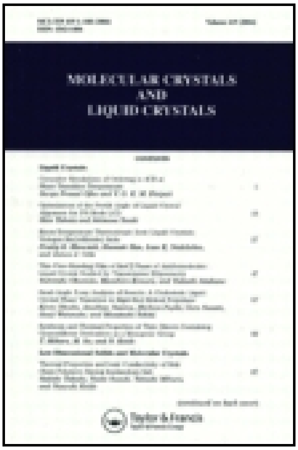

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EMPIRICAL RELATION BETWEEN ORDER PARAMETER AND NEMATIC-ISOTROPIC TRANSITION TEMPERATURE

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For the calculation of anisotropic properties of nematics the knowledge of the order parameter is necessary. The order parameter is not a universal function for all nematics, but there are substance specific differences. As an approximation, we have developed an empirical relation between the order parameter at room temperature and the nematic-isotropic transition temperature.

Keywords: order parameter; nematic-isotropic transition temperature; nematics

INTRODUCTION

The order parameter $\overline{P_2}$ of nematic liquid crystals is a measure for the anisotropy of the structure. Therefore it is connected with all anisotropic properties, important for practical applications, like dielectric and optical anisotropy, electrical conductivity, viscosity and elastic constants. Using well known theories, it is possible to calculate some of these properties without need of experiments [1,2,3]. The calculations often are hindered by the lack of experimental data for the order parameter. In order to close this gap, we developed an empirical relation between the order parameter at room temperature and the nematic-isotropic transition temperature (T_{NI}) of the compound. The T_{NI} are the best known data of liquid crystalline compounds. Even when they are lacking, they can be approximately determined by group contribution methods [4,5], without need of experiments.

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DERIVATION OF THE EMPIRICAL RELATION

The orientational order parameter $\overline{P_2}$ of nematic liquid crystals can be defined by [6]

$$\overline{P_2} = \langle (3/2 \cos^2 \Theta - 1/2) \rangle.$$

Here Θ is the angle between the molecular long axis of rod-like molecules and the director of the nematic liquid crystal; $\overline{P_2}$ is an average of the second order Legendre polynomial in cosΘ. Because real molecules are not simple stiff rods, different methods for determination of $\overline{P_2}$ can deliver different results.

The order parameter $\overline{P_2}$ at room temperature can be measured directly only in very seldom cases, when the material is nematic at room temperature. In most cases it must be extrapolated from data measured at higher temperatures. The temperature dependence of $\overline{P_2}$ can be reproduced by mean field procedures like the Maier-Saupe theory [6,7] or the fitting method of Tough and Bradshaw [8]. Pohl *et al.* [9] used the more simple function

$$\overline{P_2} = \mathrm{S}_0(1 - \mathrm{yT/T_{NI}})^{\beta}, \quad (1)$$

$S_0 = 1$, $\beta = 0.13 - 0.18$ depending on the specific material, $y = 0.98$

This formula allows to calculate $\overline{P_2}$ in reasonable approximation, except the region near to T_{NI}, which is less important for our purposes. Equation (1) is equivalent to the procedure of Hanson and Shen [10], which was proposed by Haller *et al.* [11]. It is frequently used for the "Haller extrapolation" in order to evaluate $\Delta\alpha/\alpha$ and $\overline{P_2}$ from the temperature dependence of refractive indices. Specially Tough and Bradshaw [8] point at the fact, that Eq. (1) has several failings. Near T_{NI} it cannot represent the temperature dependence of $\overline{P_2}$, and therefore we avoided to use it in this temperature region. The range for β indicated in [9] is not sufficient, and it must be extended to about 0.35 in order to describe small order parameters. In most cases β is 0.20 to 0.23.

Figures 1 and 2 show representative examples of using Eq. (1) in its logarithmic form Eq. (2).

$$\log \overline{P_2} = \beta \log(1 - 0.98\ \mathrm{T/T_{NI}}). \quad (2)$$

Taking the data from Figure 1, except the two being nearest to the clearing temperature, we obtained $\beta = 0.250$ with a regression factor $R = 0.00234$. This shows that in the region more than about 5 K below T_{NI}, Eq. (1) can be used with good accuracy for extrapolating order parameter data down to room temperature. Especially at low temperatures Eq. (1) reproduces the data well.

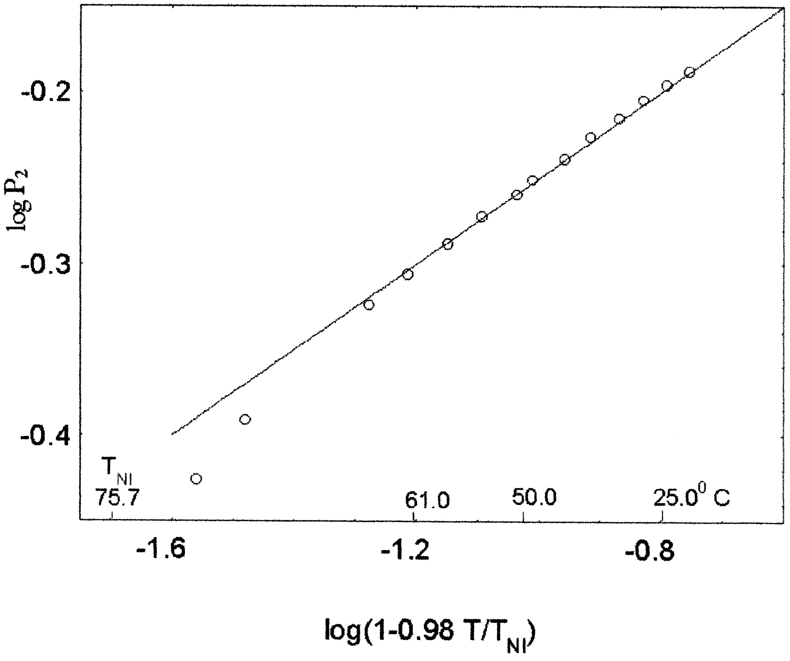


FIGURE 1 Plot of Eq. (2) for 4-ethoxyphenyl 4-n-butylcyclohexanoate. Experimental data (circles) from Hauser *et al.* [12], drawn line corresponds to Eq. (2).

In Figure 2 older $\overline{P_2}$ data obtained from diamagnetic anisotropies [13] are displayed. The data show some scattering due to larger limits of error, but in the region lower 5 K than T_{NI} again Eq. (1) delivers a satisfying fit ($\beta = 0.200$; $R = 0.00852$).

It should be emphasized that $\overline{P_2}$ data at room temperature are controlled by the temperature difference to T_{NI}, and by the individual properties of the compounds. Maier and Saupe in their mean field theory [6] claim that the order parameter at the clearing temperature at constant pressure is a function of the relative volume change $\Delta V_k/V_{N,k}$. The deviations of this volume change in the investigated cases were so small, that in the considered compounds the order parameters at T_{NI} practically were found to be constant ($\overline{P_2^{NI}} \cong 0.44$). In the meantime more order parameters have been determined. The results point at systematic differences of the $\overline{P_2^{NI}}$, compounds with higher T_{NI} have larger order parameters. This behaviour is supported by theoretical considerations. The hard-rod [14] as well as the van-der-Waals theories [15] predict increasing $\overline{P_2^{NI}}$ for increasing length-to-breadth ratios, in the same sense, in which T_{NI} is increasing. This

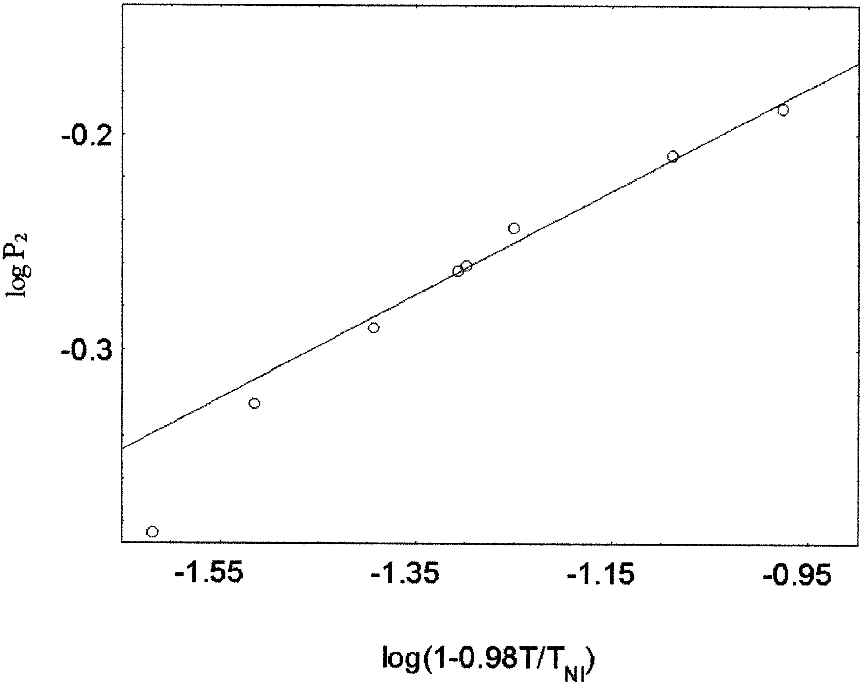


FIGURE 2 Plot of Eq. (2) 4,4′-di-methoxy-azoxybenzene (azoxyanisole). Experimental data (circles) from Saupe *et al.* [13], drawn line corresponds to Eq. (2).

means, increasing $\overline{P_2^{NI}}$ with increasing T_{NI} are to be expected, and in the whole temperature region this succession should be preserved. Figure 3 presents some examples that in fact show this predicted behaviour. Figure 2 of a paper by Bradshaw *et al.* [17] and Figure 2.2. in a chapter written by Madhusudana [18] in the case of related cyano-substituted compounds, and Figure 4 of the paper by Demus *et al.* [19] seem to confirm this fact. In the case of dyes dissolved in nematic basic mixtures a lot of experimental data are available [20,21,22]. In several cases it was shown that order parameters of the guest dyes dissolved in the same nematic solvent increase with increasing molecular length-to-breadth ratios [21,23]. Some of the investigated dyes are nematic themselves. However, there are also cases in which special interactions between the host molecules and the guest dyes disturb this picture [20,21,22].

Using literature data stemming from different authors using the same or different methods for the determination of $\overline{P_2}$ the picture looks less clear, because even for the same compound the data can be quite different.

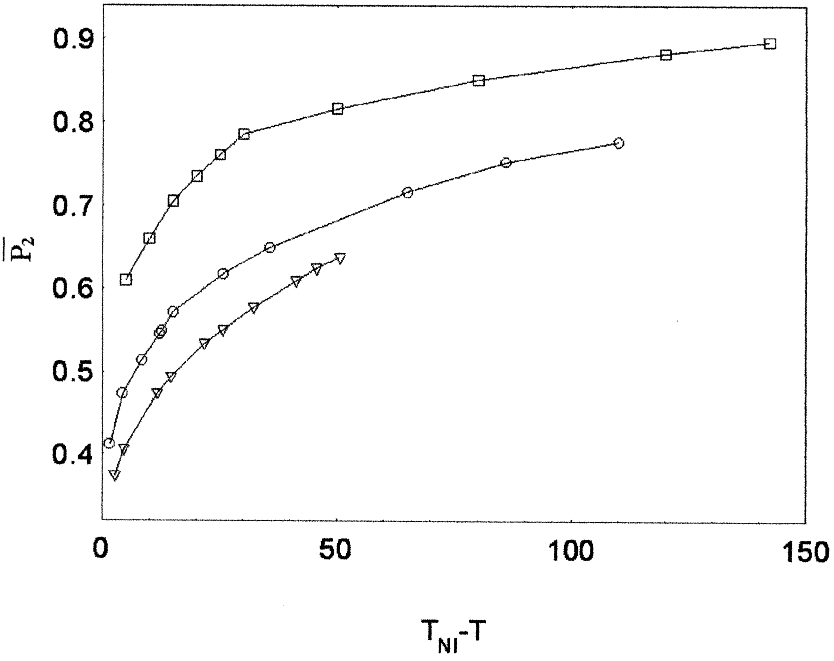


FIGURE 3 Temperature dependence of the order parameter. □ 4,4′-di-ethoxy-azoxybenzene $T_{NI} = 167.1°C$ [10]; the last 4 points are extrapolated. ○ 4,4′-di-methoxy-azoxybenzene $T_{NI} = 133.0°C$ [13]; the last 3 points are extrapolated. △ 4-ethoxyphenyl 4-butylcyclohexanoate $T_{NI} = 75.7°C$ [12,16].

We extracted $\overline{P_2}$ data from the literature for 26 compounds or mixtures, and extrapolated them to room temperature (25°C) by use of Eq. (1). The data are compiled in Table 1. They were plotted versus the T_{NI}(°C) of the compounds in Figure 4. There is a clear dependence of $\overline{P_2}$ on T_{NI}, which can be well described by Eq. (3).

$$\overline{P_2} = 0.363 \log T_{NI}. \tag{3}$$

The regression coefficient for Eq. (3) is R = 0.0207, the maximal deviation being 0.0570.

Using this relation, order parameters of arbitrary compounds at 25°C can be calculated, when the T_{NI} are known. When data for T_{NI} are lacking, they can be approximately evaluated by the procedure included in the data base "LIQCRYST" [4], or for two ring compounds by the method of Vill [5].

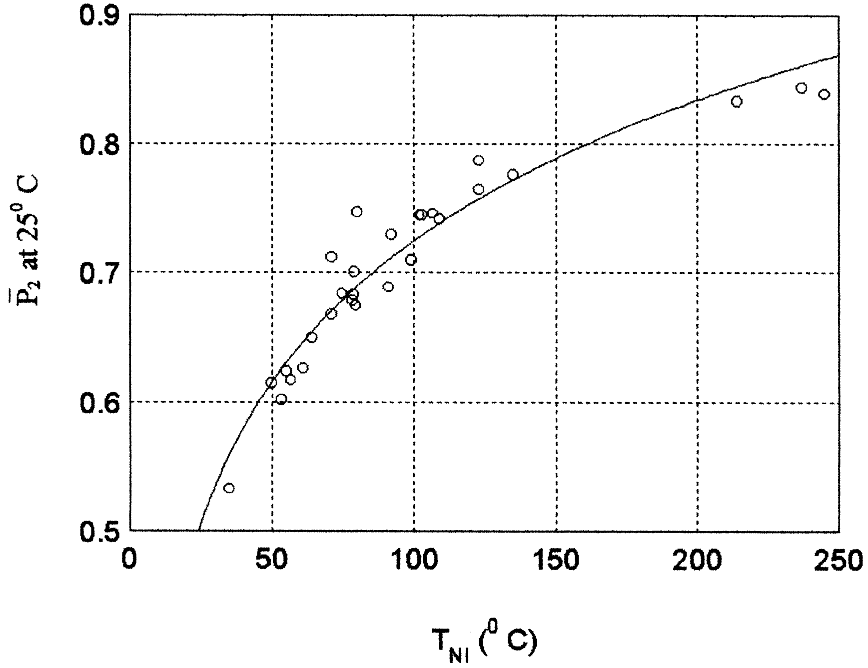


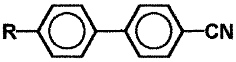
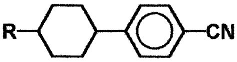
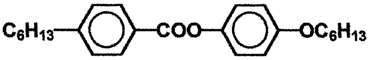
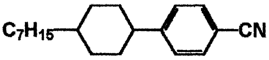
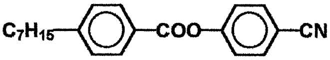
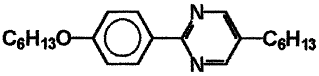
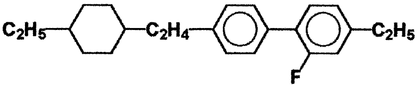
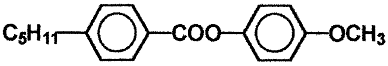
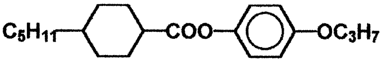
FIGURE 4 Order parameters at 25°C in dependence on T_{NI}.

DISCUSSION

The data for $\overline{P_2}$ available in the literature in many cases are not very accurate and they are not always reliable. This becomes obvious when for the same compound data from different sources, measured with the same or different methods, are available. It is well known that different methods can produce systematically different data for the order parameter. We tried to use reliable data for our considerations. It should be mentioned that in several cases we were forced to extract the $\overline{P_2}$ data from figures, because numerical data were lacking in the papers. This causes additional errors.

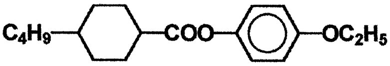
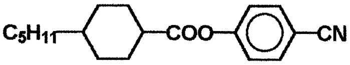
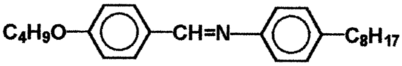
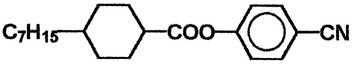
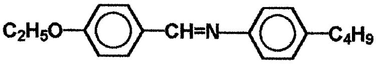
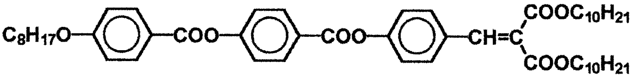
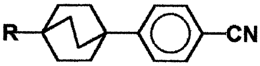
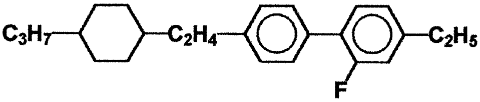
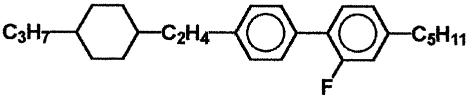
Taking these sources of errors for the order parameters in mind, it becomes clear that using more and improved $\overline{P_2}$ data, the curve presented in Figure 4, and the function derived from it, may suffer slight changes. Also the use of another mathematical function for the description of the data is possible. Because of its simplicity, we choose the logarithmic function. For our purposes, the calculation of dielectric and optical anisotropies of nematics, the accuracy of the derived function is satisfying. The empirical relation has been derived for a temperature of 25°C. There is no doubt, that analogous relations can be derived for different temperatures.

TABLE 1 Order Parameters, $\bar{P}_2$, of Nematic Liquid Crystals at 25°C

	T_{NI}/°C	$\bar{P}_2$	Ref.
1.  $R = C_3, C_5, C_7$ (mixture 30, 40, 30 weight%)	35	0.533	[17]
2.  R = see 1.	50	0.615	[17]
3. 	53.2	0.602	[12]
4. 	55	0.624	[8]
5. 	56.5	0.617	[12]
6. 	60.8	0.626	[12]
7. 	64	0.65	[24]
8. 	71.1	0.712	[25]
9. 	71.1	0.668	[25]

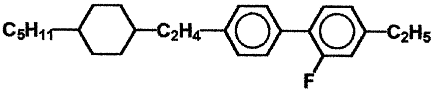
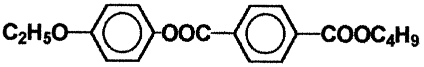
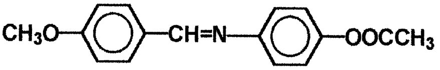
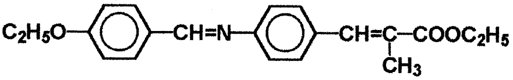
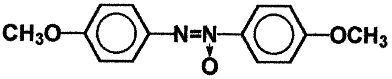
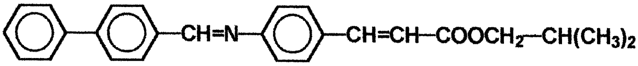
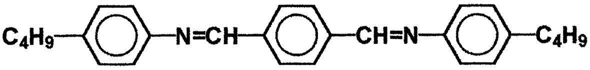
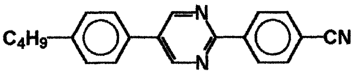
(*Continued*)

TABLE 1 Continued

	T_{NI}/°C	$\bar{P}_2$	Ref.
10. 	74.6	0.684	[25]
		0.637	[12]
11. 	78.7	0.683	[25]
	79.2	0.679	[8]
12. 	79	0.701	[26]
13. 	79.5	0.675	[12]
14. 	80	0.747	[27]
15. 	91	0.689	[28]
16. 	92	$0.80^{1)}$	[17]
R = see 1.	92	$0.73^{1)}$	[8]
17. 	99	0.71	[24]
18. 	102	0.745	[24]

(*Continued*)

TABLE 1 Continued

	T_{NI}/°C	$\bar{P}_2$	Ref.
19. 	103	0.745	[24]
20. 	106.5	0.746	[29]
21. 	109	0.742	[30]
22. 	123.0	0.787	[31]
	123.0	0.76[2)]	[10]
23. 	135	0.776	[13]
24. 	214	0.759	[26]
25. 	237	0.844	[26]
26. 	244.7	0.839	[32]

1) The value of $\overline{P_2} = 0.8$ obtained by the Haller extrapolation does not fit well in equation (3); $\overline{P_2} = 0.73$ obtained by mean field extrapolation [8] fits well.

2) In this substance is a SmA-N transition at 77°C. Therefore pretransition effects in $\bar{P}_2$ will cause too high values, extrapolated from values near to 77°C to room temperature. Using in Eq. (1) $\bar{P}_2$ values for different temperatures delivers the following data:

T/°C	$\bar{P}_2$	β	$\bar{P}_2$ at 25°C
78	0.76	0.1315	0.8345
105	0.58	0.1988	0.765
115	0.485	0.2245	0.7405

The point with $\beta \cong 0.2$ fits best in the general curve.

In Table 1 the order parameters of some mixtures are listed. Because in many cases the order parameters are derived from macroscopic properties like the birefringence, the properties of the individual compounds are automatically averaged.

It should be emphasized that for $\overline{P_2}$ data at room temperature, in addition to the main effect of the temperature difference to T_{NI}, the individual properties of the compounds are important. This is illustrated in Figure 3. The three curves are ranging from T_{NI} to $T = 25°C$ in each case. When we compare the data for equal $\Delta T = T_{NI} - T$, say $\Delta T = 50\,K$, we clearly see the distinct influence of the different molecular structures on $\overline{P_2}$. The further increase of $\overline{P_2}$ in the two upper curves demonstrates the influence of the distance to T_{NI}, which of course is also substantial. The middle curve (4,4′-di-methoxyazoxybenzene) corresponds quite well to the Maier-Saupe theory and thus allows the comparison to this theory.

It is not possible to extract from a universal curve for the temperature dependence of the order parameter the substance specific order parameters for 25°C. The shapes of the curves for the temperature dependence of $\overline{P_2}$ do not follow a simple logarithmic law like Eq. (3).

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