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Theory of Systems of Rodlike Particles

II. Thermotropic systems with orientation-dependent interactions

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A system of rigid, inpenetrable, rodlike molecules subject to orientation-dependent mutual attractions is treated by extension of the theory presented in the preceding paper. This energy is formulated, for a system at constant volume, by considering interactions between pairs of segments in contact, rather than in terms of interactions between entire molecules. The orientation-dependent energy between a pair of segments is taken to be proportional to $\cos^2 \psi_{ij}$ where ψ_{ij} is the angle between the principal axes of their polarizability tensors, assumed to be cylindrically symmetric with respect to the molecular axis. A characteristic temperature T^* measures the intensity of these interactions. The orientational energy of the system as a whole is of the form derived by Maier and Saupe. The orientation distribution with respect to the domain axis and the partition function are formulated with T^* and the axial ratio x as parameters. Steric effects of molecular shape asymmetry, embodied in x, are of foremost importance. The reduced temperature $\tilde{T}_{ni} = T_{ni}/xT^*$ at which the nematic-isotropic transition takes place in the neat liquid decreases with decrease in x below its athermal limit $x_{\text{crit}} = 6.417$ for $\tilde{T}_{ni}^{-1} = 0$. Both the entropy difference between isotropic and nematic phases and the orientational heat capacity C_p are monotonic through the transition; C_p diverges at a temperature appreciably above $\tilde{T}_{ni}$, where the metastable anisotropic state becomes unstable. Comparison of theory with experiments on those nematogens whose molecules can be approximated by rigid rods lends encouragement to the prospect of relating characteristics of the nematic-isotropic transition to molecular structure.

INTRODUCTION

Nematic fluids characteristically undergo transformation to the isotropic state when heated above a well defined transition temperature T_{ni} for the given nematogen. This fact alone implies that the order-disorder process

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involves a change in energy. The energy latent at the transition amounts to only several percent of the latent heat of fusion of the crystalline solid.[1-3] The latent volume change typically is on the order of 0.2 to 0.4 percent of the volume. A rough estimation of the change of energy specifically attributable to the change in volume shows it to be only a minor fraction of the energy latent at the nematic-isotropic transition. Hence, an increase in the intermolecular cohesion resulting directly from the higher degree of order in the nematic state appears to be mainly responsible for its lower energy, this being reflected in the latent heat at the transition as well as in the occurrence of the transformation upon raising the temperature.

In passing from the isotropic to the nematic state, the dispersion interactions, or van der Waals attractions, between a pair of neighboring anisodiametric molecules may be markedly increased as they become more nearly parallel primarily as a consequence of the greater area of contact between them. The increase in contacts, however, is gained at the expense of contacts with other molecules. As should be obvious, these two effects of ordering are mutually compensatory at constant volume. Hence, no net increase in intermolecular contacts should be expected to occur with improvements in the degree of order. From the near constancy of the density through the transition, it follows at once that intermolecular contacts summed over all molecules are virtually the same on either side of the transition.

If the van der Waals attractions between molecules were isotropic, then these elementary considerations would lead to the conclusion that the nematic-isotropic liquid transition would be iso-energetic when allowed to take place at constant volume. The small latent volume change must indeed impart a corresponding change in the intermolecular energy. Explanation of the latent heat on this basis is unsatisfactory for two reasons. First, as noted above, the latent heat thus estimated is too small, and, second, such an explanation would be nugatory unless the latent volume change were explicable.

The reasons outlined lead to the conclusion that the dependence of the intermolecular energy on the degree of order is accountable only if attributed to the anisotropy of the London dispersion interactions between molecules. The anisotropy to which we refer must be intrinsic to the nematogenic molecules and not merely on artefact of their shape. The observation that typical nematogens contain phenylene residues, and often other groups as well that have highly anisotropic polarizabilities,[3] is in harmony with the foregoing arguments leading to the conclusion that the order-dependent energy arises from the anisotropy inherent in the molecules. Additional support is provided by the work of van der Veen[4] showing that the increase in the transitive temperature T_{ni} caused by a substituent appended coaxially to a nematogen molecule is greater the larger the anisotropy of the polarizability of the substituent.

Maier and Saupe[5,6] postulated that the orientation-dependent interactions between nematogenic molecules arise from the anisotropy of their dispersion interactions. They developed their well-known theory on this premise. Proceeding along the lines of the London theory of dispersion forces between isotropic molecules, Maier and Saupe[5] applied second-order perturbation theory to the orientation-dependent interactions between molecules whose polarizabilities are anisotropic. They sought to account for the stability and properties of nematic phases solely on the basis of the anisotropy of the forces of attraction, disregarding the steric, or space filling, characteristics of the asymmetric molecules comprising typical nematogenic substances.

In this paper we combine an orientation-dependent energy with the partition function derived in the previous paper[7] for a system of "hard" rodlike molecules in which the intermolecular energy is the same for all configurations (at constant volume) that are devoid of overlaps. The energy that is introduced is of the form prescribed by the Maier–Saupe[5,6] theory, apart from minor modifications. Although the orientation-dependent energy is required to account for thermotropic transformation to the isotropic state, the partition function is dominated by the steric contribution not properly taken into account in most theories of the nematic state.

The treatment that is presented here addresses, primarily, systems at constant volume. The effect of the small volume change that accompanies the ordering process, and that is manifested in the latent volume, can be incorporated as a secondary refinement if desired.

THEORY

The orientational energy

Departing from the theory of Maier–Saupe[5,6] and other theories that consider the interactions between pairs of molecules,[1,2,8] each molecule being included in its entirety, we focus on the interaction between a pair of segments, i and j, whose centers of force are separated by a distance r_{ij}. The dispersion interaction between these segments, expressed in the usual approximation, is

$$\varepsilon_{ij} = -C r_{ij}^{-6}\,\mathrm{trace}(\hat{\boldsymbol{\alpha}}_i \hat{\boldsymbol{\alpha}}_j) \tag{1}$$

where $\hat{\boldsymbol{\alpha}}_i$ and $\hat{\boldsymbol{\alpha}}_j$ are the anisotropic parts of the polarizability tensors for the respective segments and C is a constant. If cylindrical symmetry may be assumed,

$$\varepsilon_{ij} = -C r_{ij}^{-6}\,\Delta\alpha_i\,\Delta\alpha_j(\cos^2\psi_{ij} - \tfrac{1}{3}) \tag{2}$$

where $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ is the difference between the polarizabilities along and perpendicular to the cylindrical axis of the indexed segment, and ψ_{ij} is the angle between these axes for the two segments.

The angle ψ_{ij} between the cylindrical axes of two segments is related to the respective angle ψ_i and ψ_j between these axes and the domain axis X, and to the angles ϕ_i and ϕ_j locating their projections in the transverse YZ plane according to

$$\cos\psi_{ij} = \sin\psi_i \sin\psi_j \cos(\phi_i - \phi_j) + \cos\psi_i \cos\psi_j \tag{3}$$

Let the orientation of segment i be fixed. Then the average of $\cos^2\psi_{ij}$ over the distribution of orientations for segment j is

$$\langle\cos^2\psi_{ij}\rangle_i = \tfrac{3}{2}\langle\sin^2\psi\rangle\sin^2\psi_i - \langle\sin^2\psi\rangle - \sin^2\psi_i + 1$$

the subscript j identifying the neighboring segment being dropped on the presumption that the directions of two segments are uncorrelated, apart from the correlation of each with the preferred axis, even when they are in close proximity. Upon introducing the order parameter s defined by

$$s = 1 - \tfrac{3}{2}\langle\sin^2\psi\rangle \tag{4}$$

one obtains for the statistical mechanical average with respect to the chosen segment i

$$\langle\cos^2\psi_{ij}\rangle_i = \tfrac{2}{3}s(1 - \tfrac{3}{2}\sin^2\psi_i) + \tfrac{1}{3} \tag{5}$$

Throughout the sequel the cylindrical axis of the polarizability tensor is tacitly assumed to be parallel to the geometric long axis of the rodlike particle. The molecules of typical nematogens may depart appreciably from this assumption, a fact that should be weighed in comparing theory with experiment.

Because of the inverse dependence of the interaction energy on r_{ij}^6, it suffices to consider only those pairs of segments that are first neighbors. It follows from Eqs. (2) and (5) that the average orientation-dependent energy of interaction for a segment inclined at angle ψ_i to the domain axis X is of the form

$$\varepsilon(\psi_i) = -(2Cz_c/3r_*^6\tilde{V})(\Delta\alpha_i\Delta\alpha)s(1 - \tfrac{3}{2}\sin^2\psi_i) \tag{6}$$

where z_c is the number of first neighbors surrounding a given segment, r_* is the inter-segment distance for dense packing of the rods, $\tilde{V} = V/V^*$ is the reduced volume of the fluid and $\Delta\alpha$ is the mean anisotropy of all segments. It is assumed that segments of diverse kinds, if present, are distributed at random in the shell of neighbors about the given segment. Dependence on the inverse of the total volume V is prescribed in Eq. (6), rather than on V^{-2} as in the Maier–Saupe formulation. The plausible assumption that the pair correlation function $g_2(r)$ is approximately independent of density over the relevant range leads to $\varepsilon(\psi_i) \sim 1/V$.

The subscript on $\Delta\alpha_i$ may be deleted if $\varepsilon(\psi)$ is construed as the mean orientational energy of a segment. Then

$$\varepsilon(\psi) = -\left(\frac{kT^*}{\tilde{V}}\right)s(1 - \tfrac{3}{2}\sin^2\psi) \tag{7}$$

where k is the Boltzmann constant and

$$kT^* = \left(\frac{2Cz_c}{3r_*^6}\right)(\Delta\alpha)^2 \tag{8}$$

The quantity $kT^*x/\tilde{V}$ corresponds to Maier and Saupe's[1,5,6] A/V^2.

The orientation-dependent energy for the system as a whole obtained by summing Eq. (7) over all segment pairs, $xn_x/2$ in number, is

$$E_{\text{orient}} = -\left(\frac{xn_x}{2}\right)\left(\frac{kT^*}{\tilde{V}}\right)s^2 \tag{9}$$

n_x being the number of molecules. (The symbol n_x and others introduced in the preceding paper,[7] identified by I, retain their previous definitions, except where stated otherwise.) Equation (9) may be obtained directly from Eq. (2) and the definitions of s and T^* according to Eqs. (4) and (8).

As we shall not be concerned with changes in volume, it is expedient to replace the reduced volume $\tilde{V}$ by unity within the scope of the present paper. On this basis Eqs. (7) and (9) may be replaced, respectively, by

$$\varepsilon(\psi) = -kT^*s(1 - \tfrac{3}{2}\sin^2\psi) \tag{7'}$$

and

$$E_{\text{orient}} = -\tfrac{1}{2}xn_x kT^*s^2 \tag{9'}$$

The same modifications may, of course, be effected through redefinition of T^*.

The distribution of orientations at equilibrium

Adaptation of Eq. I–12 of the preceding paper to the present case is achieved through multiplication of that equation by $\exp[-x\varepsilon(\psi)/kT]$. Adoption of Eq. (7′) for $\varepsilon(\psi)$ yields

$$\frac{n_{xy}}{n_x} \propto \omega_y \exp[-\alpha \sin\psi_y + s\tilde{T}^{-1}(1 - \tfrac{3}{2}\sin^2\psi_y)] \tag{10}$$

where $\tilde{T} \equiv T/xT^*$ is the reduced temperature referred to the molecule as a whole, and

$$\alpha = \left(\frac{4}{\pi}\right)ax = -\left(\frac{4}{\pi}\right)x \ln\left(\frac{\bar{y}}{x}\right) \tag{11}$$

as follows from Eq. I-32 with $v_x = 1$. Equation (10) is conveniently written explicitly as follows:

$$\frac{n_{xy}}{n_x} = f_1^{-1}\omega_y \exp[-\alpha \sin\psi_y - \tfrac{3}{2}s\tilde{T}^{-1}\sin^2\psi_y] \tag{12}$$

$\exp(s\tilde{T}^{-1})$ having been incorporated in the normalization factor f_1^{-1}, here redefined by

$$f_p = \int_0^{\pi/2} \sin^p\psi \exp[-\alpha\sin\psi - \tfrac{3}{2}s\tilde{T}^{-1}\sin^2\psi]\mathrm{d}\psi \tag{13}$$

with $p = 1$.

As in I,

$$\frac{f_2}{f_1} = \langle \sin\psi\rangle = \left(\frac{\pi}{4}\right)\frac{\bar{y}}{x} \tag{14}$$

(see Eqs. I-34 and I-36). Also

$$\frac{f_3}{f_1} = \langle \sin^2\psi\rangle = \tfrac{2}{3}(1-s) \tag{15}$$

The free energy and entropy

Combination of Eq. (9′) with Eq. I-7 gives for the reduced molar free energy of the neat liquid ($v_1 = 0$, $v_x = 1$)

$$\begin{aligned} -n_x^{-1}\ln Z_M &= (n_x kT)^{-1}A \\ &= \bar{y} - 1 - \bar{y}\ln\left(\frac{\bar{y}}{x}\right) - \sum_y \left(\frac{n_{xy}}{n_x}\right)\ln\left(\frac{\omega_y n_x}{n_{xy}}\right) \\ &\quad - \ln(x\sigma) - \tfrac{1}{2}s^2\tilde{T}^{-1} \end{aligned} \tag{16}$$

where A is the Helmholtz free energy. Substitution of Eq. (12) in (16) yields

$$(n_x kT)^{-1}A = \bar{y} - 1 - \bar{y}\ln\left(\frac{\bar{y}}{x}\right) - \alpha\langle\sin\psi\rangle - s\left(1 - \frac{s}{2}\right)\tilde{T}^{-1} - \ln(x\sigma f_1) \tag{17}$$

for the liquid at orientational equilibrium. With the aid of Eqs. (11) and (14) this result reduces to

$$(n_x kT)^{-1}A = \bar{y} - 1 - s\left(1 - \frac{s}{2}\right)\tilde{T}^{-1} - \ln(x\sigma f_1) \tag{18}$$

which differs from the Maier-Saupe result[1,5,6] through the terms $\bar{y} - 1$ and $-\ln(x\sigma)$; the former is important and the latter is arbitrary.

The reduced entropy is

$$(n_x k)^{-1}S = 1 - \bar{y} + s(1-s)\tilde{T}^{-1} + \ln(x\sigma f_1) \tag{19}$$

In the isotropic states $s = 0, f_1 = 1$ and $\bar{y} = x$ (see I). Hence, Eqs. (18) and (19) yield for the isotropic liquid

$$(n_x kT)^{-1} A_{\text{iso}} = -(n_x k)^{-1} S_{\text{iso}} = x - 1 - \ln(x\sigma) \qquad (20)$$

The reduced entropy difference between the two states (not necessarily at equilibrium) is

$$(n_x k)^{-1}(S_i - S_n) = [\bar{y} - x - s(1 - s)\tilde{T}^{-1} - \ln f_1] \qquad (21)$$

Biphasic equilibrium

Equating Eqs. (18) and (20), one obtains for the condition for coexistence of isotropic and anisotropic (nematic) phases

$$x - \bar{y} + s\left(1 - \frac{s}{2}\right)\tilde{T}_{ni}^{-1} + \ln f_1 = 0 \qquad (22)$$

or

$$x - \bar{y} + \tfrac{1}{2}(1 - \tfrac{9}{4}\langle\sin^2\psi\rangle^2)T_{ni}^{-1} + \ln f_1 = 0 \qquad (22')$$

The reduced latent entropy at the nematic-isotropic transition is

$$(n_x k)^{-1}\Delta S_{ni} = -E_{\text{orient}}/n_x kT_{ni} = \tfrac{1}{2}s^2\tilde{T}_{ni}^{-1} \qquad (23)$$

the symbol ΔS_{ni} being reserved exclusively for the transformation at biphasic equilibrium. The same result follows from Eqs. (21) and (22).

Approximate forms

On the premise that the precise form of the orientational distribution is only of secondary importance, one may dismiss the second term in the exponents in Eqs. (12) and (13). These equations then revert, respectively, to Eq. I-30 or 31 and to Eq. I-33 and 35. Equation (16), with substitutions from Eqs. (11) and (14), yields

$$(n_x kT)^{-1} A = \bar{y} - 1 - \tfrac{1}{2}s^2\tilde{T}^{-1} - \ln(x\sigma f_1) \qquad (24)$$

instead of Eq. (18) in this approximation. Equation (24) is just the combination of the reduced entropy according to Eq. I-16 for hard rods (with $v_x = 1$) and the orientation-dependent reduced energy according to Eq. (9′). It is the analog therefore of the Bragg and Williams approximation or of the corresponding approximation invoked in regular solution theory.

Adoption of Eq. (24) and the relations that follow from it has, as expected, only a minor effect on numerical calculations for small relative energies, i.e., for small $\tilde{T}^{-1}$. Simplifications thus achieved are marginal, however. For this reason calculations carried out in this approximation are not included below.

The asymptotic approximation presented in I becomes operable in the context of the present paper only upon adoption of the foregoing approximation, according to which the term in $\sin^2\psi$ in the exponents of Eqs. (12) and (13) is neglected.

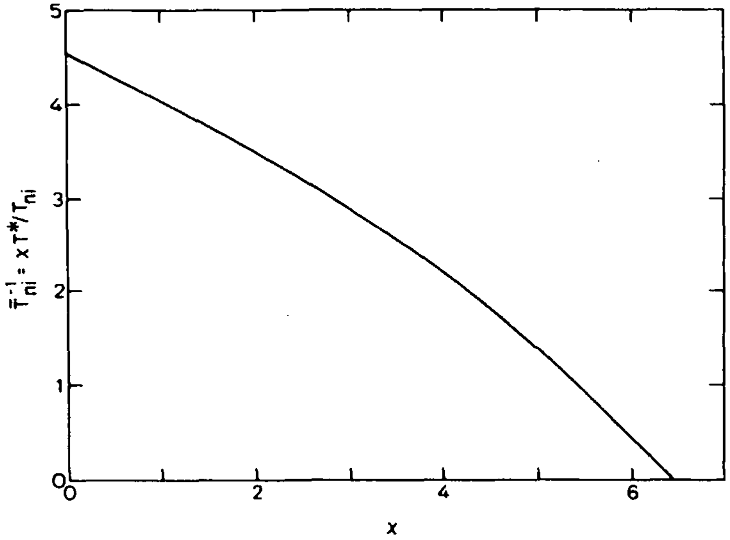


FIGURE 1 Reciprocal of the reduced temperature plotted against the axial ratio calculated according to Eq. (22) with aid of Eqs. 11, 13–15.

NUMERICAL CALCULATIONS

Calculations for systems in which isotropic and anisotropic phases coexist at equilibrium are conveniently carried out for selected values of α. With choice of a trial value of $s\tilde{T}^{-1}$, Eqs. (13), (14) and (15) then give f_1, $\bar{y}/x$ and s. Equation (11) provides $\bar{y}$ and x. Substitution of x, $\bar{y}$, $1 - s/2$ and f_1 in Eq. (22) yields $s\tilde{T}^{-1}$, which may be compared with the trial value.

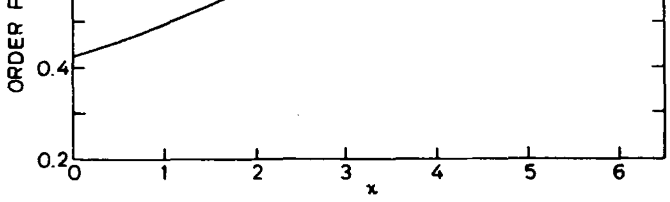


FIGURE 2 The order parameter, see Eq. (4) at coexistence plotted against the axial ratio.

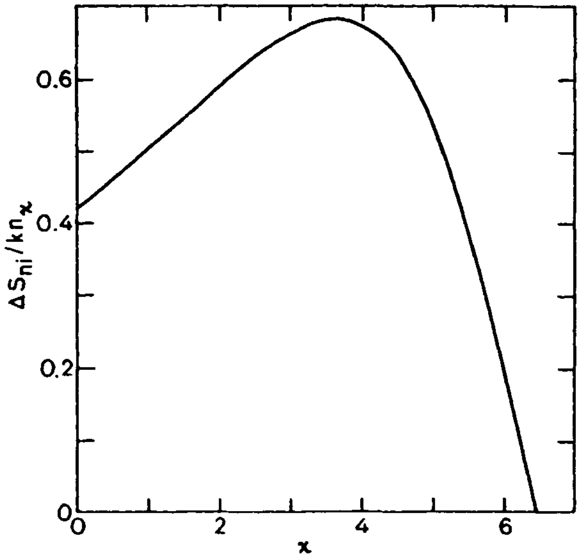


FIGURE 3 The reduced latent entropy at the transition, calculated according to Eq (23), as a function of the axial ratio.

In Figure 1 the reciprocal reduced temperature $\tilde{T}^{-1} = xT^*/T$ is plotted against the axial ratio x. The curve intersects the abscissa at $x = 6.417$, the limit for $T^* = 0$ found in I. The required orientational energy, measured by $\tilde{T}^{-1}$, rises with decrease in x. It reaches the Maier–Saupe[5] limit $\tilde{T}^{-1} = 4.541$ at $x = 0$.

In Figure 2 we show the order parameter s at the transition plotted against the axial ratio. The reduced latent entropy at the transition, calculated according to Eq. (23), is plotted against the axial ratio in Figure 3. It rises rapidly with decrease in x below $x_{\text{crit}} = 6.417$, attaining values of 0.65–0.68 for axial ratios of 3–4. For smaller axial ratios it decreases, reaching the Maier–Saupe[1,5,6] limit, 0.4291, at $x = 0$.

The dependence of the order parameter on temperature is illustrated in Figure 4, where s is plotted against $\tilde{T}^{-1}$ for three values of x. Solid lines are drawn for temperatures below the transition temperatures T_{ni}, i.e., for $\tilde{T}^{-1} > \tilde{T}_{ni}^{-1}$. Dashed lines represent the metastable ranges in which $T > T_{ni}$ (i.e., $\tilde{T}^{-1} < \tilde{T}_{ni}^{-1}$). The dashed lines cover the range of metastability. They are bounded by $\tilde{T}_{ni}^{-1}$ and by the reciprocal reduced temperature where the nematic phase becomes unstable; i.e., by the temperature above which the free energy is monotonic with order. This temperature has the characteristics of a critical point.

The difference between the reduced entropies in the isotropic and nematic states calculated according to Eq. (21) is plotted against $\tilde{T}^{-1}$ for $x = 4$ in

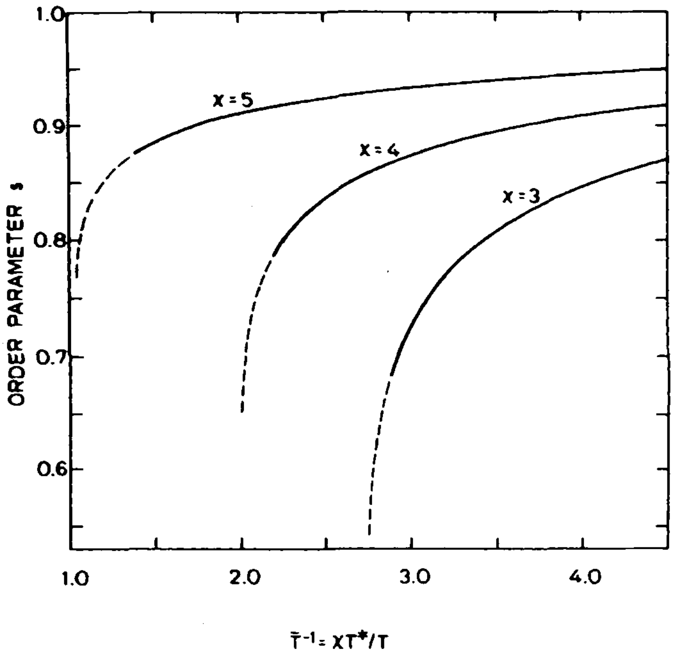


FIGURE 4 The order parameter s plotted against the reciprocal of the reduced temperature for three values of the axial ratio x. The solid lines represent temperatures below the transition; dashed lines cover the metastable range above the transition temperature T_{ni}. The termini of the dashed lines represent critical points at which the anistropic phase becomes unstable.

Figure 5. Also shown is the reduced molar orientational heat capacity $R^{-1}C_p$ of the nematic phase calculated from the temperature coefficient of Eq. (21), or, equivalently, from $-(n_x k)^{-1}\,\partial S/\partial \ln \tilde{T}^{-1}$, where R is the gas constant and S is given by Eq. (19). These relationships are depicted by dashed lines for temperatures within the metastable range, as in Figure 4. The entropy and the heat capacity, like the order parameter (Figure 4), vary continuously through the transition. The only discontinuity occurs at the termination of the metastable range, where the heat capacity diverges. This critical point, noted above, occurs in the neighborhood of the phase transition temperature T_{ni}, but is appreciably displaced from it. The orientational heat capacity x small for temperatures up to and somewhat beyond the nematic-isotropic transition.

Corresponding relationships for $x = 3$ and 5 are similar to those shown in Figure 5 for $x = 4$, apart from displacements along the axes. The heat capacity at coexistence decreases rapidly with x; at the coexistence point $(n_x k)^{-1}C_p = 2.69$, 0.975 and 0.169 for $x = 3$, 4 and 5, respectively.

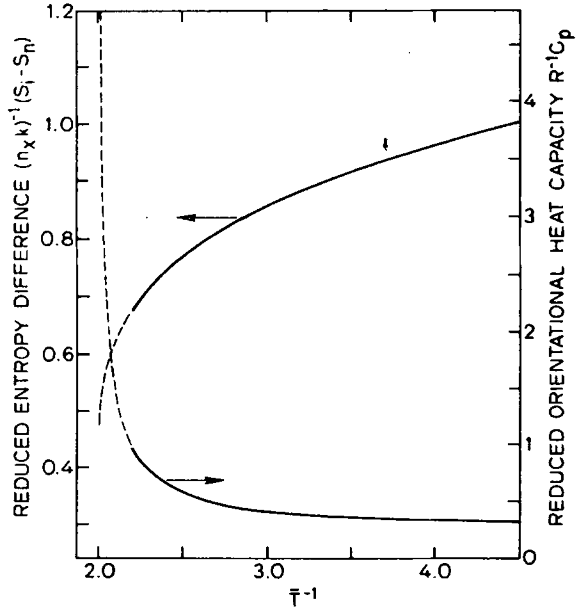


FIGURE 5 The reduced entropy difference between isotropic and anisotropic phases and the corresponding reduced orientational heat capacity as functions of the reciprocal reduced temperature for an axial ratio of four. Solid lines are shown for temperatures below the transition; dashed lines, commencing at the transition, and continuing to the critical point, embrace the range of metastability of the anisotropic phase.

COMPARISON OF THEORY WITH EXPERIMENTS

Nematogenic molecules characteristically are highly anisodimensional. Often they are approximately rodlike in shape; the assumption of cylindrical symmetry about the long axis is an irresistible further approximation. Significant departures from these simple geometric features should not be ignored however. Principal groups (e.g., phenylene) comprising the molecule usually are not arranged collinearly, hence the molecule may lack an axis of symmetry connecting its extremities. Often the molecule of the nematogen may be articulated through rotations about one or more of the chemical bonds of its backbone structure. Quantitative comparisons between theories, which rest necessarily on models involving idealization to some degree, and experimental results for real substances must therefore be undertaken with circumspection.

Poly-*p*-phenylenes

Molecules of the series

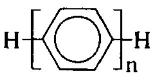


TABLE I

Transitions between crystalline, nematic and isotropic phases in compounds of the series

n	T_{cn} °C	T_{ci} °C	T_{ni} °C	axial ratio x	$\tilde{T}_{ni}^{-1}$ calc'd	T_{ni}, °C$_a$ estimated
2		70		2.25		
3		210		3.1		
4		$320^{11,12}$		4.1	2.1	117
5	$401^{11,12}$		445^{11}	5.0	1.39	(445)
6	$475^{11,12,b}$		$>600^{11}$	5.9	1.54	1900
7	$\sim 545^{12,c}$			6.8		

[a] Estimated from x, $\tilde{T}^{-1}$ and $T^* = 200$K.

[b] The phase first formed (at 475°C) may have been smectic; transformation to a nematic phase occurred at a somewhat higher temperature.[11]

[c] Although reported[12] as the "melting point," the melted phase may be assumed to have been mesomorphic.

provide examples that are most nearly rodlike and approximately cylindrically symmetric. The structural units are joined coaxially, and the rigidities of the bonds prevent appreciable bending for members of the series with $n \leq 7$, this being the range of interest. The phenylene group C_6H_4 does indeed depart significantly from cylindrical form about the molecular axes; its transverse dimensions in the plane and perpendicular thereto are approximately 6.1 and 3.8 Å, respectively. However, steric interactions between hydrogen atoms attached to adjoining phenylene residues enforce rotations of about 35°–40° about the molecular axis in the vapor[9] and liquid[10] states. In a poly-*p*-phenylene with $n \geq 3$, the signs of these rotations about successive inter-unit bonds may be assumed to be random; i.e., their directions within a given molecule should be virtually uncorrelated. Consequently, the form of the molecule as a whole, with $n \geq 4$, may be considered to be effectively cylindrical.

This series of rodlike molecular homologs was investigated more than half a century ago by D. Vorlander.[11] Experimental results are summarized in Table I. Members with $n \leq 4$ exhibit normal melting behavior; their crystal-isotropic liquid melting temperatures are given in the third column of the table. Quinquephenyl melts to a nematic liquid at $T_{cn} = 401$°C and exhibits a nematic range of 44°.[11] Sexiphenyl was reported to melt to a mesomorphic phase[11] at *ca.* 475°C,[12] which eventually became fluid (nematic) with further heating. When heated in a flame the material became "amorphous" (i.e., non-birefringent), though discolored due to decomposition.[11] Reversion to the liquid crystalline state occurred upon cooling. The effect of decomposition in promoting the transformation to an isotropic fluid is unknown. We may conclude from Vorlander's observations, however, that the nematic-isotropic transition temperature T_{ni} for sexiphenyl exceeds 600°C; it may be much higher.

Busch and Weber[12] reported a "melting point" of *ca.* 545°C for septiphenyl, isolated in small quantity. The melted phase was not characterized, but may be presumed to have been mesomorphic.

Axial ratios given in the fifth column of Table I were calculated from structural data as follows: $d_{C_1 \cdots C_4} = 2.78$ Å, $d_{C_1-C_4'} = 1.50$ Å, $d_{C-H} = 1.08$ Å, a van der Waals radius of 1.0 Å for H, and 4.8 Å for the mean diameter of phenylene. Reciprocal reduced temperatures in the sixth column are from the curve shown in Figure 1. The transition temperature T_{ni} for quinquephenyl admits of evaluation of the characteristic temperature $T^* = T_{ni}\tilde{T}^{-1}/x$. The result is $T^* = 200$ K. If the same value of T^* is assumed to hold for the homologs with $n = 4$ and 6, as the theory set forth above implies, then the transition temperatures in the last column of Table I are obtained. These values are, of course, subject to errors arising in the estimation of x, as well as from limitations of the theory itself. Nevertheless, the marked dependence of T_{ni} on the axial ratio is believed to be significant.

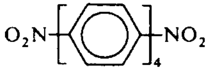
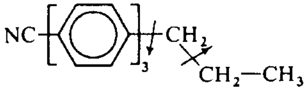
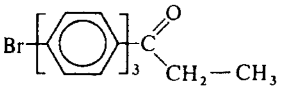
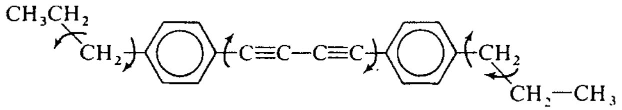
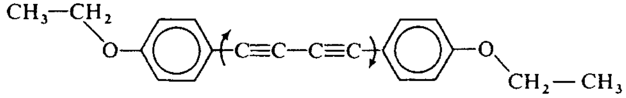
The experiments cited indicate that the axial ratio in the athermal limit, approached as $T \to \infty$, must exceed $x = 6$. The evident steep rise in T_{ni} with axial ratio suggests that $x_{\text{crit}} < 7$. Hence, experimental results for this series of homologs that most closely approach cylindrical, rodlike form support the theoretical result, $x_{\text{crit}} = 6.4$.[7]

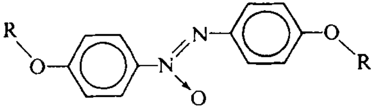
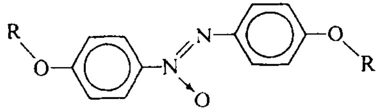
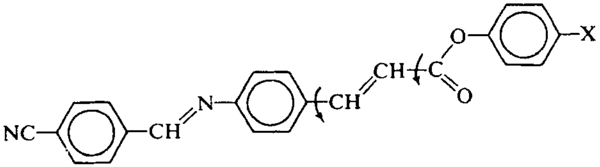
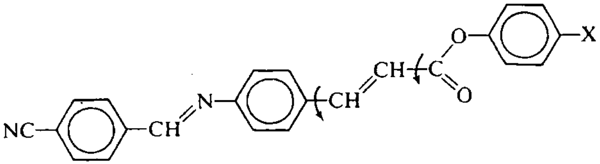
Axial ratios and transition temperatures for typical nematics

Data for additional examples are summarized in Table II. Compound **1**, 4.4″-dinitro-*p*-tetraphenyl, possesses a rigid rectilinear axis with the planar nitro groups approximately coplanar with the respective phenylene groups to which they are attached. Thus, the approximation involved in its representation as a cylindrically symmetric rod should be comparable to that for the poly-*p*-phenylenes. The next lower member of the series, 4,4″-dinitro-*p*-terphenyl, for which $x = 3.9$, melts to an isotropic liquid[13] at 273°C.[14] Vorlander[13] observed that compound **1** melts at 257–260° to a liquid crystalline phase which becomes isotropic at 285–290°. The temperatures reported were uncorrected for the emergent stem of the thermometer; they may be low by 20–30° on this account. Harley-Mason and Mann[15] reported a "melting point" of 317–320°C (corrected) with no mention of a mesomorphic phase. In light of Vorlander's observations, the "melting point" reported by Harley-Mason and Mann probably pertains to the nematic-isotropic transition; it may however be the crystal-nematic transition, in which case T_{ni} should be some 25–30° higher. In either case, the value of T^* deduced from the axial

TABLE II

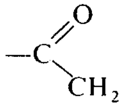
Nematic-isotropic transitions for representative nematogens

	Nematogen	Axial Ratio x	$\tilde{T}^{-1}$ calc'd	T_{ni} obsd., °C	T^*, K
1.		4.8	1.56	$\geq 320^{13,15}$	≥ 195
2.		4.2	2.03	257^{16}	255
3.		4.3	1.96	283^{16}	255
4.		4.7	1.65	132^{17}	140
5.		5.0	1.39	210^{17}	135

6.  R = CH_3	3.6	2.48	135.5[3,19]	280
7.  R = $CH_2—CH_3$	4.2	2.03	167.5[3,19]	215
8.  X = H	5.0	1.39	188[16]	130
9.  X = CH_3	5.2	1.21	226[16]	115

ratio and T_{ni} approximates $T^* = 200$ K obtained similarly for quinquephenyl (Table I).

In 4-cyano-4″-*n*-propyl-*p*-terpyhenyl, compound **2** in Table II, the cyano group is collinear with the terphenyl units but the propyl group is articulated. Admissible rotations about skeletal bonds that significantly affect the form of the molecule are indicated by curved arrows in the formulas presented in Table II. Rotations about the bond Ph—CH_2 adjoining the ring in compound **2** is believed to be nearly free; i.e., the rotational potential, inclusive of steric interactions, is small for all torsions ϕ_α. Rotations ϕ_β about the penultimate bond, CH_2—CH_2, of the propyl group are subject to a threefold potential with minima at $\phi_\beta = 0°$ and *ca.* $\pm 120°$. Barriers separating the minima are on the order of 3 kcal mole^{-1}. If ϕ_α is in the neighborhood of 0°, so that the CH_2—CH_2 bond is approximately coplanar with the phenylene ring, then gauche rotations $\phi_\beta \approx \pm 120°$ about this bond are opposed by steric overlaps of the terminal CH_3 group with the ring. Hence, the incidence of these conformations is severely reduced. In nonplanar conformations with ϕ_α in the vicinity of 90°, rotations ϕ_β are not impeded by steric interactions. They are affected only by the "inherent" torsional potential causing the energy of the gauche conformations ($\phi_\beta \approx \pm 120°$) to exceed that of trans ($\phi_\beta = 0°$) by 300 to 500 cal mole^{-1}, i.e., by *ca.* $\frac{1}{2}kT$ at relevant temperatures. The combined population of the two gauche conformations for the CH_2—CH_2 bond should exceed that of trans when ϕ_α is in the neighborhood of 90°. Averaging over ϕ_α, we expect comparable incidences of trans and gauche conformations for the CH_2—CH_2 bond. We thus estimate a mean length of 20.3 Å and an axial ratio of 4.2 for compound **2**. The value of T^* calculated on this basis, 255 K, is somewhat greater than that for quinquephenyl and for compound **1**. The difference does not, however, exceed the error due to the uncertainty in x, to which the calculation is most sensitive (see Figure 1).

Electron delocalization in 4-bromo-4″-*n*-propanoyl-*p*-terphenyl, compound **3** in Table II, favors coplanarity of the  $-C(=O)CH_2$ group with the third phenylene residue. However, steric interactions may be expected to enforce a rotation of *ca.* 15–20° from the coplanar conformation. Gauche rotations (*ca.* $\pm 120°$) about the C—CH_2 bond nevertheless are effectively precluded by steric interactions between the terminal methyl group and the phenylene ring. Hence, we treat the conformation as approximately coplanar with significant rotations about skeletal bonds suppressed. The value estimated for T^* is again somewhat greater than for compound **1** and for quinquephenyl.

Compounds **4** and **5**, recently reported by Grant,[17] possess a rigid rectilinear backbone, apart from articulations of the terminal groups. The central diacetylenic bridge is somewhat smaller in diameter than pendant portions of the molecule, but it accounts for only *ca.* 17% of the length of the chain. The estimated mean diameter is *ca.* 4.6 Å, compared with 4.8–4.9 Å for the examples above. Bond rotations in the *n*-propyl groups in compound **4** permit a range of conformations, as indicated above for compound **2**. The axial ratio was estimated from the mean length for trans and gauche conformations about the $CH_2—CH_2$ bonds.

Electron delocalization at the phenylene-oxygen bonds in compound **5** enforces coplanarity of the phenylene—O—CH_2 systems.[18] Gauche conformations of O—CH_2 are therefore precluded, and the alkoxy groups consequently may be assumed to be coplanar with the respective phenylene groups. The axial ratio was estimated on this basis.

The values of T^* for compounds **4** and **5** are substantially lower than those for the examples considered above, suggesting smaller orientation-dependent interactions for the diacetylenic group than for phenylene. The marked difference between the transition temperatures for these two compounds is attributable to the difference in their axial ratios which, in turn, is due to the greater flexibility of the *n*-propyl terminal groups in **4** compared to the oxyethyl groups in **5**.

In *p*-azoxyanisole (PAA), compound **6**, and *p*-azoxyphenetole (PAP), compound **7**, the axes of the phenylene residues are displaced *ca.* 1 Å the one from the other. Delocalization favors coplanarity of the phenylene and azoxy groups. Steric interactions should be expected to introduce small departures from coplanarity, however. The crystallographic investigations of these nematogens by Krigbaum and Barber[20] show one of the phenylene groups in PAA to be rotated 23° with respect to the other. Coplanarity was found[20] in crystalline PAP. This may be due to intermolecular forces that affect the molecular conformation in a manner that is peculiar to the crystal of this compound. The O—R groups may be assumed to be coplanar with the phenylene residues for the reasons pointed out above for compound **5**.

The value of T^* for PAA is surprisingly large, especially in view of the low anisotropy of the polarizability of the terminal groups $—OCH_3$ that comprise 24% of the molecule. For this reason a smaller T^* than for compounds **1**, **2** and **3** should have been expected. The T^* deduced for PAP is more nearly in accord with expectation although a lower value would have been predicted from the fact that the terminal groups, the polarizability anisotropies of which are small, comprise 31% of this molecule.

The unexpectedly large T^*'s for PAA and PAP may arise in part from the more marked departures of these molecules from cylindricity. The approximate coplanarity of the phenylene rings and the azoxy linkage, and the displacement of the phenylene axes from collinearity, impart platelike shape to an appreciable degree. Consequently, the molecules possess greater asymmetry than is taken into account by the axial ratio. The effect of this additional asymmetry should be qualitatively equivalent to an increase in x. Consequently, the values of T^* given in Table II for compounds **6** and **7** may be too large on this account, i.e., the asymmetry is under-estimated and, hence, the contribution of the orientational energy is over-estimated. Another possible cause for the apparent elevation of T^* in PAA and PAP is considered in the following section.

The smaller value of T^* for PAP compared with that for PAA may reasonably be attributed to the low anisotropy of the polarizability of the added CH_2 groups in PAP. In other words, the elevation of T_{ni} brought about by the substantial increase in axial ratio gained by introduction of $CH_2—CH_2$ bonds at either end of the molecule is moderated by the smaller anisotropy of $—CH_2—$.

The p-phenylene residues in compounds **8** and **9** (Table II) define three axes that are approximately parallel but not collinear. Twofold rotations about the axes indicated in Table II allow a variety of conformations. Mutual alignment of these molecules in the nematic state may require adoption of a degree of uniformity in conformation that is not obligatory in the isotropic state. The entropy associated with the broader distribution of conformations in the isotropic state may therefore lower the transition temperature. The orientational energies indicated by the values of T^* for compounds **8** and **9** probably are fictitiously low on this account.

The effect of intramolecular changes in the population of conformations at the transition could be incorporated in the theory in ways both obvious and straightforward. We have chosen however to limit the theory in the present paper to rigid molecules. Apart from the limitations imposed by this deliberate omission, the theory seems to provide a rational account of the results presented in Table II. The critical role of the axial ratio is supported by these comparisons of theory with experiment.

The transition entropy

Calorimetric measurements over the range of the nematic-isotropic transition have been carried out by Arnold[19] on PAA and PAP and by Barrall, Porter and Johnson[21] on PAA. The heat capacities exhibit marked pre- and post-transition enhancements. Torgalkar, Porter, Barrall and Johnson[22] showed the heat capacity for PAA to be quantitatively correlated, throughout the range of the transition, with the coefficient of thermal expansion according to the Frenkel theory[23] of heterophase fluctuations. The breadth of the range, extending more than 20° below the transition and nearly 10° above it,[24] is a consequence of the small magnitude of the entropy of transition and the low interfacial free energy.[22]

Inasmuch as the transition involves a change of phase and, hence, is of first order, the integral changes in V, H and S over the full range of the transition are the relevant first-order quantities. The larger of the two estimates of the latent enthalpy offered by Arnold[19] for PAA is $\Delta H_{ni} = 690$ J mole^{-1}. Barrall and coworkers[21] obtained 730 J mole^{-1}. The latter result yields $\Delta S_{ni} = 0.22$ R for the transition entropy, which is considerably smaller than the value $\Delta S_{ni}/\mathrm{R} \approx 0.65$ predicted by theory for $x = 3.6$ (see Figure 3).

Before comparing this result with theory, the latent enthalpy and entropy determined at constant pressure should be corrected to constant volume. According to Torgalkar *et al.*,[22] the latent volume change for PAA is $\Delta V_{ni} = 0.94$ cm^3 mole^{-1}. The required coefficient $\gamma = (\partial p/\partial T)_V = (\partial S/\partial V)_T$ has not been determined for PAA, but it may be estimated from the characteristic pressure p^* for related (aromatic) compounds.[25] Alternatively, the value of γ may be inferred from the volume-pressure-temperature measurements of Kuss[26] on MBBA [*N*-(*p*-methoxy benzylidene)-*p*-*n*-butyl aniline] and on EBBA [*N*-(*p*-ethoxy benzilidene)-*p*-*n*-butyl aniline] in the nematic and in the isotropic states. (Equation-of-state parameters deduced from the results of Kuss[26] are nearly identical in the nematic and isotropic states, apart from the small difference in density.) From these two approaches we arrive at the estimate $\gamma = 1.3(\pm 0.2)$ J cm^{-3} deg^{-1}. The contribution to the entropy from the change in molar volume is therefore 1.2 J deg^{-1} mole^{-1}. Hence, for PAA

$$(\Delta S_{ni})_V \approx 0.07 \mathrm{~R}$$

which is only a tenth of the theoretical value, *ca.* 0.65 R (see Figure 3).

According to the results of Arnold,[19] the latent enthalpy for the transition in PAP is 1500 J mole^{-1}, more than twice the value for PAA. This gives

$$\Delta S_{ni} = 0.41 \mathrm{~R}$$

The latent volume change is not reliably known in this instance. Assuming the same value as for PAA, we obtain

$$(\Delta S_{ni})_V = 0.26 \mathrm{~R}$$

which, though larger than for PAA, is much below prediction according to theory (see Figure 3).

Association of molecules in the isotropic state would afford an explanation for the low entropies of the nematic-isotropic transition in PAA and, to a lesser degree, in PAP. The presence of the polar N → O bond, and the dipole moment of 2.2 D for PAA[27] lend plausibility to this explanation. Both ΔH_{ni} and ΔS_{ni} would thereby be diminished, the latter perhaps to a greater degree by the geometric anisotropy of the shape of the complex. The values of T^* estimated above for the transitions in PAA and PAP would be invalidated if complex formation occurs to any considerable extent.

Recently, Barrall, Grant and Gregges[28] have reported enthalpies and entropies of transition for homologous *p,p′*-di-*n*-alkyldiphenyldiacetylenes and for *p,p′*-di-*n*-alkoxydiphenyldiacetylenes, including compounds **4** and **5** in Table II. They find $\Delta S_{ni} = 0.41$ R for compound **4** and 0.61 R for compound **5**. These values are in reasonable agreement with theory. Correction for the latent volume changes (not determined) would lower them somewhat.

Obviously, calorimetric measurements are needed on the transitions in other nematogens that more nearly conform to cylindrical rods and that are less susceptible to specific intermolecular interactions.

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