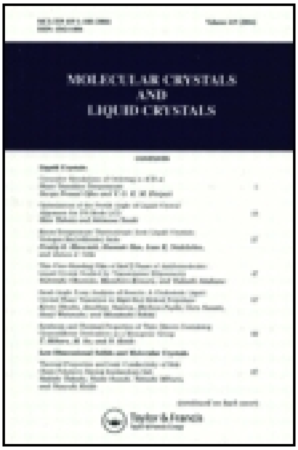

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Molecular Structure and Nematic Liquid Crystalline Behaviour†

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In this review some experimental results on the variation of the nematic-isotropic transition temperature T_{NI} with molecular structure will be evaluated with the aid of expressions for T_{NI} from molecular-statistical theories. The effect of terminal substituents on T_{NI} and some typical trends in the values of T_{NI} for the members of homologous series can be understood from changes in the anisotropic dispersion forces as discussed in Maier and Saupe's theory. The effects of some other structural changes in the molecules on T_{NI}, as for example the variation of central groups, cannot be explained on this basis. Probably it is necessary to take into account as well the molecular repulsions due to the excluded volume.

I INTRODUCTION

Characteristic of the various liquid crystalline phases[1,2] is the occurrence of long-range orientational order. In these phases the anisotropic elongated molecules are, on average, aligned with their long axes parallel to a preferred direction in space. In the nematic phase the centres of mass of the molecules are distributed at random, as in the isotropic liquid. The local preferred direction can be described by specifying a unit vector **n**, the director. Around **n** there exists uniaxial symmetry, while the directions **n** and −**n** are equivalent. The variations of **n** over molecular dimensions are small; the orientational order extends over large distances. The degree of order can be described by an order parameter S, defined as[1-3]

$$S = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle, \tag{1}$$

where θ is the angle between the long axis of a molecule and the director. The brackets denote a statistical average. In the isotropic liquid phase $S = 0$,

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whereas S has a finite value in the nematic phase. In the limit of a nematic with perfect orientational order $S = 1$.

The nematic-isotropic transition temperature T_{NI} of a mesogenic compound can be guessed reasonably well with the aid of empirical rules based on the analogy with related substances.[4,5] Whether a sizeable nematic temperature range is found is uncertain due to the hitherto unpredictable value of the melting point and due to the sometimes unexpected occurrence of smectic phases. A detailed understanding of the nature of the NI transition in terms of molecular properties is lacking, which holds in particular if one wants to predict the value of T_{NI} from molecular properties. In the following we shall discuss some typical trends in the NI transition temperatures of nematogenic compounds and examine the extent to which these results can be understood on the basis of existing molecular-statistical theories. We shall not attempt to give a full account of the experimental data on T_{NI}, nor shall we seek to evaluate in detail the merits of the various models of the nematic phase.

Before embarking upon this discussion it will be useful to recall the various intermolecular forces that may come into play in the nematic phase. Consider a molecule like *p*-azoxyanisole (PAA), which substance gives a nematic phase from 116 to 135°C. It is generally assumed that in the nematic phase such a molecule rotates freely around the long molecular axis, leading effectively to axial symmetry. It seems reasonable to represent the molecule by a homogeneously polarizable ellipsoid or spherocylinder. The elongated shape thus leads to an anisotropy of the electric polarizability. From measurements of the refractive indices (see Appendix B) one can derive the static values of the molecular polarizability, α_l and α_t, where the indices l and t refer to the directions parallel and perpendicular to the long molecular axis:

$$\alpha_l = 54\ \text{Å}^3,$$
$$\alpha_t = 22\ \text{Å}^3.$$

These values are about what one would expect from a homogeneously polarizable ellipsoid with the dimensions of PAA (length ~ 20 Å, width ~ 5 Å, giving a molecular volume $v \approx 300\ \text{Å}^3$). Furthermore, PAA has a permanent dipole moment $\mu \approx 2$ Debye $(= 2 \times 10^{-18}$ esu. cm). The corresponding effective polarizability would be $\mu^2/3kT \approx 20\ \text{Å}^3$ in the nematic temperature region. Disregarding multipoles of higher order than dipoles, the interactions between the molecules may be of the following type:

i) interaction between permanent dipoles ($W_{\mu\mu}$),

ii) interaction between the permanent dipole of one molecule and the induced dipole of another ($W_{\mu\alpha}$),

iii) interaction between the induced dipoles ($W_{\alpha\alpha}$),

iv) short-range interactions due to the repulsive forces between the molecules as they touch each other (excluded volume effects).

In order to estimate the relative importances of the first three interactions we introduce:

—a bond length $a \sim 1$ Å,
—an intermolecular distance $R \sim v^{1/3} \sim 10$ Å,
—a molecular excitation energy $I \sim e^2/a$,
—a permanent dipole moment $\mu \sim 0.5ea$ (see PAA),
—an anisotropy of the molecular polarizability $\alpha_a \sim 0.1v$ (see PAA).

The various interaction energies are:

i) $W_{\mu\mu} \sim \mu^2/R^3 \sim e^2/4000a$,
ii) $W_{\mu\alpha} \sim \alpha_a(\mu^2/R^6) \sim e^2/40000a$,
iii) $W_{\alpha\alpha} \sim \alpha_a^2 I/R^6 \sim e^2/100a$.

The dominant interaction is associated with $W_{\alpha\alpha}$. The reason is that α_a is in a good approximation proportional to the anisotropy of the volume of the molecule, while the net permanent dipole moment is always of the order of a few Debye units, irrespective of the size of the molecule. Hence it is reasonable to consider the interactions between the induced dipole moments of the molecules (dispersion or London-Van der Waals forces) as the origin of the nematic ordering (see sections II and III). Besides we have to consider the possible role of the molecular repulsions on T_{NI} (Section IV).

II MAIER AND SAUPE'S THEORY AND NEMATIC BEHAVIOUR

Maier and Saupe consider the interaction between the induced dipoles of the molecules as basic in their molecular-statistical theory of the nematic phase.[6] In the model it is assumed that the distribution of the centres of mass around a molecule has spherical symmetry. This simplifies the calculations considerably, the relative positions of neighbouring molecules now being independent of their orientations. However, it can certainly be expected to be a severe approximation for the anisotropic molecules under consideration. Maier and Saupe try to justify the assumption by taking units of several molecules as the statistical entity. Attempts to verify the correctness of the assumption experimentally[7] have failed so far. However, there is no doubt that the model is excellent for spherical molecules with an anisotropic point polarizability in its centre. In a mean field approximation each molecule is assumed to experience an average potential $W_i(\theta)$. Maier and Saupe find[6]

$$W_i(\theta) = -\frac{A}{V^2} S(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}), \tag{2}$$

where A is the strength of the potential depending only on molecular properties, while V is the molar volume. The number of molecules pointing with their long axis in the solid angle $d\Omega = 2\pi \sin\theta \, d\theta$ is given by $f(\theta)d\Omega = (1/Z)\exp(-W_i/kT)d\Omega$. Z normalizes the distribution function $f(\theta)$. The order parameter can now be defined self-consistently as

$$S = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} \rangle = \int f(\theta)(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})d\Omega. \tag{3}$$

By solving this implicit equation for S, one in turn obtains $W_i(\theta)$.

The difference in free energy between the nematic and the isotropic phase is given by

$$F_{\text{nem}} - F_{\text{is}} = \Delta F = \Delta U - T\Delta\Sigma. \tag{4}$$

The internal energy difference is given by $\Delta U = \frac{1}{2}\langle W_i \rangle = -AS^2/2V^2$, which is minimal for perfect alignment ($S = 1$). The orientational entropy difference $\Delta\Sigma$ counteracts the tendency towards more perfect alignment and is given by $\Delta\Sigma = -k\langle \ln f(\theta) \rangle$, where k is Boltzmann's constant. The NI transition takes place at $\Delta F = 0$, which leads to[6]

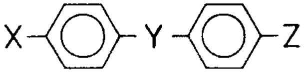
$$\frac{A}{kT_{\text{NI}} V^2} = 4.54 \quad \text{and} \quad S_{\text{NI}} = 0.43. \tag{5}$$

Using an approximate expression for A (see Appendix A) Maier and Saupe's theory predicts a NI transition temperature

$$T_{\text{NI}} = \frac{1}{4.54} \frac{4\pi^2}{135} \frac{(\alpha_l - \alpha_t)^2 I}{kV^2}. \tag{6}$$

In this expression I is the ionization potential that stands for the average excitation energy approximating the complete sum-over-states in the expression for A (see Appendix A).

We shall use Eq. (6) as a starting point for our discussion on NI transition temperatures. One would expect $\alpha_l - \alpha_t$, the anisotropy of the molecular polarizability, to correspond roughly to the anisotropy of the molecular shape. Indeed nematogenic molecules are strongly elongated, and in principle a large length/width ratio will give a high NI transition temperature. In order to increase T_{NI} further one should look in addition for functional groups whose polarizability has a high anisotropy. In this respect aromatic rings, or more generally systems with π-electrons, are to be considered. For example, benzene has a relatively large polarizability in the plane of the ring (~ 12.3 Å^3) and a much smaller one in the direction perpendicular to this plane (~6.7 Å^3).[8] Many of the compounds known to give a liquid crystalline phase contain two or three benzene rings, and have for example a molecular structure like



Often the bridging group Y contains double bonds, giving rise to conjugation between the benzene rings, which causes an even larger value of α_l and thus of $\alpha_l - \alpha_t$. The importance of conjugation can be demonstrated by a comparison of *ortho* and *meta* substitution of a group R in such systems. In these cases the angle between the CR bond and the long molecular axis is about 60°, which is close to the "magic angle" of 54.7° where the polarizability of this bond would contribute equally to α_l and α_t. Therefore one expects that $\alpha_l - \alpha_t$ will not change much. If the substituent is situated *meta* to the bridging group the width of the molecule increases. If the substituent is situated *ortho* to the bridging group in addition the molecule becomes nonplanar. In that case the conjugation and thus $\alpha_l - \alpha_t$ is reduced, and T_{NI} decreases strongly compared with the *meta* substituted compound.[9] Further examples can be found in the work of Dewar and Goldberg,[10] who studied the effect on T_{NI} when an aromatic ring in a particular compound is replaced by a saturated ring of approximately equal size. This also leads to a marked decrease of T_{NI}.

So far the available information on T_{NI} of liquid crystalline compounds seems to be consistent with the idea that the interaction between induced dipole moments is important for determining the stability of the nematic phase. In the next section we shall investigate whether the proportionality between T_{NI} and $(\alpha_l - \alpha_t)^2/V^2$, as given by Eq. (6), indeed holds in more detail. It is more difficult to obtain information on the possible variations of the ionization potential I. It seems likely, however, that I is mainly determined by the aromatic π-electrons, and will vary relatively little in the various compounds that will be considered. This assumption is supported by the available data for I of monosubstituted benzenes.[11]

III CORRELATIONS BETWEEN T_{NI} AND THE ANISOTROPIC POLARIZABILITY

Consider Figure 1 where the values of T_{NI} for some members of two series of *p,p'* substituted azoxybenzenes are shown. These series will be indicated as series I and II, respectively. The change of the NI transition temperatures

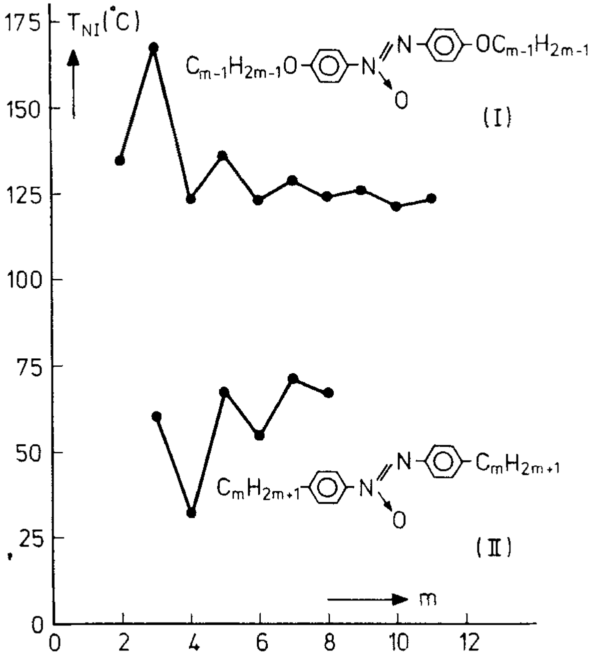


FIGURE 1 NI transition temperatures of some homologous series of alkyl- and alkoxy substituted azoxybenzenes (Ref. 12, 13).

when varying the chain length can be considered as typical of many other series. We shall denote the number of carbon atoms in the chain by *m*, while the oxygen atom, if present, is counted as a carbon. The following features now have to be explained:

i) The difference in T_{NI} between the series, or more generally the difference between T_{NI} of compounds with different end groups;

ii) The alternation of T_{NI} within each of the series;

iii) The overall decrease of T_{NI} with increasing *m* for series I where T_{NI} is initially high, and the overall increase of T_{NI} for series II, where T_{NI} is initially low.

Concerning point (i) we note that an oxygen atom, when attached directly to a benzene ring, is strongly conjugated with the aromatic system. Consequently the oxygen contributes especially to α_l, and replacement of a CH_2 group by an oxygen atom can be expected to give a substantial increase of $\alpha_l - \alpha_t$ and thus of T_{NI}. The importance of the conjugation with the benzene ring can be explicitly demonstrated by comparison with a molecule where the oxygen atom is situated somewhere in the parafinic chain. In that case a reduction of T_{NI} is generally observed, compared with the analogous compound with a CH_2 group.[14]

The influence of various end groups X on T_{NI} has been studied in detail by Van der Veen.[15] He considered some series of molecules that differed only in one end group X. In that case the variations of both I and V can be expected to be small. Furthermore he assumed, as is accepted generally, that the polarizability of a molecule can be obtained by addition of bond polarizabilities. From Eq. (6) one would then infer that $T_{NI} \propto \Delta\alpha_{CX}$, where $\Delta\alpha_{CX}$ is the anisotropy of the polarizability of the $C_{ar}X$ bond. For some end groups X this value can be obtained from measurements of the Kerr effect of X-substituted benzenes in solution. The resulting plot of T_{NI} versus $\Delta\alpha_{CX}$ is indeed approximately linear (see Figure 2). In this way it is also possible to understand why, for example, substitution of a CF_3 group as end group leads to relatively low values of T_{NI}.[16] The value of $\Delta\alpha_{CCF_3}$ is very small, being only about 0.25 Å^3.[17]

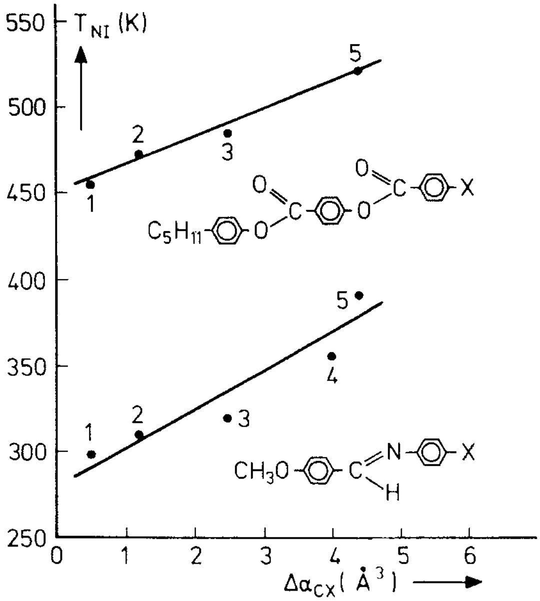
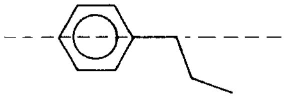


FIGURE 2 Relation between NI transition temperatures and the anisotropy of the polarizability of the $C_{ar}X$ bond (Ref. 15).

1 : F, 2 : CH_3, 3 : Cl, 4 : NO_2, 5 : CN.

We now return to Figure 1. With regard to (ii) we first assume that the parafinic chains exist in the all-trans zig-zag conformation. Then the effect on T_{NI} of addition of a CH_2 group depends on *m*. When *m* is even, an additional CC bond is approximately parallel to the long-molecular axis (at least for short chains):



The increment in α_l then turns out to be about twice that of α_t.[18] In the other case the increments of α_l and α_t are about equal. Table I gives values of the anisotropy of the polarizability for the members of series I and II, obtained from the refractive indices at 546 nm in the nematic phase. The polarizabilities are denoted by α_l^* and α_t^* in order to distinguish them from the static polarizabilities. These experimental values depend on specific assumptions about the internal field (see Appendix B). From Table I we note that the increment in

TABLE I

Values of $\alpha_l^* - \alpha_t^*$ of series I and II in Figure 1, as obtained from the refractive indices at 546 nm in the nematic phase (Ref. 19).

	$\alpha_l^* - \alpha_t^*$ ($Å^3$)	
m	series I	series II
2	40.7	—
3	47.0	41.0
4	46.0	44.9
5	52.2	51.6
6	55.5	53.6
7	60.2	60.8
8	61.0	60.1
9	67.2	—

$\alpha_l^* - \alpha_t^*$ is indeed relatively large when going from even *m* to odd *m*, while it is small or negative in the other case. According to Eq. (6) this could explain the alternation of T_{NI} with increasing *m*. Furthermore it proves that the assumption of a zig-zag conformation of the parafinic chains is approximately correct. As the angle between the CC bonds in the parafinic chains is about 109°, the difference in the increment of $\alpha_l - \alpha_t$ for even and odd *m* becomes less for longer chains. This effect is reinforced by the increasing flexibility of the chains, which is especially marked at higher temperatures. Indeed the alternation of T_{NI} diminishes at longer chain lengths and tends to be somewhat less pronounced for series I where T_{NI} is found at higher temperatures (see Figure 1).

Finally we consider point (iii), the overall increase or decrease of T_{NI} with increasing *m*. Marcelja[20] has attributed this difference in behaviour of series I and II to a difference in the relative magnitude of $(\alpha_l - \alpha_t)^2/V^2$ of the central part of the molecule and the average value of this quantity for a CH_2 group. If the latter is larger than the first one, additional CH_2 groups give an increase of the average anisotropic interaction and T_{NI} increases. In Figure 3 we have plotted $(\alpha_l^* - \alpha_t^*)^2/V^2$ versus *m* for series I and II using the results of Table I and the known densities.[19] Apart from the alternation $(\alpha_l^* - \alpha_t^*)^2/V^2$ decreases in both series with increasing *m*, the decrease being much more pronounced in series I. The overall trend in the curves of $(\alpha_l^* - \alpha_t^*)^2/V^2$ versus *m* resembles that of T_{NI} versus *m*, but there is no quantitative agreement. Apart from the uncertainties in the values of $\alpha_l^* - \alpha_t^*$ this could be related to the assumption of spherical symmetry of the centres of mass in the molecular field calculation, which is increasingly incorrect for larger *m*.

Next we consider the manner in which T_{NI} is influenced by variation of the bridging group. In Figure 4 some results are given for T_{NI} of various di-alkoxy substituted compounds; the relative order of the values of T_{NI} depends little

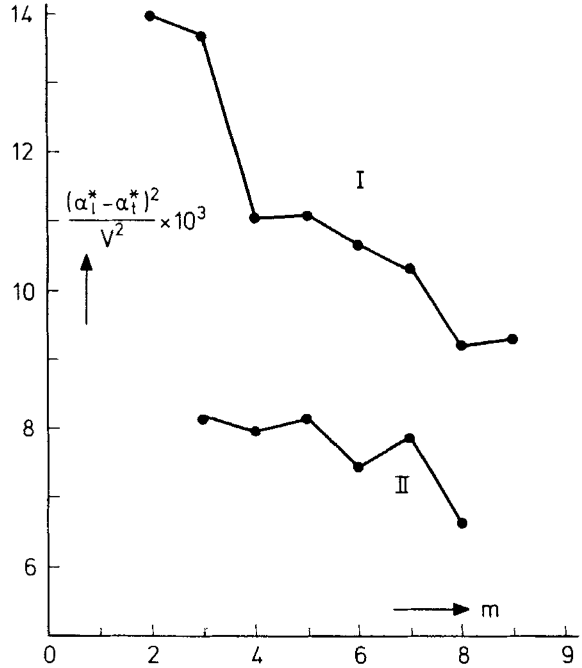


FIGURE 3 Anisotropy of the polarizability per unit volume for series I and II.

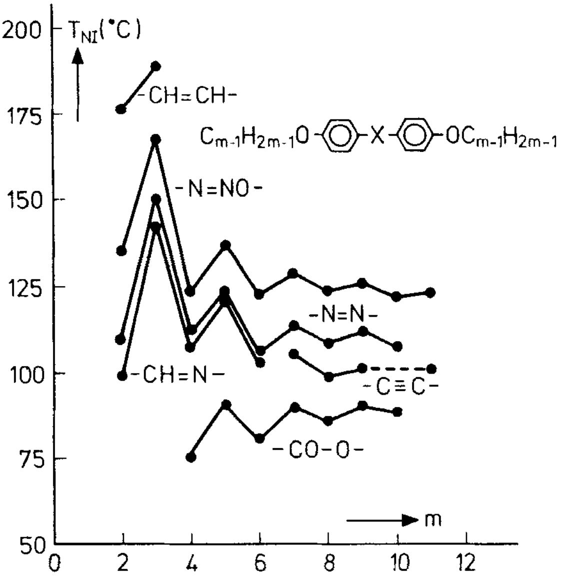


FIGURE 4 NI transition temperatures for some homologous series with different bridging group (compiled from Ref. 21).

on the specific end substituents. It is difficult to obtain reliable information about the values of $\alpha_l - \alpha_t$ for the various bridging groups. In these systems the interpretation of experimental data for the molar refraction and the Kerr constant, which in principle would give such information, depends on ad hoc assumptions about the direction of the dipole moment (if present), the conformation of the molecule, and especially the amount of conjugation between the two benzene rings.[22,23] However, it is often found that even the direction in which $\alpha_l - \alpha_t$ can be expected to vary upon a change in a bridging group does not agree with the direction of the corresponding change in T_{NI}. For example, going from azobenzene to non-planar azoxybenzene one may suppose the conjugation between the two benzene rings to decrease.[24] Consequently one would expect $\alpha_l - \alpha_t$ to decrease somewhat, which is not reflected in the observed change in T_{NI}. Data on $\alpha_l - \alpha_t$ and l are compared in Table II for stilbene and azobenzene. In addition the length L and the diameter D of the molecule are given. D is defined as the diameter of a cylinder with the pp' direction as the axis, in which the molecule can just rotate. Even when taking the uncertainties in the various estimates into consideration we must conclude that the higher T_{NI} values of the stilbene derivatives cannot be explained taking only the anisotropic dispersion forces into account. It appears necessary to consider other mechanisms as well.

TABLE II

Some molecular data for stilbene and azobenzene.

	$\alpha_l - \alpha_t(\text{Å}^3)$	I(eV)	L(Å)	D(Å)
Stilbene	7.5(a)	7.87(c)	13.5	6.48(d)
Azobenzene	11.2(b)	8.46(c)	13.1	6.65(e)

(a) Ref. 24; (b) Ref. 23; (c) Ref. 25;
(d) calculated using the conformation of the bridging group as determined by X-ray diffraction (Ref. 26), and for the benzene rings a CC-distance of 1.35 Å, a CH distance of 1.1 Å, and for H a Van der Waals radius of 1.0 Å;
(e) As (d), Ref. 27.

IV EXCLUDED VOLUME EFFECT AND T_{NI}

We shall now discuss the possible role of the repulsive forces between the molecules. Starting with the work of Onsager[27] several authors[28] have considered the hard-core repulsions between anisotropic bodies (rigid rods). In these theories the excluded volume of two rods plays an essential role. The excluded volume is given by the volume of the body defined by the locus of the centre of a second rod moving around a first rod while touching it, the mutual orientations of these rods being fixed at an angle γ. For rods with length L and diameter D, taking D very small so that end effects can be ignored, this volume is easily calculated to be[28,29]

$$\beta(\gamma) = 2L^2D|\sin\gamma|. \tag{7}$$

The smaller the excluded volume the greater the number of ways of accommodating another rod. The excluded volume reaches a minimum value for parallel rods, and with increasing density a transition is predicted from a disordered phase to an ordered phase, which can be identified with a NI transition. This type of theory is athermal (the temperature does not explicitly come into play), and is therefore not directly applicable to thermotropic liquid crystals. Nevertheless the predicted phase transition indicates that the repulsive forces between the molecules could be important for determining the stability of the nematic phase.

In practice it will be difficult to distinguish between the effect of the repulsive and the attractive forces on T_{NI}. This can be illustrated as follows. It is well known that bulky side groups on an elongated molecule lead to a low T_{NI}. This has been nicely demonstrated by Gray[4,30] who studied the influence of various *meta*-substituents (see Figure 5). In that case $\alpha_l - \alpha_t$ will not be influenced much by the nature of X. However, D varies strongly for the various substituents. D will approximately be equal to the distance of

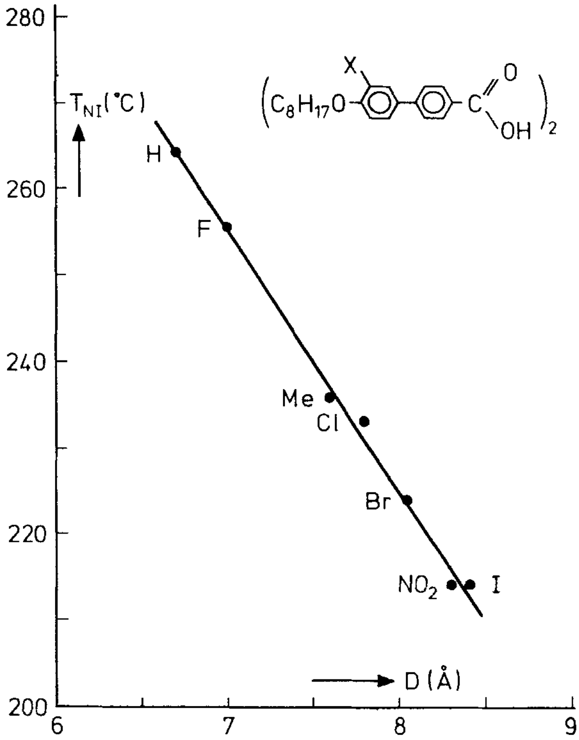


FIGURE 5 Relation between NI transition temperature and the width of the molecule (Ref. 29).

closest approach of two molecules, and hence will influence the magnitude of the attractive dispersion forces. Consequently these will decrease with increasing D in spite of the constancy of $\alpha_l - \alpha_t$. On the other hand, an increase of D (at constant length L) will diminish a possible contribution of excluded volume effects to the stability of the nematic phase. Qualitatively both effects could play a role in explaining the experimentally observed decrease of T_{NI} with increasing D.

Obviously one would like to combine the effect of the attractive dispersion forces and the molecular repulsions in one single theory. The free energy difference between the nematic and the isotropic phase can then be expressed as[31]

$$\Delta F = -\tfrac{1}{2}S^2\left(\frac{A}{V^2} + BT\right) - T\Delta\Sigma. \qquad (8)$$

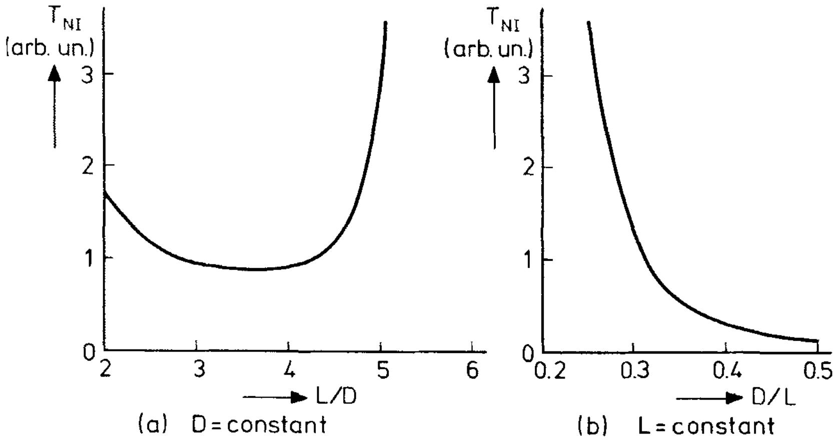
As compared with Eq. (4) there is a new term related to the packing entropy $-\tfrac{1}{2}BS^2$ due to the excluded volume effect, that favours the tendency towards more perfect alignment. Analogous to Maier and Saupe's result for T_{NI} we now find[32]

$$T_{\mathrm{NI}} = \frac{A/V^2}{4.54k - B} \quad \text{and} \quad S_{\mathrm{NI}} = 0.43. \tag{9}$$

Kimura[33] has given an explicit expression for B, using a combination of Onsager's treatment of the molecular repulsions and of Maier and Saupe's theory. The molecules are treated as spherocylinders. His result is

$$T_{\mathrm{NI}} = \frac{A}{kV^2}\left(4.54 - \frac{5\pi}{32}\frac{\beta_0}{v}\right)^{-1}, \tag{10}$$

where $v = (\pi/4)D^2L(1 - D/3L)$ is now the volume available to one molecule and $\beta_0 = 2DL^2(1 - D/L)^2$ is the coefficient of $\sin\gamma$ in the complete expression for the excluded volume (compare Eq. (7)). The dependence of T_{NI} on L and D is quite complicated; some results are given in Figure 6. Figure 6b closely resembles the experimental trend of T_{NI} in Figure 5. It is interesting to apply Eq. (10) to dimethoxystilbene and dimethoxyazobenzene. We take L and D from Table II and add 3.4 Å to L for the two methoxy groups. Then Eq. (10) gives a ratio of the T_{NI}'s for these two compounds of 1.1, which compares reasonably well with the ratio 1.17 found experimentally (see Figure 4). However, one may wonder whether the model is not too crude to be trusted for quantitative estimates of T_{NI}. For example, for $L/D > 5.2$ the nematic phase is predicted to be stable at all temperatures (see Figure 6a). This could be associated with the use of Onsager's theory, which retains only the first term in a virial expansion of the free energy. It



(a) D = constant (b) L = constant

FIGURE 6 NI transition temperatures for different L/D ratios according to Eq. (10) (Ref. 32).

has been argued that this is quantitatively correct only for large L/D ratios (say $L/D > 100$).[34] Furthermore the attractive forces are still treated within an isotropic model. Hence one would expect the dependence of T_{NI} on L and D to be more complicated than the relation given in Eq. (10).

V CONCLUSIONS

Progress in liquid crystal research over the past decade has been made especially in the *phenomenological* description of liquid crystals. In this field methods from solid state physics and from the general theory of phase transitions have been introduced with great success. Less progress has been made with respect to the *molecular* physics of liquid crystals. The types of interactions between the molecules that determine the stability of the various liquid crystalline phases are not yet fully understood. In this review we have shown that Maier and Saupe's theory provides a framework that forms a good first approximation for correlating NI transition temperatures with molecular properties. On the other hand it is not possible to reach a quantitative understanding of NI transition temperatures on this basis. For example, if we try to calculate T_{NI} for PAA from Eq. (6), using $(\alpha_l - \alpha_t)/V = 0.1$ and $I = 8$ eV (see Figure 3 and Table II), we obtain $T_{NI} \approx 60$ K, a factor of 6 too low.[35]

In the foregoing we have concentrated on some general aspects of the relation between T_{NI} and molecular structure, and have not touched on isolated peculiar cases of nematogenic compounds. It should be kept in mind, however, that even the variation of T_{NI} in a homologous series can be much less regular than in the examples shown here.[36] In spite of the usefulness of Maier and Saupe's theory it is clear that other factors than the anisotropic dispersion forces must also enter into the picture. This becomes even more evident if other quantities that T_{NI} are also considered at the NI transition, for example the entropy difference $\Delta\Sigma_{NI}$, or the value of the order parameter S_{NI}. We have emphasized the possible additional role of the repulsive forces between the molecules. The relatively large number of papers on the molecular theory of the nematic phase at this conference shows that various other approaches are possible. At any rate, it is clear that our understanding of the molecular factors that influence the thermal stability of the nematic phase is by no means complete.

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Appendix A. T_{NI} in Maier and Saupe's theory

The result for T_{NI} from Maier Saupe's molecular-statistical theory is given in Eq. (6). The factor A/V^2 can be written explicitly as[6]

$$\frac{A}{V^2} = \sum_{\mu,\nu}{}' \frac{\delta_{0\mu}\delta_{0\nu}}{E_{00} - E_{\mu\nu}} \sum_j \left(1 - 8\frac{Z_{ij}^2}{R_{ij}^2} + 9\frac{Z_{ij}^4}{R_{ij}^4}\right)\Big/R_{ij}^6. \tag{A1}$$

The first summations run over all wave functions ϕ_μ and ϕ_ν of molecule i and j, respectively, with an associated energy $E_{\mu\nu}$ for the two molecules together. The prime indicates that the combination $\mu = 0$, $\nu = 0$ is excluded from the summation. Using a coordinate system (ξ, η, ζ) fixed to one of the molecules with the long molecular axis as the ζ-axis, $\delta_{0\mu}$ is given by

$$\delta_{0\mu} = |\zeta_{0\mu}|^2 - \tfrac{1}{2}(|\xi_{0\mu}|^2 + |\eta_{0\mu}|^2), \qquad \text{(A2)}$$

where $\xi_{0\mu}$, etc., are the molecular transition moments defined by

$$\xi_{0\mu} = \sum_k \int \phi_0 e_k \xi_k \phi_\mu \, d\tau. \qquad \text{(A3)}$$

The summation extends over all electronic charges e_k in the molecule. The second summation in Eq. (A1) runs over all molecules j surrounding the central molecule i, the distance between the centres of mass being given by $R_{ij} = (X_{ij}, Y_{ij}, Z_{ij})$. Assuming a spherical distribution of these centres of mass, this summation can easily be evaluated to give $32\pi^2/135\ V^2$.

For practical purposes Eq. (A1) can be approximated as follows.[37] The polarizability of the molecule in the direction ξ is given by

$$\alpha_\xi = 2 \sum_\mu{}' |\xi_{0\mu}|^2/(E_\mu - E_0), \qquad \text{(A4)}$$

and similarly for α_η and α_ζ. Assuming that the energies E_μ and E_ν lie in a narrow band, we can use for all μ and ν $E_\mu - E_0 \approx E_\nu - E_0 \approx I$. Using the notation $\alpha_l = \alpha_\zeta$ and $\alpha_t = \frac{1}{2}(\alpha_\xi + \alpha_\eta)$ this gives

$$A = \frac{4\pi^2}{135}(\alpha_l - \alpha_t)^2 I. \qquad \text{(A5)}$$

The excitation energy, I, is often identified with the ionization potential. Substitution of Eq. (A5) in Eq. (5) leads to Eq. (6) for T_{NI}.

Appendix B. Refractive index and molecular polarizability

In Section III we used values for the polarizabilities α_l and α_t of the members of series I and II obtained from the refractive indices in the nematic phase. The relation between these quantities is given by

$$\frac{n_\lambda^2 - 1}{4\pi} \mathbf{E}_\lambda = N\alpha \mathbf{E}_\lambda^i, \qquad \lambda = \parallel, \perp, \qquad \text{(B1)}$$

where N is the number of molecules per unit volume, $\mathbf{E}^i_\lambda$ is the internal field working on a molecule in the direction λ, that differs from the external field $\mathbf{E}_\lambda$, while the indices $\parallel$ and $\perp$ refer to the directions parallel and perpendicular to the director. $\alpha_\parallel$ and $\alpha_\perp$ are related to the molecular polarizabilities α_l and α_t by

$$\begin{aligned} \alpha_\parallel &= \bar{\alpha} + \tfrac{2}{3}(\alpha_l - \alpha_t)S, \\ \alpha_\perp &= \bar{\alpha} - \tfrac{1}{3}(\alpha_l - \alpha_t)S, \end{aligned} \tag{B2}$$

where $\bar{\alpha} = (\alpha_l + 2\alpha_t)/3$. In order to calculate the internal field in a semi-empirical way a molecule is considered as a homogeneously polarizable ellipsoid. For an anisotropic *solid* crystal this gives:

$$\alpha_\lambda = \frac{1}{4\pi N} \frac{n_\lambda^2 - 1}{1 + \Omega_\lambda(n_\lambda^2 - 1)}, \qquad \lambda = x, y, z \tag{B3}$$

where the Ω_λ are shape-factors or depolarization factors that depend only on the axes ratio of the ellipsoid.[38] This equation cannot be directly applied to the nematic phase. When $S \neq 1$ the long axis of the molecular ellipsoid does not coincide with the director, and it is not clear how to calculate the denominator of Eq. (B3). This problem can be overcome if the internal field is written in a slightly different way:[19]

$$\begin{aligned} \mathbf{E}^i_\lambda &= [1 + \Omega_\lambda(n_\lambda^2 - 1)]\mathbf{E}_\lambda \\ &= [1 - 4\pi N \alpha_\lambda \Omega_\lambda]^{-1}\mathbf{E}_\lambda. \end{aligned} \tag{B4}$$

The latter form leads to an expression that is completely equivalent to Eq. (B3)

$$n_\lambda^2 - 1 = \frac{4\pi N \alpha_\lambda}{1 - 4\pi N \alpha_\lambda \Omega_\lambda}, \qquad \lambda = x, y, z. \tag{B5}$$

However, Eq. (B5) can also be applied to nematics where $S \neq 1$, because the right-hand side contains quantities that can all be related to the molecular quantities α_l, α_t, Ω_l and Ω_t with the aid of the order parameter. Equation (B5) has been used to calculate α_l and α_t from the refractive indices and the values of S obtained from magnetic susceptibility measurements. The results for the members of series I and II have been given in Table I. A fuller discussion of the various approximations involved will be given elsewhere.[19]