# Thermal conductivity and thermal diffusivity of the cyanobiphenyl ($n$CB) homologous series

M. Marinelli, F. Mercuri, U. Zammit, and F. Scudieri

*Dipartimento di Ingegneria Meccanica and Sezione INFM Roma II, Università di Roma ''Tor Vergata,''*

*Via di Tor Vergata, Roma, Italia*

The thermal conductivity and the thermal diffusivity of aligned $n$CB samples ($n=5,\ldots,9$) has been measured with a photopyroelectric technique. An odd-even effect has been found in the values of these two quantities for homeotropic samples with increasing $n$. The results can be interpreted in terms of a model proposed by Urbach, Hervet, and Rondelez. This model, which takes into account not only the geometrical dimensions of the liquid crystal molecules but also their average mutual distances, has been also used to account for the observed anisotropy in the thermal diffusivity. [S1063-651X(98)13010-6]

## I. INTRODUCTION

It is well known [1] that the heat conduction in liquid crystal (LC) ordered phases is anisotropic, but the physical mechanisms that govern such anisotropy are not yet completely understood. The data reported in the literature [1–9] show that, in all the measured compounds, $D_\parallel$, which is the thermal diffusivity measured in a direction parallel to the director, is larger than $D_\perp$, which is the one measured in a direction perpendicular to it. A semiquantitative approach, based on the extension of the Eyring model for the thermal diffusivity of simple fluids to anisotropic media, has been proposed to explain some experimental observations [1]. This model, in which LC molecules are considered as rigid rods, is based on two simple assumptions. The first one is that, for example in the nematic phase, where all the molecules have, on the average, their long axis aligned parallel to the director, the ''empty space'' between molecules measured along the long axis is not the same as the one perpendicular to it. The second assumption is that the energy is not instantaneously transferred from one molecule to the surrounding ones, but it propagates with finite speed as in the case of convective conduction. The conclusions derived from the explanation of the experimental results in terms of the proposed model are the following: (i) $D_\parallel/D_\perp$, which has been found to be greater than 1 for all the measured compounds, linearly depends on the molecular length; (ii) $D_\parallel$ and $D_\perp$ do not depend on the long-range order of the system and thus do not vary significantly from one mesophase to another, showing no pretransitional effects; (iii) the dependence of the value of $D_\parallel$ on the length of the central rigid core of the molecule is more important than that due to the length of the aliphatic end chain.

Some open questions, however, remain. Following the above-mentioned modeling of the heat conduction in LC, it turns out that the ordering of the molecules, which is expected to affect the amount of empty space between them, should have an influence on $D$. Packing of the molecules, on the other hand, depends on their symmetry and is responsible for the so-called odd-even effect on the nematic-isotropic (NI) transition temperature ($T_{NI}$) found in several LC compounds [10]. An odd-even effect also in the anisotropy of $D$ may therefore be expected. The absence of pretransitional effects has, moreover, been contradicted by some recent high resolution results on the critical behavior of $D$ close to several phase transitions of various compounds [11,12] and it has also been shown that the variation of $D$ from one mesophase to another is not always negligible [13].

Another interesting aspect is how the heat conduction anisotropy in LC can be related to the molecular dimensions. Some authors [8] have suggested that the same expression relating the mass diffusion coefficient $D_m$ and the molecular dimensions, via the microscopic order parameter $S$, may be valid also for the thermal diffusivity. These models, however, do not consider the symmetry of the molecules, which, as stated before, is known to affect the ordering process. Only a few experimental results on this issue are available in the literature and, to date, no definite conclusion has been drawn.

In this paper we report on the simultaneous measurement of the thermal conductivity ($k$) and the thermal diffusivity as a function of temperature for the $n$CB ($n=5,\ldots,9$) homologous series. The data have been compared with those existing in literature. An odd-even effect, similar to the one reported for $T_{NI}$ [10] has been found in $k$ and $D$ and have been explained in terms of the model proposed in Ref. [1]. It has been concluded that it is not only the length to width ratio of the molecules that influences the heat conduction, but also the intermolecular distances, and therefore the packing of the molecules, which is affected by the ordering due to the molecular symmetry. Data on the dependence of the heat conduction anisotropy as a function of $n$ are also presented. It is shown that these data can be only accounted for with the above-mentioned theoretical model, while the expressions that have been proposed for $D_m$ do not seem to be adequate.

## II. EXPERIMENT

Measurements have been performed in the photopyroelectric setup described previously [12], which enables the simultaneous measurement of specific heat, thermal conductivity, and thermal diffusivity. The heating rate was between 20 and 40 mK/min. Samples homeotropic alignment was obtained by treating the cell walls with a trimethylcetylammonium bromide solution in chloroform. The concentration of the surfactant was adjusted to have a maximum value for $D_\parallel$ at a reference temperature, a circumstance which, as discussed later on, ensures optimum alignment. In all cases a
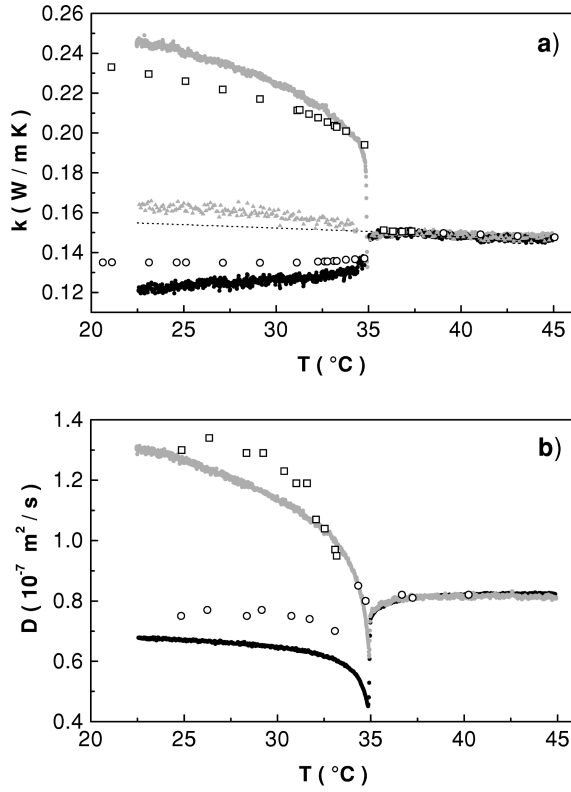
FIG. 1. (a) Thermal conductivity as a function of temperature for homeotropic (gray dots) and planar (dark dots) 5CB samples. Open squares and circles represent data taken from Ref. [7]. Light gray triangles show calculated values of the average thermal conductivity for nonaligned samples. (b) Thermal diffusivity as a function of temperature for homeotropic (gray dots) and planar (dark dots) 5CB samples. Open squares and circles represent data taken from Ref. [1].

value of 5% in weight proved to be the best choice to have monodomain samples. A polarizing microscope was then used to check the alignment. Planar samples were obtained by depositing on the cell walls a thin layer of quartz at a grazing angle. Also in this case the alignment was checked by a polarizing microscope and the sputtering conditions were adjusted to have a minimum values for $D_\perp$ at a reference temperature.

### III. RESULTS

Figure 1(a) shows the thermal conductivity data versus temperature for two 5CB samples with planar and homeotropic alignment. The two data sets coincide in the isotropic phase where the thermal conductivity slightly decreases with increasing temperature. A discontinuity, as expected for a first order phase transition such as the NI one, is clearly evident at $T_{NI}$. Below this temperature $k_\parallel$ increases with decreasing temperature, while $k_\perp$ decreases. A comparison between the data obtained in the present work and the ones reported in Ref. [7] is also contained in Fig. 1(a). Although the qualitative behavior is similar, the thermal conductivity values we have obtained in the nematic phase are systematically larger in the case of $k_\parallel$ and smaller in the case of $k_\perp$. This could be due to a poorer alignment of the sample in Ref. [7]. Data available in the literature suggest that the thermal

conductivity value is close to $\frac{1}{3}(k_\parallel + 2k_\perp)$ for nonaligned samples and $k_\parallel > \frac{1}{3}(k_\parallel + 2k_\perp) > k_\perp$. This leads to the conclusion that the better the alignments, the larger (the smaller) the value of $k_\parallel$ ($k_\perp$). As pointed out by the authors in Ref. [7], in their case the sample had been aligned by a magnetic field. With such a method and with their experimental setup the extent of the molecular alignment could not be checked. In our case, as stated earlier on, the sample alignment was carefully checked. Figure 1(a) also shows calculated values of $\frac{1}{3}(k_\parallel + 2k_\perp)$ versus temperature in the nematic phase. This quantity is supposed to give the average value for the thermal conductivity in nonaligned samples, based on the assumption that LC molecules can be represented as simple rods. One might therefore expect that the $\frac{1}{3}(k_\parallel + 2k_\perp)$ quantity should coincide with the extrapolation below $T_{NI}$ of the data in the isotropic phase. The data, as in Ref. [7], do not confirm this and we believe that the observed deviation is due to the true conformation of the molecules that can be considered as rigid ellipsoids only as a first approximation. It should be, moreover, considered that the sample density has a discontinuity at $T_{NI}$, the value in the nematic phase being larger than the one in the isotropic phase [14] so that a closer packing of the molecules in the nematic phase can be responsible for the larger average $k$ value observed in such a phase.

Figure 1(b) shows the thermal diffusivity versus temperature for planar and homeotropic aligned samples. In both cases, a dip in $D$ at the transition temperature can be observed. Again the data coincide in the isotropic phase while $D_\parallel$ and $D_\perp$ increases below $T_{NI}$ with decreasing temperature, the increase in $D_\perp$ being less pronounced. Also shown in Fig. 1(b) are data reported in Ref. [1]. Though a good agreement has been found in the isotropic phase, the data taken from Ref. [1] are systematically larger than the ones we have obtained in the nematic phase for both planar and homeotropic alignments. It should be pointed out, however, that while we have used pure compounds in our measurements, in Ref. [1] a dye has been added to the samples. Pretransitional effects in $D$ are, moreover, clearly visible in our data close to the NI transition. This contradicts the conclusion reported in Ref. [1] concerning the absence of any pretransitional effect near phase transition in $D$ probably due to the much lower temperature resolution of such measurements in the vicinity of the phase transition and possibly also to the lower sample purity due to the presence of the dye.

For 5CB and for all of the other investigated samples we have also obtained the specific heat data (not shown), which in all cases where our technique was applied are in a very good agreement with the ones reported in literature.

Figures 2 and 3 show the thermal conductivity and the thermal diffusivity versus temperature for 6CB and 7CB, respectively. The same considerations as for 5CB apply to the data reported in these figures. Two data points for $D_\parallel$ and $D_\perp$ of 6CB, taken from Ref. [6], are reported in Fig. 2(b). Both are considerably larger than the corresponding ones obtained in the present work.

The temperature dependence of the thermal conductivity and thermal diffusivity for aligned 8CB and 9CB samples, already reported in Refs. [12] and [13], are shown in Figs. 4 and 5. Also reported in Fig. 4(b) are data taken from Ref. [5] which show a reasonable agreement with the ones we have obtained. The behavior of $D_\parallel$ and $D_\perp$ below $T_{NI}$ in these two
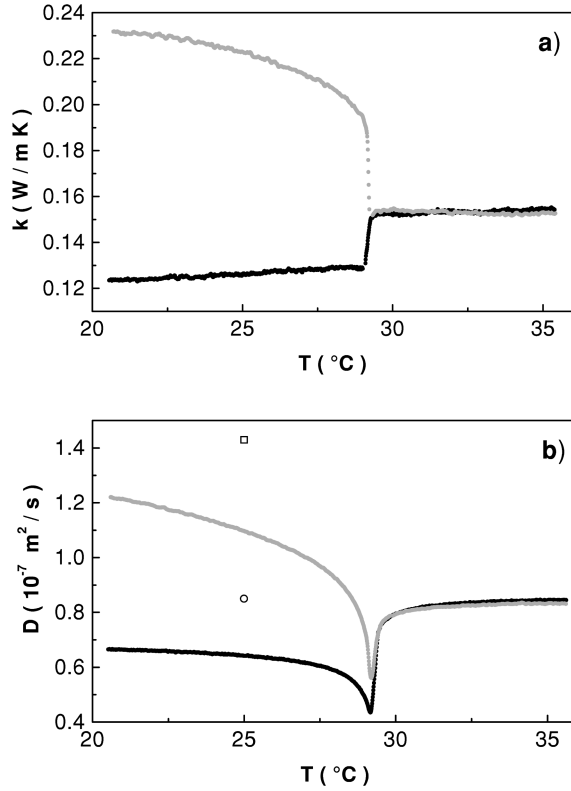
FIG. 2. (a) Thermal conductivity as a function of temperature for homeotropic (gray dots) and planar (dark dots) 6CB samples. (b) Thermal diffusivity as a function of temperature for homeotropic (gray dots) and planar (dark dots) 6CB samples. Open symbols represent data taken from Ref. [6].
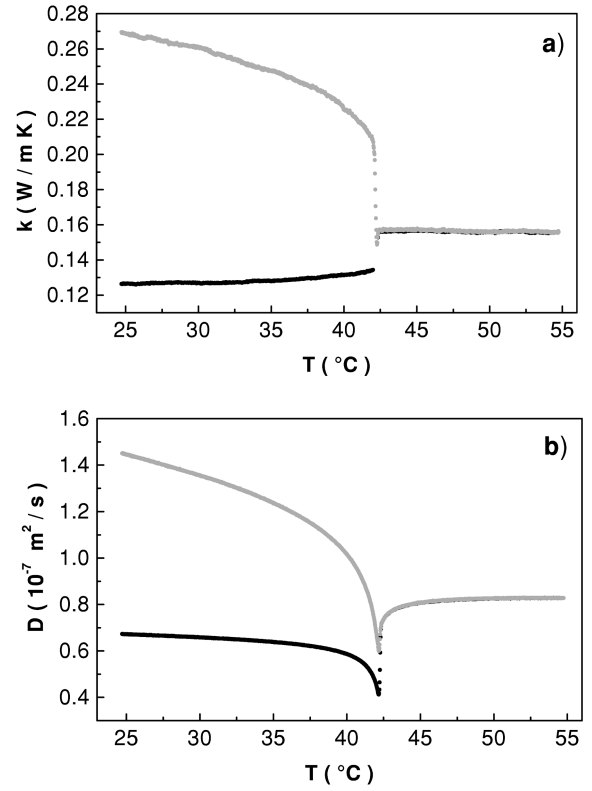


FIG. 3. (a) Thermal conductivity as a function of temperature for homeotropic (gray dots) and planar (dark dots) 7CB samples. (b) Thermal diffusivity as a function of temperature for homeotropic (gray dots) and planar (dark dots) 7CB samples.

compounds is different with respect to the other compounds of the series since, below the NI transition, the smectic A–nematic (AN) phase transition takes place. In both cases below $T_{AN}$, a sudden increase of $k_\parallel$ with decreasing temperature, due to the smectic ordering contribution to the orientational order parameter, as explained in Ref. [13] is evident in Figs. 4(a) and 5(a). This effect is more pronounced in the case of 9CB because of the narrower nematic range. Such an effect is difficult to detect in the thermal diffusivity because of the dip at the AN transition shown in Figs. 4(b) and 5(b), which is associated with the critical behavior of the specific heat [12]. These results demonstrate that, unlike what was reported in Ref. [1], the thermal diffusivity has a critical behavior at the AN transition and that the smectic ordering can affect the thermal transport especially in compounds with a narrow nematic range [13]. It should finally be noted that the temperature resolution of our measurements is about three orders of magnitude larger than the one of Ref. [1].

## IV. DISCUSSION

### A. Thermal parameters as a function of molecular length

As already stated in the Introduction, a simple kinetic model based on an extension of the Eyring theory for the thermal diffusivity of isotropic fluids to anisotropic ones has been proposed for the thermal diffusivity of LC [1]. There are two basic assumptions: the first one is that the empty space between molecules in the nematic phase, for example,

is not the same in a direction parallel to the long axis of the molecule and in the perpendicular one, while the second concerns the energy that is not instantaneously transferred from one molecule to the surrounding ones. The first assumption is strictly connected to the elongated shape of LC molecules, while the second one derives from the analysis of experimental data which suggest that, generally speaking, the LC molecules have a highly conducting rigid core and a less conducting alkyl chain [1]. If we assume that a LC single molecule or a single dimer in the case of polar compounds can be represented by a cylinder, then in the case of a perfect alignment ($S=1$), according to the model reported in Ref. [1], we have

$$D_\parallel^* \simeq \frac{L^2}{3d_\parallel}, \quad D_\perp^* \simeq \frac{a^2}{3d_\perp}. \tag{1}$$

The quantities in Eq. (1) are average values of the distances indicated in Fig. 6.

If $S<1$ then:

$$D_\perp = \frac{D_\parallel^*(1-S)+D_\perp^*(2+S)}{3}, \tag{2}$$

$$D_\parallel = \frac{D_\parallel^*(1+2S)+D_\perp^*(2-2S)}{3}.$$

The above expressions clearly indicate that the influence of the molecular length on the thermal diffusivity can be derived from the experimental data from different com-
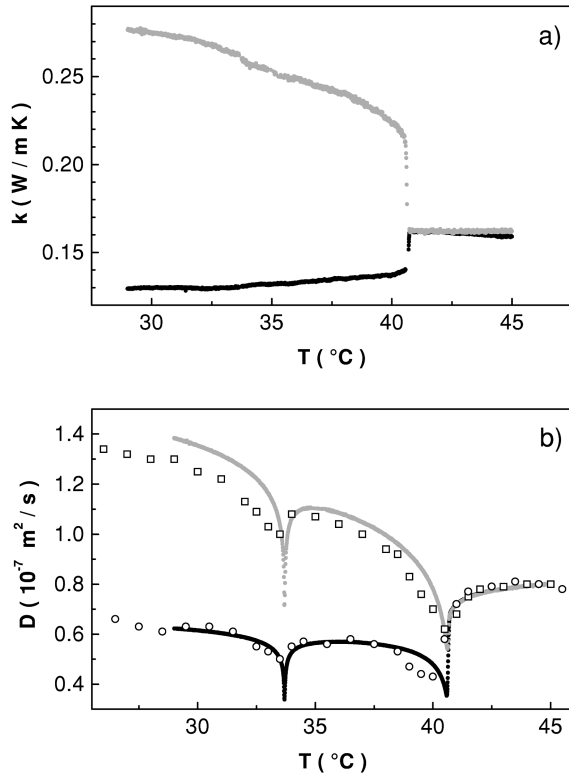
FIG. 4. (a) Thermal conductivity as a function of temperature for homeotropic (gray dots) and planar (dark dots) 8CB samples. Data are taken from Ref. [12]. (b) Thermal diffusivity as a function of temperature for homeotropic (gray dots) and planar (dark dots) 8CB samples. Data are taken from Ref. [12]. Open squares and circles represent data taken from Ref. [5].
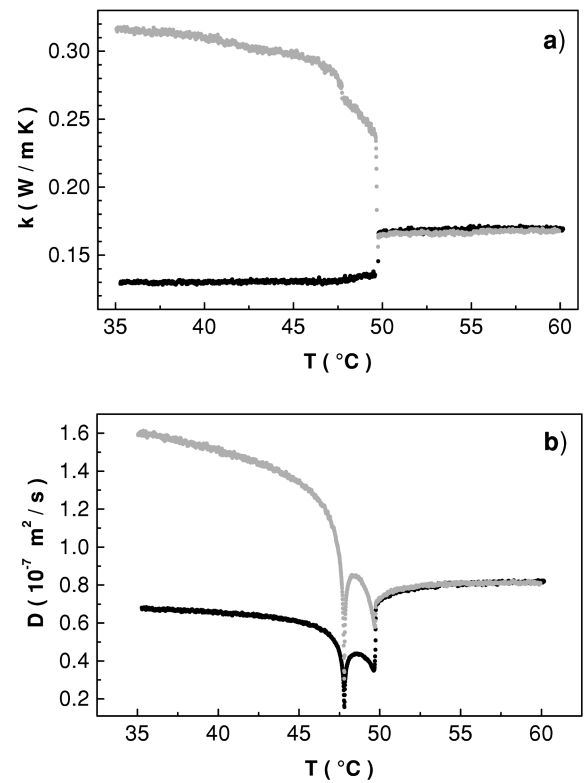


FIG. 5. (a) Thermal conductivity as a function of temperature for homeotropic (gray dots) and planar (dark dots) 9CB samples. Data are taken from Ref. [13]. Thermal diffusivity as a function of temperature for homeotropic (gray dots) and planar (dark dots) 9CB samples. Data are taken from Ref. [13].

pounds. The thermal diffusivity strongly depends on the orientational order of the system, which is temperature dependent, but if we assume, as in the case of the Maier-Saupe theory [14], that the molecular interactions are temperature independent, then the microscopic order parameter $S$ is a universal function of $T/T_{NI}$. Following this assumption, which will be discussed again later on, and to allow a comparison among the different compounds, the data will be plotted as a function of the reduced temperature $t = (T - T_{NI})/T_{NI}$.

In Ref. [1] the authors claim that $D_\parallel$ increases linearly with $n$ while $D_\perp$ does not change substantially. Considering Eqs. (1) and (2) this would be consistent with both $L$ and $d_\parallel$ increasing linearly with $n$, since $D_\parallel \simeq L^2/d_\parallel$. If one, however, looks more carefully at the data on the PAA series (Fig. 7 of Ref. [1]) one sees that the $D_\parallel$ values are affected by the so-called odd-even effect, which, in their case, produces an increase (decrease) of $D_\parallel$ when moving from one compound with an odd (even) number of methyl groups in the alkyl chain to one having an even (odd) number.

Figure 7 shows $T_{NI}$ versus $n$ for the $n$CB series where the so-called odd-even effect is clearly visible. This effect has been related to the symmetry of the molecule, which is changed by the progressive addition of alkyl groups [10]. This effect becomes less evident as the molecular length increases because of the flexibility of the alkyl chain.

In Fig. 8 we have reported the values of $D_\parallel$ as a function of $n$ calculated at $t = -0.033$, which correspond to the largest

common distance from $T_{NI}$ achievable for all compounds in our measurements. An odd-even effect is clearly visible also in the $D_\parallel$ values. It should be noted that while 5CB, 6CB, and 7CB are always in the nematic phase for all the negative values of $t$, 8CB, and 9CB are in the smectic A phase for $t \leqslant -0.022$ and $t \leqslant -0.006$, respectively. Since in these two compounds there is an additional contribution to the orientational order due to the smectic layering [13], the relevance of the odd-even effect in $D_\parallel$ is reduced and it therefore appears less evident than in $T_{NI}$. It is very difficult for these two compounds to have values for the diffusivity in the nematic phase to be easily comparable with those of the other compounds of the homologous series because of their narrow nematic range and because of the pretransitional effects found in $D$.
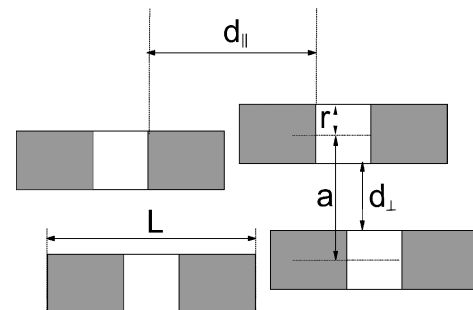


FIG. 6. Schematic representation of rodlike LC molecular dimensions. White areas represent rigid cores while shaded areas represent alkyl chains.
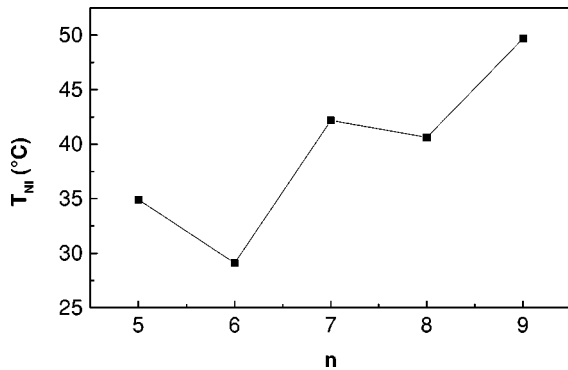
FIG. 7. Nematic-isotropic transition temperature as a function of $n$.

While in the case of the PAA series $D_\parallel$ decreases going from an even to an odd compound, the opposite occurs in the $n$CB series. This is obviously due to the different molecular structure and therefore to the different molecular symmetry of the two series.

Also shown in Fig. 8 is $D_\perp$ versus $n$. A variation of about 10%, smaller than the one found in $D_\parallel$, has been obtained for different compounds. The data, however, do not allow us to draw any definite conclusion regarding the trend of the $D_\perp$ with $n$, as also in the case of Ref. [1]. What may appear as a nonmonotonous behavior, particularly for 8CB, is due to the vicinity of the AN transition, which induces an anomalous decrease of $D_\perp$. Thermal diffusivity data for 8CB taken at lower temperatures, further away from $T_{AN}$, are quite close to the 9CB value and this leads to the conclusion that the variation of $D_\perp$ could be smaller than that reported in Fig. 8 if data could be taken for all the compounds at a smaller $t$.

Figure 9 shows $k_\parallel$ versus $n$. Though the odd-even effect is less evident, $k_\parallel$ behaves qualitatively like $D_\parallel$ and this is not surprising if we consider that $k_\parallel = \rho c D_\parallel$. Figure 9 shows also the approximately linear increase of $k_\perp$ with $n$. When compared with the one of $D_\perp$ the behavior of $k_\perp$ can be explained only if we assume an increase of $\rho$ and $c$ with $n$. While, as discussed later on, $\rho$ decreases slightly with $n$ [15], $c$ increases [16] and its increase can account for the observed behavior of $k_\perp$.

Let us now try to analyze the results we have obtained in terms of Eqs. (1) and (2). If we consider the LC molecules as rigid rods, then an increase of the length $L$ must produce an
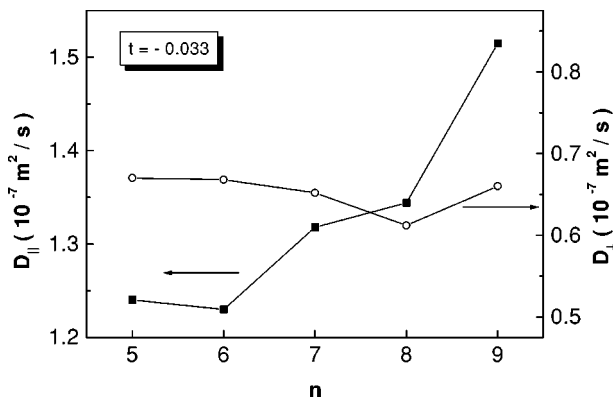
increase in $D_\parallel$. The presence of the odd-even effect, however, suggests that we have to take into account also the symmetry of the molecule, since it affects the ordering process and therefore their average separation. In other words the observed odd-even effect suggests a nonmonotonous variation of $d_\parallel$ with increasing $L$. We can then look at the $D_\parallel$ dependence on $n$ as the combination of two contributions: one given by the increase in $L$, which gives a linear background increase in $D_\parallel$, plus the oscillation induced by the nonmonotonous variation of $d_\parallel$.

The above-mentioned results may raise some doubts about the choice we have made to plot the thermal conductivity and thermal diffusivity data as a function of the reduced temperature to allow a comparison between different compounds. This choice was based on the Maier-Saupe theory [14] that considers LC molecules as rigid rods. The results we have obtained show, however, that the symmetry of the molecule affects, together with other possible effects such as, for example, the smectic contribution to orientational order, the ordering process. This would imply that the microscopic order parameter $S$ would no be longer a universal function of $t$. In other words, the presence of the odd-even effect may give rise to different values of $S$ at the same $t$ for different compounds. In the following it will be shown that the difference between the orientational order parameter among the various compounds of the $n$CB series at $t = -0.033$ are small enough to confirm all the conclusions we have drawn on the basis of the normalization procedure we have chosen.

### B. Thermal anisotropy

It is well known that the anisotropic part of a tensorial quantity can be used to define a macroscopic order parameter which is usually assumed to be proportional to the microscopic one [17]. Strictly speaking, this is true only when the field produced by molecular interactions, as in the case of the magnetic susceptibility, is negligible with respect to the external one. In all the other cases, to preserve the proportionality, arbitrary assumptions must be made on the correlation function, even though, after a suitable normalization, macroscopic order parameters obtained from different experimental technique show a reasonable agreement [17].
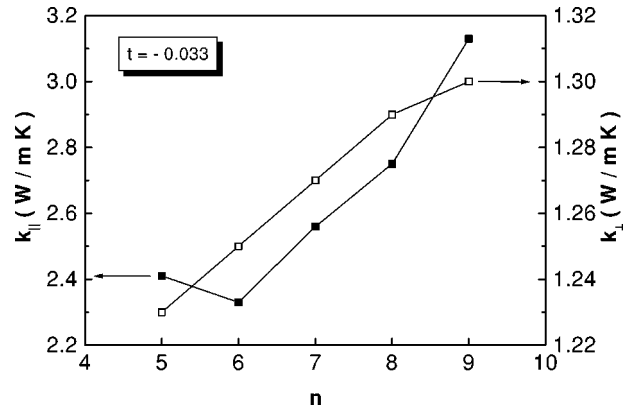


FIG. 9. Thermal conductivity of homeotropic (squares) and planar (circles) samples as a function of $n$ at $t = -0.033$.



FIG. 8. Thermal diffusivity of homeotropic (squares) and planar (circles) samples as a function of $n$ at $t = -0.033$.
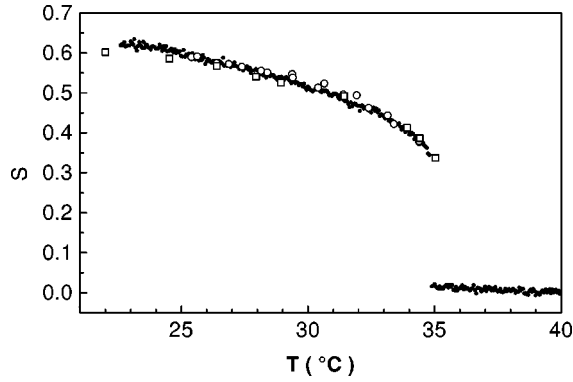
FIG. 10. Orientational order parameter as a function of temperature for 5CB. Open squares and circles represent data taken from Refs. [18] and [19], respectively.



FIG. 11. Thermal anisotropy as a function of $n$.

Figure 10 shows the behavior of $S$ as a function of $T$ obtained in 5CB assuming the anisotropy in the thermal conductivity $\Delta k = k_\parallel - k_\perp \simeq S$. The data have been normalized at 28 °C with a data point taken from Ref. [18]. Also shown in the figure are data taken from the literature [18,19] and the agreement with those we have obtained is fairly good. Similar agreement (not shown) has been obtained for the other compounds of the homologous series, this leading to the conclusion that the assumption we have made about the proportionality between $k_\parallel - k_\perp$ and $S$ is reasonable. Moreover, small differences have been observed in the behavior of $S$ as a function of $t$ obtained from $k_\parallel - k_\perp$ for the different compounds of the $n$CB series, thus justifying the choice we have made to represent the data on $k$ and $D$ for the various compounds as a function of $t$. We would like to emphasize once again the very large temperature resolution in the $S$ data as a function of temperature that can be obtained from the thermal conductivity anisotropy via the photopyroelectric measurements, an aspect that is very important when one is interested in the critical behavior of $S$ to evaluate its critical exponent $\beta$. A discussion on this point is, however, beyond the scope of this work and will be presented elsewhere.

Equations (1) and (2) can be used to predict the behavior of the thermal anisotropy as a function of $n$. If we define

$$R = \frac{D_\parallel - D_\perp}{D_\parallel + 2D_\perp}, \qquad (3)$$

then we obtain

$$R = S \frac{Q^2 - 1}{Q^2 + 2}, \qquad (4)$$

where, assuming $d_\perp \ll 2r$, then $a^2 = (2r + d_\perp)^2 \sim 4r^2$ and $Q^2 = D_\parallel^* / D_\perp^* = (L^2/4r^2)(d_\perp/d_\parallel)$.

It has been suggested that the anisotropy in $D$ and that in the mass diffusion coefficient $D_m$ should be described by the same expression [8]. The expression for the anisotropy of $D_m$ obtained in Ref. [20] from an affine transformation model, is indeed equal to Eq. (4), where, however, $Q^2 = (L/2r)^2$. Also, in the case of Ref. [21], the prediction for the anisotropy in $D_m$ is again equal to Eq. (4) but with $Q^2 = (L/2r)$.
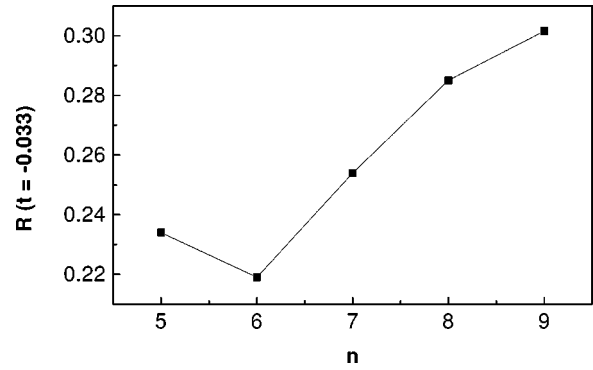
Figure 11 shows the $R$ versus $n$ behavior we have obtained from our data. The behavior of $R$ is similar to that for $k_\parallel$. A semiquantitative calculation based on Eq. (4) will give in the following an estimate of the value of $d_\perp/d_\parallel$ and its dependence on $n$. We will not use data obtained for 8CB and 9CB, compounds with a larger anisotropy, since, as discussed before, they have smectic phases with $T_{AN}$ quite close to $T_{NI}$. At $t = -0.033$ we have, considering, for example, 5CB and 7CB, $R_{5CB} = 0.23$ and $R_{7CB} = 0.25$. Combining these two numbers with the $S$ values obtained from $\Delta k$ data at the same $t$, which are $S_{5CB} = 0.59$ and $S_{7CB} = 0.64$, respectively, from Eq. (4) we have $Q^2_{5CB} = Q^2_{7CB} = 2.92$. Since $n$CB are polar compounds and are known to form dimers, then assuming that $2r \sim 9$ Å [22] for all the investigated compounds and $L_{5CB} \sim 25$ Å and $L_{7CB} \sim 29.8$ Å [23], we obtain $(d_\perp/d_\parallel)_{5CB} \sim 0.38$ and $(d_\perp/d_\parallel)_{7CB} \sim 0.26$. In both cases the variation of the geometrical dimensions and, in particular, the increase of the molecular length that affects $d_\parallel$, cannot account for the decrease of $d_\perp/d_\parallel$. We believe that, with $d_\perp$ approximately constant in the nematic phase, there is an increase of the average distance between molecules in a direction parallel to the molecular long axis. This conclusion is supported by the decrease of the sample density with increasing $n$ reported in Ref. [15] for the $n$CB series and it is also consistent with what is reported in Ref. [1] for the PAA series. Though the calculations have been performed for 5CB and 7CB only for the reasons reported above, the data shown in Fig. 11 suggests that the variation of $R$ with $n$ cannot be explained only in terms of the variation of the geometrical dimensions for all the investigated molecules. The results we have presented lead us to conclude that the models for the thermal diffusivity based on the molecular dimensions only, such as those for $D_m$, are not adequate.

It is interesting to note that from $D_\parallel^*/D_\perp^* = (L^2/4r^2)(d_\perp/d_\parallel)$ it follows that the conclusion $D_\parallel > D_\perp$, unlike that reported in Ref. [1], may not be a general one in all the mesophases. $D_\parallel/D_\perp$ in fact depends on the geometrical dimensions of the molecules but also on $d_\perp/d_\parallel$. In other words, it may be possible, at least in principle, that $d_\perp/d_\parallel$ is small enough to give $D_\parallel < D_\perp$. This possibility cannot be excluded, for example, in highly symmetric smectic phases, in which smectic layering could produce a close packing of the molecules [17] within the plane, thus reducing considerably $d_\perp/d_\parallel$.

## V. CONCLUSIONS

The measurements of the thermal diffusivity and thermal conductivity of the $n$CB series have been presented. It has been shown that, for homeotropic samples, both quantities are affected by the odd-even effect. This implies that any theoretical interpretation of the results must take into account, not only the geometrical dimensions, but also the symmetry of the molecules and their average distances. This has been confirmed by data on the thermal transport anisotropy, which, moreover, show that models for the anisotropy used for the mass diffusion coefficient cannot be applied to the thermal diffusivity. It has been, moreover, shown that the ratio of the average distance between molecules along a direction perpendicular to the molecular long axis and perpendicular to it is smaller than 1 and decreases with $n$. The effect of long-range order has been found to be important in the thermal transport parameters in the cases of 8CB and 9CB, where an increase in the anisotropy just below $T_{AN}$ has been found. Pretransitional effects are clearly visible in the thermal diffusivity but are absent in the thermal conductivity.

[1] W. Urbach, H. Hervet, and F. Rondelez, J. Chem. Phys. **78**, 5113 (1983).

[2] R. Vilanove, E. Guyon, C. Mitescu, and P. Pieranski, J. Phys. (Paris) **35**, 153 (1974).

[3] W. Urbach, H. Hervet, and F. Rondelez, Mol. Cryst. Liq. Cryst. **46**, 409 (1978).

[4] F. Rondelez, W. Urbach, and H. Hervet, Phys. Rev. Lett. **41**, 1058 (1978).

[5] T. Akahane, M. Kondoh, K. Hashimoto, and M. Nakagawa, Jpn. J. Appl. Phys. **26**, L1000 (1987).

[6] Y.G. Fuh and R.F. Code, Can. J. Phys. **63**, 282 (1985).

[7] G. Ahlers, D.S. Cannel, L.I. Berge, and S. Sakurai, Phys. Rev. E **49**, 545 (1984).

[8] A.C. Bento, A.J. Palgana, L.R. Evangelista, M.L. Baesso, J.R.D. Pereira, E.C. da Silva, and A.M. Mansanares, Appl. Phys. Lett. **68**, 3371 (1996).

[9] J. Caerels, E. Schoubs, and J. Thoen, Liq. Cryst. **22**, 659 (1997).

[10] S. Marčelija, J. Chem. Phys. **60**, 3500 (1974).

[11] G. Nounesis, C.C. Huang, and J.W. Goodby, Phys. Rev. Lett. **56**, 1712 (1986).

[12] M. Marinelli, F. Mercuri, S. Foglietta, U. Zammit, and F. Scudieri, Phys. Rev. E **54**, 1604 (1996).

[13] F. Mercuri, U. Zammit, and M. Marinelli, Phys. Rev. E **57**, 596 (1998).

[14] W. Maier and A. Saupe, Z. Naturforsch. A **13**, 564 (1958); **14**, 882 (1959); **15**, 287 (1960).

[15] D.A. Dunmur and W.H. Miller, J. Phys. Colloq. **40**, C3-141 (1979).

[16] J. Thoen, Int. J. Mod. Phys. B **9**, 2157 (1995).

[17] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).

[18] J.W. Emsley, G.R. Luckhurst, and C.P. Stockley, Mol. Phys. **44**, 565 (1981).

[19] G. Vertogen and W.H. de Jeu, *Thermotropic Liquid Crystals, Fundamentals* (Springer-Verlag, Berlin, 1988).

[20] S. Hess, D. Frenkel, and M.P. Allen, Mol. Phys. **74**, 765 (1991).

[21] K.S. Chu and D.S. Moroi, J. Phys. Colloq. **36**, C1-99 (1975).

[22] A.J. Leadbetter, J.L.A. Durrant, and M. Rugman, Mol. Cryst. Liq. Cryst. **34**, 231 (1977).

[23] A.J. Leadbetter, J.C. Frost, J.P. Gaughan, G.W. Gray, and A. Mosley, J. Phys. (Paris) **40**, 375 (1979).