At some intermediate chain length the smectic phase appears, leading to the sequence: smectic-nematic-isotropic. The smectic-nematic transition temperature rises steeply with increasing chain length and eventually converges with the gradually descending nematic-isotropic curve. Prior to the point where the nematic phase disappears entirely, the nematic-isotropic curve approaches a limiting temperature, which is maintained by the smectic-isotropic transition. Many examples of this general phase behavior can be found in the more recent literature. [25-28]

Young, Haller and Aviram[6] prepared and characterized a homologous series of nematogenic nitrones. They observed that both the nematic-isotropic (beyond a certain minimum chain length) and smectic-isotropic transition entropies increased more or less linearly with increasing carbon number, yielding $d\Delta S/dn$ values of 0.13 and 0.15 e.u., respectively. Similar linear ΔS vs. n behavior was found for other homologous series in the literature. For example, for the dialkoxyazoxybenzene series, [29] one obtains a value of 0.21 ± 0.03 e.u. for $d\Delta S_{NI}/dn$ from a least squares linear fit of the results for diheptyl through didecyl (where the nematic phase last appears), and a $d\Delta S_{SI}/dn$ value of 0.56 e.u. (from two points only – diundecyl and didodecyl). Comparing these transition entropy increments per methylene group with the much higher value for n-alkane melting (1.95 e.u.), they concluded that the alkyl pendant groups in smectic and nematic phases cannot exist in a single elongated conformation. This conclusion was based on the assumption that the alkyl pendant groups in the isotropic phase are not subject to external constraints, i.e., that they are conformationally as free as liquid n-alkane molecules. Hence, they regarded the mesophase-isotropic transitions as involving anisotropic states where the hydrocarbon chains were somewhat restricted by external constraints, but hardly as restricted as in solid state n-alkanes. The other supporting evidence for this view has already been cited. [1-3, 5, 8, 9, 12]

Let us consider this question of molecular flexibility in more quantitative detail, using Arnold's results [29] as our basis. Concurrent with the linear increase

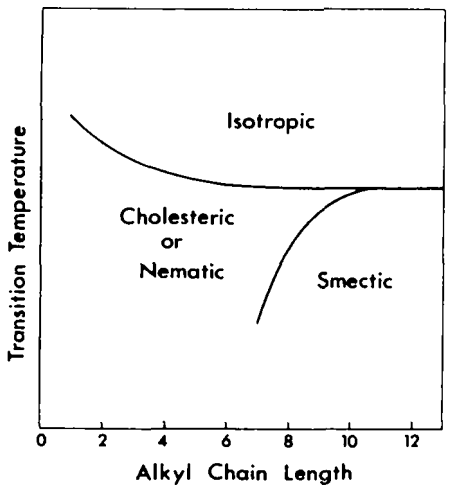

FIGURE 1. Typical phase diagram for homologous series. Transition temperature vs. number of carbon atoms in alkyl pendant groups.

in ΔS with increasing carbon number, inspection of Arnold's data reveals that the mesophase-isotropic transition temperature (N→I or S→I) levels off at about 123.0 ± 1.5°C, beginning with the diheptyl derivative (see Figure 1). This ΔS and T behavior is reminiscent of what is observed for n-alkane melting.[13] In the case of the nematic-isotropic transition, utilizing Eqs. 1-6, one can write:

$$\frac{d\Delta S_{NI}}{dn} = \frac{d\Delta S^{t}}{dn} + \frac{d\Delta S^{r}}{dn} + \frac{d\Delta S^{s}}{dn} = \frac{d\Delta S^{t+r}}{dn} + \frac{d}{dn}\left[RT\left\{\frac{\partial \ln (Q_I^s/Q_N^s)}{\partial T}\right\} + R\ln\left(\frac{Q_I^s}{Q_N^s}\right)\right] \tag{15}$$

As in the case of n-alkane melting, we will attribute the transitional entropy increment per methylene group to the onset upon transition of increased rotational freedom about C-C bonds, i.e., $d\Delta S^{t+r}/dn$ is taken to approach zero once a sufficiently long chain length has been attained.[2,4,13] Accordingly, (a) assuming that $d\Delta S^{t+r}/dn$ is zero for the heptyl derivative and beyond, (b) taking $d\Delta S_{NI}/dn$ as 0.21 e.u.,[29] (c) letting T = 396.2°K, (d) assuming that the pendant alkyl groups are free from *external* constraints in the isotropic liquid phase, where E is taken as 500 cal., and (e) utilizing Eqs. 7 and 15 and Table 1, we obtain (by trial and error solution) a value of E′ = 1050 cal. for the effective[12] trans/gauche energy difference on the nematic side of the transition for the dialkoxyazoxybenzene series. Similar trial error procedure, using the less reliable $d\Delta S_{SI}/dn$ value of 0.56 e.u.,[29] yields a smectic phase value of E′ = 1600 cal.,

TABLE 2

Probability (as a percentage) of finding the n-alkyl chain in Dialkoxyazoxybenzene in the all-trans conformation at 123°C

Case I – Letting E = 500 cal for the Isotropic Phase

Chain	E = 0 [a]	E = 500 (iso) [b]	E′ = 1050 (nem) [c]	E′ = 1600 (smec) [c]	E′ = ∞ (solid) [d]
n-C_4	33.3	48.5	65.5	79.2	100.0
n-C_5	11.1	27.2	45.6	64.2	100.0
n-C_6	3.7	14.9	31.5	51.9	100.0
n-C_7	1.2	8.2	21.8	41.9	100.0
n-C_8	0.4	4.5	15.1	33.9	100.0
n-C_9	0.4	2.5	10.4	27.4	100.0
n-C_{10}	<0.1	1.4	7.2	22.2	100.0
n-C_{11}	<0.1	0.7	5.2	17.9	100.0

Case II – Letting E′ = ∞ for the Smectic Phase

Chain	E′ = 2600 (iso) [c]	E′ = 3150 (nem) [c]	E′ = ∞ (smec and solid) [d]
n-C_4	93.1	96.5	100.0
n-C_5	87.0	93.1	100.0
n-C_6	81.2	89.9	100.0
n-C_7	75.8	86.8	100.0
n-C_8	70.8	83.8	100.0
n-C_9	66.1	80.9	100.0
n-C_{10}	61.7	78.1	100.0
n-C_{11}	57.6	75.3	100.0

a. With no potential energy difference between trans and gauche minima, in which case the percentage is $100/3^{n-3}$ (see Eq. 8)
b. Chosen to agree with value for n-alkane liquids
c. Determined from observed d Δ S/dn values (see text)
d. Chosen to agree with effective value for n-alkane solids

which is in the same range as Seelig's more directly determined smectic values.[12] Summarized in Table 2 (Case I) is the probability of finding a given n-alkyl chain in the fully extended (all-trans) conformation for the various "effective-energy-difference" conditions (see Eq 8). Also, listed in Table 3 (Case I) are mean end-to-end distances for the n-alkyl chains, as calculated by Flory's procedure[20] for independent bond rotational potentials. Note that appreciable chain shortening is indicated as one proceeds through the phase sequence: solid-smectic-nematic-isotropic, being more pronounced for the longer n-alkyl chains (as in the melting of n-alkanes[9, 13, 30]). Also note that the values for C_4, and C_9 -C_{11} are extrapolated values, allowed by the observed linearity of $\ln Q^5$ vs. n. Accepting these findings at face value, one would conclude that an appreciable population of

TABLE 3

RMS end-to-end (Carbon-to-Carbon) distance (in A) of n-alkyl chains at 123°C

Case I – Letting E = 500 cal. for the Isotropic Phase

Chain	E = 500 (iso)	E' = 1050 (nem)	E' = 1600 (smec)	E' = ∞ (solid)
n-C_4	3.48	3.63	3.74	3.81
n-C_5	4.31	4.61	4.81	5.07
n-C_6	5.07	5.55	5.90	6.34
n-C_7	5.77	6.43	6.92	7.61
n-C_8	6.40	7.26	7.93	8.88
n-C_9	6.99	8.05	8.90	10.15
n-C_{10}	7.54	8.80	9.84	11.42
n-C_{11}	8.06	9.51	10.75	12.68

Case II – Letting E' = ∞ for the Smectic Phase

Chain	E' = 2600 (iso)	E' = 3150 (nem)	E' = ∞ (smec and solid)
n-C_4	3.80	3.81	3.81
n-C_5	4.99	5.03	5.07
n-C_6	6.22	6.28	6.34
n-C_7	7.39	7.49	7.61
n-C_8	8.59	8.74	8.88
n-C_9	9.74	9.93	10.15
n-C_{10}	10.91	11.16	11.42
n-C_{11}	12.03	12.35	12.68

The above values were calculated through the procedure described in ref. 20 (Chap. I, Sec. 10) for chains with fixed bond angles and independent bond rotational potentials. The C-C-C bond angle was taken as 112 degrees and the C-C bond length as 1.53 A. The assumption of independent rotations is justifiable for a chain of ten or less C-C bonds (See Figure 9, Chap. V, Ref. 20).

pendant-group conformations other than the all-trans one exists in both the nematic and isotropic liquid phases of this series. Further, for the nitrone series,[6] one would expect that, since $d\Delta S_{NI}/dn$ is only 0.13 e.u., E' would be less than 1050 cal. and, accordingly, the nematic phase pendant-chain flexibility should more closely resemble that of the isotropic phase.

If one agrees with this conformational interpretation of the transitional entropy increment per methylene group, then clearly the values involved imply mesophase-isotropic conformational changes far less dramatic than those observed for n-alkane melting. These changes were interpreted above by assuming that in the isotropic liquid phase the rotation of alkyl chains about C-C bonds is free of any intermolecular constraints (i.e., E = 500 cal. as in n-alkane liquids).

While existing evidence indicates that this assumption is probably valid for the dialkoxyazoxybenzene and other series, it would be unwise to generalize. For example, the X-ray results of de Vries [10] indicate that the alkyl groups in 4-alkoxybenzal-4 '-ethylanilines are predominantly in the all-trans conformation, even on the isotropic side of the nematic-isotropic transition. It is conceivable that, with certain nematogenic compounds, isotropic phase n-alkyl chains are conformationally restricted relative to liquid phase n-alkanes. These external constraints could result from short-range orientational ordering in the isotropic phase.[4, 10, 31-33] Accordingly, if it is assumed that E' approaches infinity for the smectic phase, (i.e., the pendant groups are exclusively in the all-trans conformation), then utilizing the observed $d\Delta S_{SI}/dn$ result for the dialkoxyazoxybenzene series and the procedure outlined previously, one obtains a value of E' = 2600 cal. for the isotropic phase. Further, with this new isotropic value and $d\Delta S_{NI}/dn = 0.21$ e.u., E' for the nematic phase becomes 3150 cal. As before, the fraction of n-alkyl chains in the all-trans conformation (Table 2, Case II) and the mean end-to-end distance of the chains (Table 3, Case II) can be calculated. With this new set of energy conditions, it is apparent that the lengths of pentyl, hexyl and heptyl chains in the isotropic and nematic phases would be (within experimental error) approximately equal to the fully extended lengths, as suggested by de Vries. It should be noted, however, that other nematogens (monohexyl derivatives) studied by X-ray [10] show molecular lengths in the isotropic phase roughly 0.8. Å less than the fully extended lengths. This would place the isotropic E' values for these compounds at, roughly, 1000 cal.

THERMODYNAMICS OF *n*-ALKANES DISSOLVED IN NEMATICS

Statistical Thermodynamic Relations

Let us consider solute molecules (component 2) at infinite dilution in a solvent medium (component 1), which may or may not be liquid-crystalline. It is assumed that the product $P\bar{V}_2^e$ is negligibly small (where P is the pressure and $\bar{V}_2^e$ is the solute partial molar excess volume), resulting in a near equality between the solute partial molar excess Gibbs and Helmholtz functions (i.e., $\bar{G}_2^e \approx \bar{A}_2^e$) and between the corresponding enthalpy and internal energy terms (i.e., $\bar{H}_2^e \approx \bar{U}_2^e$). It is also assumed that while the dissolved solute possibly perturbs the local structure of the solvent, the long range structure (if any) and solvent molecular energy states (on the average) are unaltered due to the infinite dilution condition of the solute.[14, 34] Accordingly, from Eqs. 2-6, we have

$$\bar{G}_2^e \approx \bar{A}_2^e = -RT\ln\left[\frac{(Q^tQ^rQ^s)_{actual}}{(Q^tQ^rQ^s)_{ideal}}\right], \qquad (16)$$

$$\bar{H}_2^e \approx \bar{U}_2^e = RT^2 \frac{\partial}{\partial T} \ln \left[\frac{(Q^t Q^r Q^s)_{actual}}{(Q^t Q^r Q^s)_{ideal}} \right] , \tag{17}$$

where the subscript "actual" (hereafter denoted by "a") refers to the solute molecular partition function in the environment of the actual solution and the subscript "ideal" (hereafter denoted by "i") refers to the solute molecular partition function in an ideal solution. Letting it be understood that the ensuing treatment is for the solute component, the subscript "2" will be dropped. Relating $\bar{G}^e$ to the infinite dilution solute activity coefficient (γ), we have from Eq. 16:

$$\begin{aligned} \gamma \equiv \exp(\bar{G}^e/RT) &\doteq \frac{Q_i^t}{Q_a^t} \cdot \frac{Q_i^r}{Q_a^r} \cdot \frac{Q_i^s}{Q_a^s} \\ &\doteq (\gamma^t) \cdot (\gamma^r) \cdot (\gamma^s) . \end{aligned} \tag{18}$$

Also, from Eq. 17:

$$\begin{aligned} \bar{H}^e &\doteq RT^2 \frac{\partial}{\partial T} \left[\ln \frac{Q_a^t}{Q_i^t} + \ln \frac{Q_a^r}{Q_i^r} + \ln \frac{Q_a^s}{Q_i^s} \right] \\ &\doteq (\bar{H}^e)^t + (\bar{H}^e)^r + (\bar{H}^e)^s . \end{aligned} \tag{19}$$

Finally, the solute partial molar heat of solution ($\Delta\bar{H}$) is given by

$$\Delta\bar{H} = \bar{H}^e - \Delta H^{vap.} , \tag{20}$$

where $\Delta H^{vap.}$ is the pure solute heat of vaporization.

Interpretation of GLC Results

Chow and Martire [14] used gas-liquid chromatography (glc) to determine the infinite dilution activity coefficients (γ) and heats of solution ($\Delta\bar{H}$) of over forty non-mesomorphic solutes in both the nematic and isotropic phases of p-azoxyanisole (PAA) and 4,4'-dihexoxyazoxybenzene (DHAB). They and others [34, 35] utilized expressions essentially equivalent to Eqs. 18-20 to present a qualitative discussion of their glc results. Let us consider, in more quantitative detail, the data for the n-alkane solutes (excluding the less reliable n-C_{11} data) with PAA and DHAB. [14] Listed in Table 4 are the experimental data of interest for PAA, i.e., the activity coefficients on the nematic and isotropic sides of the phase transition (407.4°K), and the heats of solution in the nematic phase. [14] While the final derived results will be given in graphical form for DHAB (nematic-isotropic transition temperature of 401.4°K), the experimental data [14] and intermediate derived results will not be listed.

Assume that the *external* conformational constraints (due to the alignment of the solvent) experienced by an n-alkane molecule at infinite dilution in a nema-

tic phase are comparable to those experienced by the alkyl chain of the nematogen. Taking E=500 cal. for an ideal solution and E'=1050 cal. (Case I in the previous section) for the nematic phase, it becomes possible to evaluate γ^s (or Q_i^s/Q_a^s), the conformational contribution to the activity coefficient, and $(\bar{H}^e)^s$ on the nematic side of the transition. Thus utilizing Eqs. 7 and 19, Table 1, and the linearity of $\ln Q^s$ and $T(\partial \ln Q^s/\partial T)$ vs. carbon number, γ^s and $(\bar{H}^e)^s$ were evaluated for the n-alkanes and are listed for PAA in Table 4. Note that $(\bar{H}^e)^s$ is relatively small (roughly 11% of the observed $\bar{H}^e$ [14]) and endothermic. Also, $\gamma^s > 1$, indicating a positive contribution to the deviation from Raoult's law – a counter-solubility effect. [14]

The evaluation of γ^r and $(\bar{H}^e)^r$ presents a problem. One would expect that, if, in the nematic solution, the rotational motion of the solute molecule as a whole were to be restricted (due to anisotropic repulsive interactions with the aligned rods of the nematic environment) relative to such motion in an ideal solution (free rotation assumed), the rotational partition function of such a hindered rotor should decrease, i.e., $\gamma^r \geq 1$ (see eq. 18). Unfortunately, a rigorous determination of Q_a^r is difficult, if not impossible. First, the solute moments of inertia would be expected to change somewhat (due to different conformational populations) upon "transfer" from an ideal solution to the actual nematic solution. Secondly, even if the moments of inertia were to be estimated, [20] the extraction of Q_a^r from even an approximate quantum mechanical model is hardly possible without detailed knowledge of the rotational energy barrier involved. Accordingly, two simple models will be considered, from which an empirical expression for γ^r will be deduced.

The partition function (Q_i^f) for a symmetrical linear rotor with two degrees of free rotational freedom (perpendicular to the long axis) is well known:

$$Q_i^f = \frac{4\pi^2 IkT}{h^2} \quad , \tag{21}$$

where I is the moment of inertia.

Consider now a linear rotor whose center is fixed in and whose rotational motion is restricted by a cylindrical box with infinite hard walls (see Fig. 2). By analogy to the solution for a particle undergoing translational motion in a two dimensional box (replacing the mass of the particle (m) by the moment of inertia (I), and the box dimension (ℓ) by twice the absolute value of the maximum angle of rotation about the vertical ($2|\alpha|$), where $|\alpha| < \pi/2$), the hindered rotor partition function (Q_a^r) is:

$$Q_a^r = \frac{8\pi IkT\alpha^2}{h^2} \quad . \tag{22}$$

Another possibility is to treat the restricted rotation or rotational oscillation

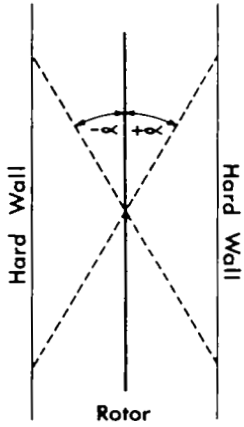

FIGURE 2 Linear rotor-in-a box. Potential energy is V=0 for $|\theta| < |\alpha|$ and V=∞ for $|\theta| > |\alpha|$, where θ is the angle off the vertical.

in terms of an Einstein model.[36] When $T >> \Theta$ (where Θ is the characteristic temperature), we have for two degrees of freedom:

$$Q_a^r \approx \left(\frac{T}{\Theta}\right)^2 , \tag{23}$$

where[36]

$$\Theta^2 \approx \frac{h^2 T}{2\pi^2 Ik\alpha^2} , \tag{24}$$

and α is, again, the maximum angle ("amplitude"). Thus,

$$Q_a^r = \frac{2\pi^2 IkT\alpha^2}{h^2} . \tag{25}$$

One can readily calculate that, with $I = 10^{-37}$ gm-cm^2, T = 400°K and $\alpha = \pi/3$ (see later), $\Theta \approx 0{,}02T$; therefore, the condition $T >> \Theta$ is satisfied, as would be expected for such a weak force constant and large amplitude.

Taking Eqs. 18, 21 and 22, and assuming that the solute moment of inertia perpendicular to its long axis is the same in an ideal solution and in the nematic solution, one obtains for the rotational contribution to the solute activity coefficient from the rotor-in-a-box model:

$$\gamma^r = \pi/2\alpha^2 . \tag{26}$$

Similarly, with Eqs. 18, 21 and 25, the Einstein model yields:

$$\gamma^r = 2/\alpha^2 . \tag{27}$$

Both expressions have the same form, i.e., $\gamma^r = \text{constant}/\alpha^2$. However, neither expression gives the correct limiting value, i.e., γ^r should be unity for free rotation ($|\alpha| = \pi/2$). This is not surprising considering the crudeness of the models. Thus, let us choose the constant empirically such that γ^r becomes unity when $\alpha^2 = \pi^2/4$, i.e., let

$$\gamma^r = \pi^2/4\alpha^2 \quad , \tag{28}$$

which implies that the "corrected" restricted rotational partition function is:

$$Q_a^r = \frac{16IkT\alpha^2}{h^2} \quad . \tag{29}$$

To evaluate γ^r on the nematic side of the transition from Eq. 28, one needs to know α^2, which is related to the solute order parameter η_2 through the expression [36]

$$\eta = \frac{\cos\alpha}{2}(\cos\alpha + 1) \tag{30}$$

The η_2 values have not been directly determined for the n-alkanes in nematic PAA and DHAB. However, they may be estimated from the glc results [14] using the following expressions derived from a "two phase" model [15]:

$$\frac{1}{\gamma_{nem}} = \frac{\eta_1}{\gamma_0} + \frac{1-\eta_1}{\gamma_{iso}} \quad , \tag{31}$$

and

$$\gamma_{nem} = \eta_2\gamma_0 + (1-\eta_2)\gamma_{iso}, \tag{32}$$

where, η_1 and η_2 are, respectively, the solvent and solute nematic order parameters at the transition; γ_{nem} and γ_{iso} are the observed solute activity coefficients on the nematic and isotropic sides, respectively, of the transition; and γ_0 is the solute activity coefficient in a hypothetical completely aligned ($\eta_1 = 1$) nematic solvent. For DHAB, $\eta_1 = 0.32$ [7], as is the average of the published values for PAA (0.31 [7], 0.34 [36], 0.30 [37]). One would expect the solute order parameters to be lower and α values to be higher than for the pure nematogens ($\alpha = 63.7°$ for $\eta_1 = 0.32$, according to Eq. 30). From Eqs. 31 and 32 with $\eta_1 = 0.32$, the solute order parameters were determined and are listed for PAA in Table 4. [Note that the η_2 value calculated in a similar manner from the glc results [14] for p-xylene in DHAB is 0.21, which compares favorably with that determined from nmr for p-difluorobenzene in DHAB (0.18) [19].] Then, from Eqs. 28 and 30, the γ^r values were calculated (see Table 4). Finally, since the ratio (Q_a^r/Q_i^r) is temperature independent, $(\bar{H}^e)^r$ is zero (see Eq. 19). Alternatively, one could argue that for both the free and restricted rotor the allowed molecular energy levels are sufficiently closely spaced that the classical result for the rotational molar internal energy obtains in both cases, i.e., $U_i^r = U_a^r = RT$, thus $(\bar{H}^e)^r = (\bar{U}^e)^r = 0$.

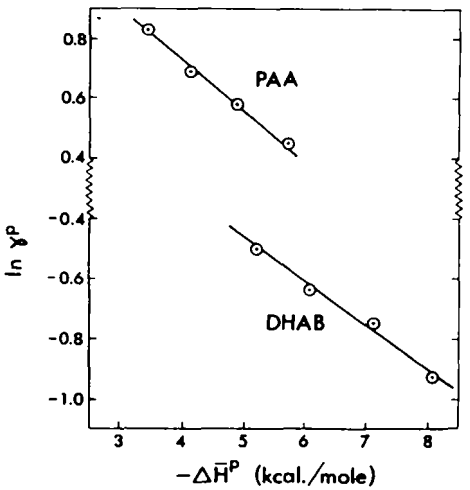

FIGURE 3 $\ln\gamma^p$ (potential energy contribution to $\ln\gamma$) vs. $-\Delta H^{pp}$ (potential energy contribution to $-\Delta H$) for n-alkanes at infinite dilution in nematic PAA and DHAB at the transition point.

Therefore, utilizing the experimental γ and ΔH results for the nematic side of the transition and the derived results for γ^s, γ^r and $(\bar{H}^e)^s$, the quantities γ^p and ΔH^{pp} were calculated via Eqs. 18-20, are listed for PAA in Table 4. The superscript "t" has been changed to "p" to denote that it is only the potential energy contribution to the translational partition function which differs in an ideal solution and the nematic solution. In an ideal solution,, the solute-solvent segmental interaction energy is equal to the arithmetic mean of solute-solute and solvent-solvent segmental interaction energies,[38] and all energy terms are isotropic. In the actual solution, solute-solvent interactions may be weaker or stronger than this arithmetic mean value and, in a nematic solvent, anisotropic forces are operative. Accordingly, (Q_i^p/Q_a^p) or γ^p may be less than or greater than unity, depending on the relative strengths of the interactions. It has been argued[14] that a measure of relative γ^p values within a series of solutes in a given solvent (or in a given phase of a liquid crystal solvent) should be the relative $\Delta\bar{H}^{pp}$ values, i.e., stronger solute-solvent interactions should lead to more negative $\Delta\bar{H}^{pp}$ values and smaller γ^p values. This argument is valid, of course, only if the negative enthalpy trend predominates over any negative entropy trend (for $-T\Delta\bar{S}^{pp}$) which may exist. Such appears to be the case for the n-alkanes in nematic PAA and DHAB, as is illustrated in Figure 3 by the excellent linear correlation between $\ln\gamma^p$ and $-\Delta\bar{H}^{pp}$. Note that the γ^p values are smaller and the $\Delta\bar{H}^{pp}$ values more negative for DHAB. This is due to weaker solvent-solvent and/or stronger solute-solvent interaction terms with DHAB.[14, 38]

In the previous section an alternative scheme (called Case II), prompted by results from X-ray analysis,[10] was considered. Consistent with a conformational interpretation of the transition entropy increments per methylene group, this alternative led to a value of $E' = 3150$ cal. for the effective trans/gauche energy difference in the nematic phase. If, as before, one employs this value to determine γ^S for the n-alkane solutes, absurdly high γ^S values (e.g., $\gamma^S \approx 58$ for n-C_{10} in DHAB) and unrealistically low γ^P values (e.g., $\gamma^P \approx 0.035$ for n-C_{10} in DHAB) are obtained. Contrasting these findings with the more reasonable interpretation developed using the previous scheme (i.e., Case I) strengthens the view that the effective intra- and inter-molecular constraints to rotation about C-C bonds are such that in the nematic and isotropic phases of dialkoxyazoxybenzenes, alkyl chains are far from exclusively in the all-trans conformation.

TABLE 4

Experimental and derived thermodynamic results for n-alkanes at infinite dilution in PAA at 407.4°K (with $E' = 1050$ cal.)

							Units of kcal./mole		
Solute	$\gamma^{14}_{nem.}$	$\gamma^{14}_{iso.}$	γ^S	η_2	γ^I	γ^P	$-\Delta\bar{H}^{14}_{nem.}$	$(\bar{H}^e)^S$	$-\Delta\bar{H}^P$
n-C_7	8.85	7.27	2.63	0.17	1.47	2.29	3.02	0.40	3.42
n-C_8	9.63	7.91	3.30	0.17	1.47	1.99	3.61	0.49	4.10
n-C_9	10.61	8.58	4.15	0.16	1.43	1.79	4.30	0.58	4.88
n-C_{10} †	11.65	9.41	5.20	0.16	1.43	1.57	5.03	0.67	5.70

† The values for n-C_{10} in nematic PAA given in Ref. 14 are incorrect. They should read $\bar{H}^e = 5.32$ kcal/mole and $\bar{S}^e = 8.18$ e.u. instead of 5.23 and 8.10, respectively.

CONCLUSION

By analogy to n-alkane melting, the observed nematic-isotropic (NI) transition entropy increment per methylene group along a homologous series has been interpreted in terms of the conformational population of the alkyl pendant groups before and after transition. From this model, one is led to the conclusion that the NI transitional conformational changes are far less dramatic than those observed for n-alkane melting. Two extremes, each of them consistent with the observed mesophase-isotropic entropy increments for the dialkoxyazoxybenzene series, were considered. The first assumed an isotropic phase where rotations about C-C bonds were unaffected by the environment ($E = 500$ cal) and indicated a nematic phase where the alkyl groups were subject to small external conformational constraints ($E' = 1050$ cal). The second consisted of an isotropic phase ($E' = 2600$ cal) and a nematic phase ($E' = 3150$ cal) with apprecia-

ble intermolecular constraints. [Between these two extremes, any combination of trans/gauche energy differences which yields a value of about 550 cal for (E'_{nem} – E_{iso}) would also fit the observed NI entropy results.] With neither extreme can the nematic or isotropic phase alkyl chains be confined *exclusively* to a single elongated conformation. The bulk of existing evidence and the findings of the present study suggest that reality lies much closer to the first extreme, which would mean that there is appreciable flexibility of the alkyl groups in both phases of the dialkoxyazoxybenzenes (see Tables 2 and 3 Case I). Conceivably there may be slight external constraints operative in the isotropic phase (see γ_{iso} values for n-alkanes in PAA – Table 3) and, for example, the values E'_{iso} = 700 cal and E'_{nem} = 1250 cal might represent a more valid set for describing the statistically-averaged conformational behavior.

The primary purpose of the present paper was to consider the question of molecular flexibility in nematogenic liquid crystals in more quantitative detail. To some extent, this has been accomplished. Admittedly, however, more extensive experimental work and more rigorous theoretical studies need to be done before conclusions may be reached with greater confidence. Additional and, if possible, more quantitative Raman work would help shed light on the trans/gauche energy difference in the various phases. Resonance experiments (nmr and/or epr) with chain labelling would also be of great value in that respect. Additional thermodynamic phase transition studies (temperature, entropy changes and density changes) should be performed on selected homologous series, up to very long alkyl pendant groups (to establish $d\Delta S_{SI}/dn$ and, if possible, the $d\Delta S/dn$ value for the solid-isotropic transition upon mesophase disappearance). One candidate for these and other (e.g., determination of oder parameters) studies would be the 4-alkoxybenzal-4'-ethylaniline series.[10] It is also clear that further X-ray determination of apparent molecular lengths in the isotropic phase would provide direct and useful information for homologous series. Finally, an extension of the Wulf-deRocco model[8] to molecules with rigid central cores and potentially flexible pendant groups might provide enlightening results.

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