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Virtual Nematic-Isotropic Transitions

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VIRTUAL NEMATIC-ISOTROPIC TRANSITIONS

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Abstract A new method for the determination of virtual nematic isotropic transitions is given. The method is based on the measurement of angular correlations in the isotropic phase by means of Depolarized Rayleigh Scattering. It provides a good tool for the study of the nematogenic power of substituents and to estimate the effect of disubstitutions on any central rigid core.

The determination of the virtual nematic-isotropic transition temperature (T_{NI} virtual) is an interesting topic both from a theoretical or practical point of view. What is the problem? An organic substance can exhibit, after melting from the crystalline phase, a nematic phase when the temperature is increased (enantiotropic) or an isotropic phase (monotropic) on cooling; moreover, upon cooling, sometimes the solid phase appears before the supposed nematic phase can be effectively observed. Let us speak in this case of the virtual transition. The determination of these transitions can be performed by several physical techniques; namely, by the study of phase diagrams[1] and by Depolarized Rayleigh Scattering.[2] This last technique has been used in our laboratory.

In fact, two different approaches to the problem can be made. One is purely macroscopic and is based on the measurement of the variation of the depolarized scattering intensity

with the temperature and the other, microscopic, interprets this intensity in terms of orientational correlations.

GENERAL TECHNIQUE

Measurements of the integrated spectra of Depolarized Rayleigh Scattering i are performed with a "gammadiffusiométre" already used[3] at the wavelength of 546.1 nm. The experimental accuracy on T is about $\pm 0.1^{\circ}C$. The apparatus is calibrated by comparison with the depolarized light scattered by a cell filled with toluene; such a compound is known to have an approximatively temperature independent scattered intensity.[4] The experimental uncertainty on the ratio $i/i_{toluene}$ is about 1%. All the substances studied have been carefully purified and filtered.[5]

MACROSCOPIC APPROACH

Several purely nematic compounds have been studied: MBBA,[2] p-methoxy-p'-pentyl benzoate[4] and p-methoxy-p'-pentyl tolan (Figure 1). The variations of i with temperature are well represented by a clasic law:[6] $i = kT/T-T^{*}$ where T^{*} is close to ($1^{\circ} \lesssim$) the clearing temperature T_{NI}. In the case of monotropic nematics, p-methoxy-p'-propyl or butyl tolan (Figure 1) one can observe a similar comportment. At last for the p-methoxy-p'-ethyl tolan "non-nematic", the parametration of i versus T by a computer least square method leads to a T_{NI} virtual temperature of $37^{\circ}C$. In the next considerations we will call ΔT_{CN} the difference between T_{NI} (real or virtual) and T_f (fusion of solid phase); ΔT_{CN} represent the nematic range.

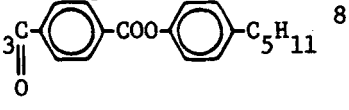
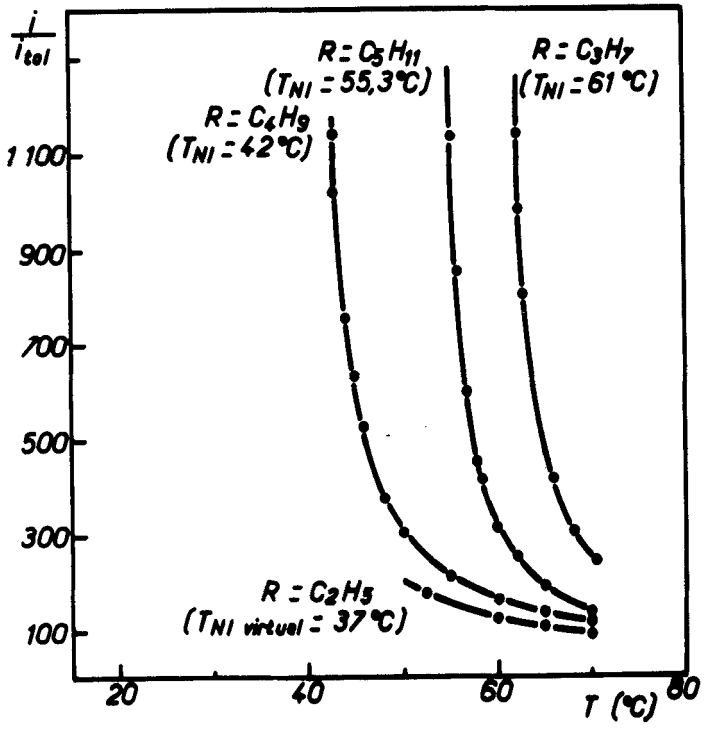
The compound  [8] provides us with

FIGURE 1 Depolarized light scattered by some p-methoxy-p'-alkyl tolans (CH_3O-⟨⟩-C≡C-⟨⟩-R) with temperature.



an interesting example; T_{NI} virtual has been found at 43°C, whereas an observation of droplets under a polarizing microscope[9] has shown the existence of a transient nematic phase at 44.2°C which agrees well with the T_{NI} virtual previously calculated.

In fact, this macroscopic procedure can be used only for substances with virtual temperature close to T_f (for the last compound $\Delta T_{CN} = -27^{\circ}$) so that the variation of i versus T is

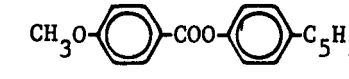
important. On the contrary when $\Delta T_{CN} < -60^{o}C$, we used another kind of approach, a microscopic one, we present now.

MICROSCOPIC APPROACH

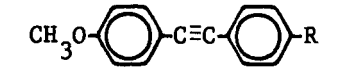
The study of the variation of the molar depolarized intensity ($y_2 = k\ i/c$ [5]) with the concentration* at one temperature shows, for mesogenic molecules, a very specific behavior.[10] The molar intensity is constant in a very short range of concentration and allows the measurement of the specific molar intensity y_2^{∞} (intensity that would be scattered at infinitely dilute solution). After a critical concentration y_2 increases strongly up to the pure liquid ($y_2^{\oplus}$). Then we can classically define, with some approximations,[9,10] the angular correlation parameter J^A_{22}.

In the microscopic model of KIELICH,[9] $J^A_{22} = (y_2^{\oplus} - y_2^{\infty})/y_2^{\infty}$, the expression of this parameter is: $\frac{1}{2} Z \langle 3\cos\theta_{22} - 1 \rangle$ where Z is the number of neighbors of one molecule having the same kind of interactions and θ_{22} is the angle between its longer axis and the Z of other molecules. J^A_{22} is an interesting parameter giving easy measurements of the short range order in the isotropic phase.

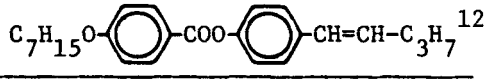
We have studied the variation of J^A_{22} with temperature for several colorless and stable nematic compounds:



[4] C $\xrightarrow{29}$ N $\underset{}{\overset{42}{\rightleftharpoons}}$ I,



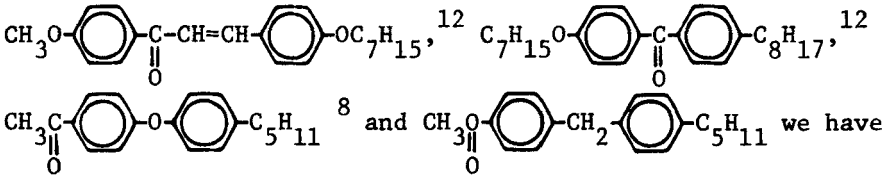
with R = C_3H_7 (C $\xrightarrow{66}$ I $\xrightarrow{61}$ [N]) and

M = C_5H_{11} (C $\xrightarrow{45.8}$ N $\underset{}{\overset{55}{\rightleftharpoons}}$ I), 

[12]

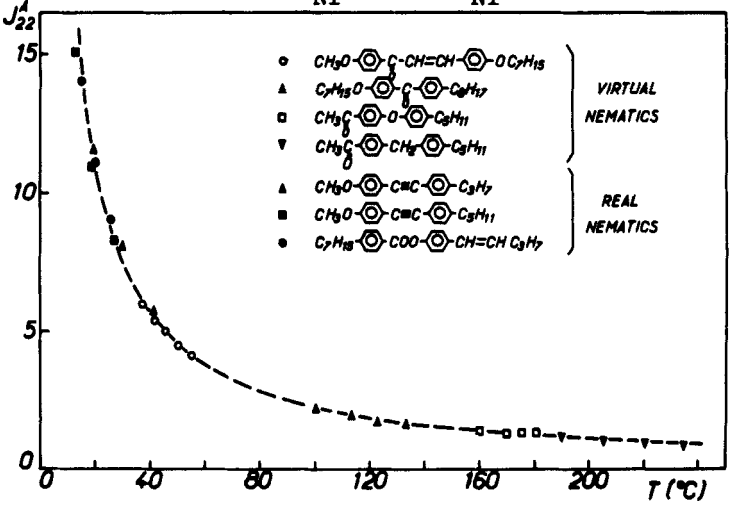
*We use a quasi isotropic solvent such as carbon tetrachloride or cyclohexane.[5,10]

C $\xrightarrow{52.8}$ N $\underset{\longleftarrow}{\overset{83.3}{\longrightarrow}}$ I. T^* has been calculated as before and we have found respectively: 312.95,[4] 333.4, 326.8 and 355.5 K. For all these substances the coefficient of the law $J_{22}^A = kT/T-T^*$ is $k = 0.675 \pm 0.005$. In fact, this simple law is valid only near the nematic-isotropic transition. Since it is obvious that at high temperatures J_{22}^A should tend to zero like $\frac{1}{T}$, we use the following relation: $J_{22}^A = 0.675\ T/T-T^*-0.675$ to calculate the function $J_{22}^A = f(T)$ from T_{NI} to $T_{NI} + 250^\circ$ (Figure 2). This curve is very useful for the determination of T_{NI} virtual temperature by comparison with the experimental value of the angular correlation parameter at one temperature. This method is illustrated in Figure 2 for the four compounds:



found for T_{NI} virtual 18, -70, -135 and -165°C.

FIGURE 2 Calculated variation of J_{22}^A with temperature from T_{NI} (o) and $T_{NI} + 250^\circ C$



Thus, this technique allows a study of the nematogenic power of monosubstituted rigid cores[10] or alternatively to estimate the effect of disubstitution on any rigid core as shown in this paper.

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