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H. J. Müller [a] & W. Haase [b]

[a] Departamento de Física, Universidade Federal de S. Catarina, SC, Brasil

[b] Institute of Physical Chemistry, Darmstadt University of Technology, Darmstadt, Germany

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REFRACTIVE INDICES, DENSITY AND ORDER PARAMETERS FOR SOME BIPHENYL CYCLOHEXANES

H. J. Müller
Departamento de Física, Universidade Federal de S. Catarina, 88040-900-Florianopolis, SC, Brasil

W. Haase
Institute of Physical Chemistry, Darmstadt University of Technology, Petersenstr. 20, Darmstadt D-64287, Germany

Measurements of densities within the nematic phase and of the main refractive indices at sodium-D line, both in the nematic and in the smectic phases, were done on some 4,4′-disubstituted biphenylcyclohexanes. The results are discussed in terms of the nature of the different substituents. By using the often applied Vuks model and some bond or fragment polarisabilities the nematic order parameter, S, could be estimated.

Keywords: nematic and smectic liquid crystals; refractive indices; density; order parameters

INTRODUCTION

4,4′-disubstituted biphenylcyclohexanes (BCHRR′) were first reported by Eidenschink *et al.* [1,2]. Transition temperatures and enthalpies for eight of the compounds from this series have been reported [3–5]. X-ray data were presented both for their liquid crystalline phases and for the solid phases [5–8]. For the compounds with $R = C_5H_{11}$, $R' = H$ (BCH5H), $R' = C_2H_5$ (BCH52), $R' = C_4H_9$ (BCH54) a crystalline B phase with a layer packing structure ABC (first one) or ABA (last two) and a nematic phase could be described [5,6]. The alignment in both of the phases smectic and nematic under cooling down from the isotropic state under applied

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Address correspondence to H. J. Müller, Departamento de Fisica, Universidade Federal de S. Catarina 88040-900-Florianopolis, SC, Brazil.

magnetic field 1.5 T is rather good [5]. In contrast, the compound with $R = C_3H_7$, $R' = H$ (BCH3H) showed only a smectic B-phase which could not be aligned [5,6]. The crystal structures were presented for the compounds BCH3H, BCH5CN ($R = C_5H_{11}$, $R' = CN$), BCH52, and BCH5F ($R = C_5H_{11}$, $R' = F$) [5–8].

The diamagnetic anisotropy in the liquid crystalline state as a function of temperature could be determined for some of the compounds for oriented samples [9]. By knowing the molecular diamagnetic anisotropy, the order parameter, S, can be estimated. Drawback of this method is on one side the incomplete alignment of the liquid crystal and on the other side the error in estimating the molecular diamagnetic anisotropy by increment methods. Only seldom are good single crystal data available. Fortunately some good data based on computer calculations are now accessible [10].

Besides extracting the order parameter from the temperature dependent diamagnetic anisotropy several other methods are in use, among them optical ones. The main refractive indices n_e and n_o can be related to the bulk polarisability components parallel $\langle\alpha_{||}\rangle$ and perpendicular $\langle\alpha_{\perp}\rangle$ to the director by adopting e.g. the Vuks [11] model:

$$\frac{n_{||,\perp}^2 - 1}{n^2 + 2} = \frac{N}{3\varepsilon_0}\langle\alpha_{||,\perp}\rangle \tag{1}$$

Here N is the number of molecules per unit volume and n^2 is

$$n^2 = \frac{1}{3}(n_{||}^2 + 2n_{\perp}^2) \tag{2}$$

$\langle\Delta\alpha\rangle$ is related to $\langle\alpha_{||}\rangle$ and $\langle\alpha_{\perp}\rangle$as:

$$\langle\Delta\alpha\rangle = \langle\alpha_{||}\rangle - \langle\alpha_{\perp}\rangle \tag{3}$$

With the help of the Vuks model, first introduced for the solid state, the internal isotropic field can be considered. It should be mentioned here, several slightly different models were used, among them a sub-model for a prolate spherical cavity [12]. To calculate N one must determine the volume density ρ.

The main problem again is to have values for the molecular properties, here the principal polarisabilities α_{xx}, α_{yy} and α_{zz}.

For rod-like liquid crystals the approximation $\alpha_{xx} = \alpha_{yy}$ holds which leads to

$$\Delta\alpha = \alpha_{xx} - \alpha_{zz} \tag{4}$$

To calculate $\Delta\alpha$, some fragment or bond polarisabilities can be used. It should be mentioned here, the often used extrapolation method after Haller *et al.* [13] is questionable because eventually phases at low temperature are not considered. We believe, this method should be applied with caution.

The order parameter S can be calculated by using the data for $\langle\Delta\alpha\rangle$ in the liquid crystalline state from

$$S = \frac{\langle\alpha_{||}\rangle - \langle\alpha_{\perp}\rangle}{\alpha_{xx} - \alpha_{zz}} \tag{5}$$

EXPERIMENTAL

The compounds investigated here in more detail have the general formula in Figure 1:

The abbreviation used, the phases and transition temperatures are presented in Table 1.

The density was measured using a bicapillary pycnometer with an accuracy of $\pm 0{,}003 g/cm^3$. The pycnometer was heated with a thermostated liquid, and the error in the temperature was $\pm 0{,}2$°C.

The refractive indices were measured as a function of temperature using a Leitz-Jelley [14] microrefractometer for sodium light (Na_D-line). The alignment of the liquid crystal samples along its long axis is achieved by rubbing the surface of the prism. The light passing through the samples is doubly refracted into extraordinary ($n_{||}$) and ordinary ($n_{\perp}$) rays. The prism was mounted in a Mettler FP-52 heating stage, the error for the temperatures was $\pm 0{,}2$°C. The accuracy of the refractive index measurements was $\pm 0{,}001$.

RESULTS AND DISCUSSION

The molar volume $\overline{V}(\overline{V} = M/\rho)$, calculated from the experimental densities ρ, are presented in Figure 2 as a function of temperature. In the nematic phase close to the nematic-smectic A transition point the dependence of $\overline{V}$ on temperature is non-linear. From the linear part in $\overline{V}(T)$ the thermal

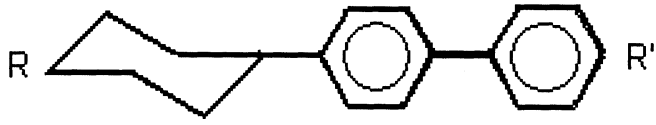

FIGURE 1 Investigated compounds; R, R′ denotes the terminal groups.

TABLE 1 Transition Temperatures and LC-Phases [4,5] of the Compounds Investigated

Abbreviation of the compound	R	R′	Phase sequence and transition temperatures(°C)
BCH5H	C_5H_{11}	H	C 57.9 SmB 81.6 N 97.9 I
BCH7CN	C_7H_{15}	CN	C 76.9 SmA 124.7 N 204.7 I
BCH5F	C_5H_{11}	F	C 94.3 N 152.8 I
BCH5Cl	C_5H_{11}	Cl	C 135.6 N 184.9 I
BCH5Br	C_5H_{11}	Br	C 153.3 N 192.6 I

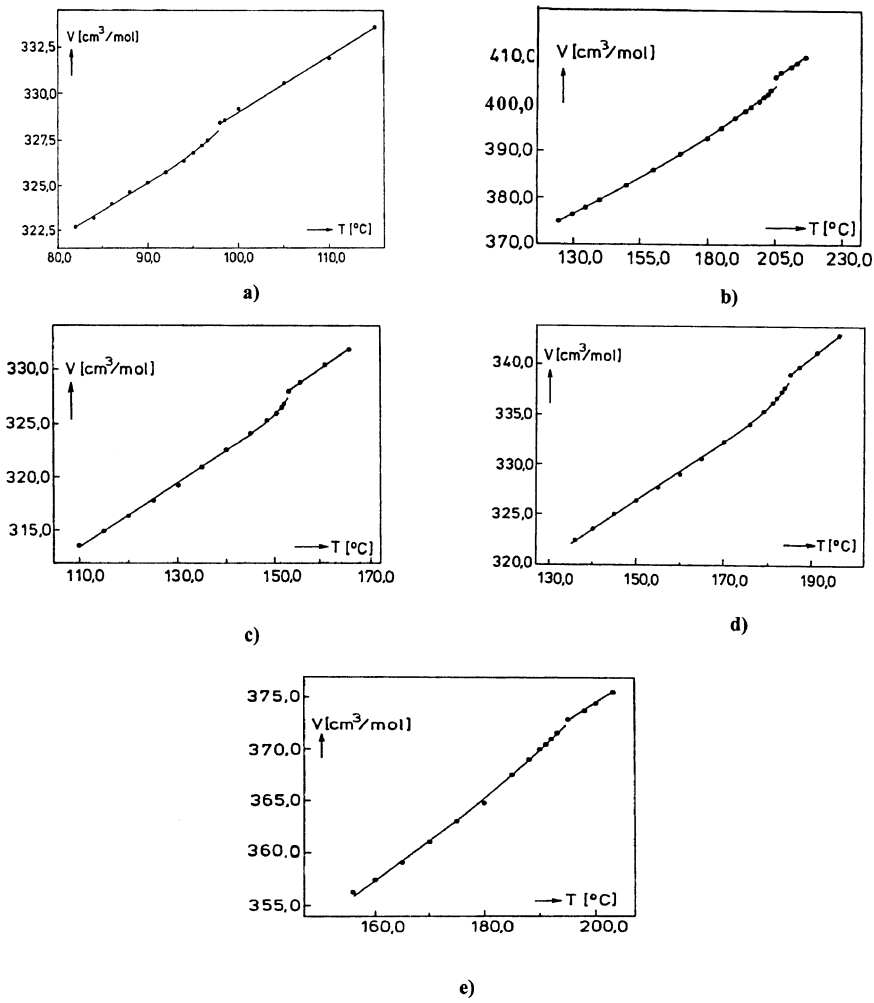

FIGURE 2 Temperature dependence of the molar volume for a) BCH5H, b) BCH7CN, c) BCH5F, d) BCH5Cl, e) BCH5Br. The solid lines are guides for the eye.

TABLE 2 Thermal Expansion Coefficients for the Nematic β_N and Isotropic State β_I

Compound	$\beta_N\ K^{-1} \times 10^3$	$\beta_I\ K^{-1} \times 10^3$
BCH5H	0.99	0.84
BCH7CN	0.85	1.02
BCH5F	0.91	0.93
BCH5Cl	0.92	1.03

expansion coefficients could be calculated for the nematic and the isotropic phases. The data are presented in Table 2.

Whereas the molar volume shows the expected increase on increasing the temperature the thermal expansion coefficients $\beta = (\partial \ln \overline{V}/\partial T)_P$ are slightly different in both of the phases. For BCH5H is $\beta_{\mathrm{N}} > \beta_{\mathrm{I}}$, but for the samples with a stronger dipole moment is $\beta_{\mathrm{N}} < \beta_{\mathrm{I}}$. It means that density change of compounds with stronger lateral dipole moment in the nematic state is weaker then in the isotropic state and vice versa. Maybe, this is due to stronger dipole correlation by compounds with stronger dipole moment inside the nematic state.

The experimental results for the determination of the refractive index $n_{||}$ and $n_{\perp}$ for smectic, nematic and isotropic phases as function of the reduced temperature $\tau = \frac{T}{T_{NI}}$ (T, $\mathrm{T_{NI}}$ in K) are presented in Figure 3. This figure shows also $n_{||}^2 - n_{\perp}^2$. This quantity is proportional to the dielectric anisotropy $\Delta\varepsilon$ and to the order parameter S (Eq.6):

$$\Delta\varepsilon \sim n_{||}^2 - n_{\perp}^2 \sim \rho S \tag{6}$$

In Figure 3 one can see the extraordinary refractive index $n_{||}$ decreases strongly in the nematic as well in the smectic A phase (BCH7CN) by increasing the reduced temperature, whereas for the smectic SmB phase (BCH5H) this decrease is rather small. One can see for a reduced temperature, e.g. τ between 1.0 and 0.96, $n_{\perp}$ decreases whereas for τ less than 0.96 $n_{\perp}$ increases slightly. This stems from the overcompensation of the contribution of increasing the density over increasing the order parameter by decreasing of τ. There is no jump in $n_{||}$ or $n_{\perp}$ for the SmA-N phase transition (BCH7CN), but a jump for the SmB-N transition (BCH5H). $\Delta n = n_{||} - n_{\perp}$ for the SmB phase of BCH5H increases only slightly by decreasing τ indicating that the density and compactness dependence in the SmB phase by changing the temperature is smaller. In comparison to this, increase is more pronounced for the SmA phase (BCH7CN). The

LC-state of BCH7CN is rather broad with 128 K and in particular in the nematic state (80 K).

The data given in Figure 3 demonstrate the increase of the order parameter in the nematic state by reducing the temperature. By comparing the homologous compounds BCH5H, BCH5F, BCH5Cl, BCH5Br the birefringence at $\tau = 0.96$ slightly increases in the given series indicating an increase of the order parameter S in the given sequence. This can be even demonstrated in Figure 3, where $n_{\|}^2 - n_{\perp}^2$ is presented.

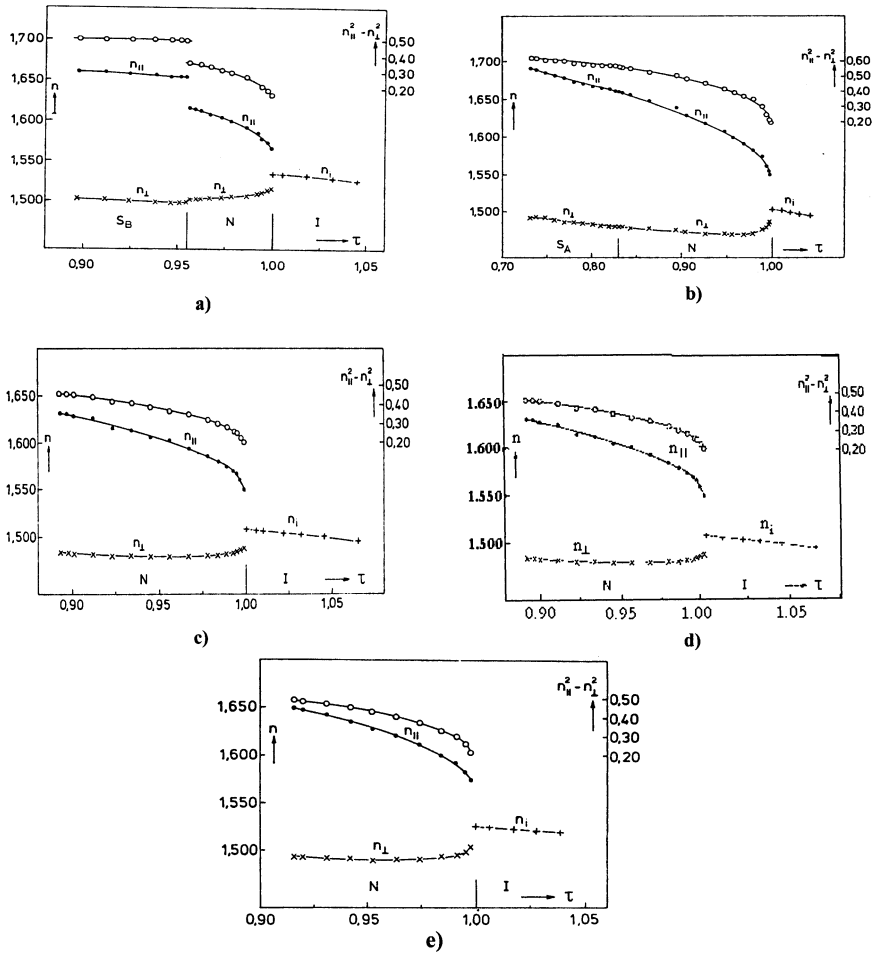

FIGURE 3 Dependence of the refractive indices on reduced temperature a) BCH50, b) BCH7CN, c) BCH5F, d) BCH5Cl, e) BCH5Br.

TABLE 3 Used Bond or Fragment Polarisabilities

Bonds	α_{xx}/A^3	$\alpha_{zz}/\text{Å}^3$
$C_{al}-C_{al}$	0,97	0,25
$C_{ar}-C_{ar}$	2,25	0,48
$C_{ar}-C_{al}$	1,40	0,30
C≡N	3,13	1,34
C−F	1,50	0,40
C−Cl	3,67	2,08
C−Br	5,04	2,88
C−H	0,82	0,60
C_6H_6	12,31	6,35
C_6H_{12}	11,17	9,75

The order parameter S was estimated using the Vuks method (Eq. 1) by calculating $\langle\Delta\alpha\rangle = \langle\alpha_{||}\rangle - \langle\alpha_{\perp}\rangle$. Because of the lack of molecular data, we calculated the molecular polarisability anisotropy by using the bond anisotropies presented in Table 3.

From this we could calculate $\Delta\alpha$ presented for the compounds under investigation in Table 4.

The values in Table 4 are reasonable. They can in principle compared with data quoted in [15]. By inspection of the data in Table 4 we can conclude

- In the halogen compounds, $\Delta\alpha$ increases in the sequence F, Cl, Br;
- The anisotropic polarisability is larger in the compounds with cyano end groups compared to ones with halogen end groups.

In Figure 4 and 5 we present the obtained order parameters calculated via (Eq. (5)) using the $\Delta\alpha$ value in Table 4 and the $\langle\Delta\alpha\rangle$ values based on $n_{||}$ and $n_{\perp}$ measurements (Eq. (1–3)). In Figure 4, the calculated order parameter S for BCH7CN as a function of reduced temperature is presented. S is slightly larger as the Maier-Saupe values, what is normal for p-CN

TABLE 4 Calculated Molecular Anisotropic Polarisability

Compounds	$\Delta\alpha/\text{Å}^3$
BCH50	18,5
BCH7CN	22,1
BCH5F	19,5
BCH5Cl	20,0
BCH5Br	20,5

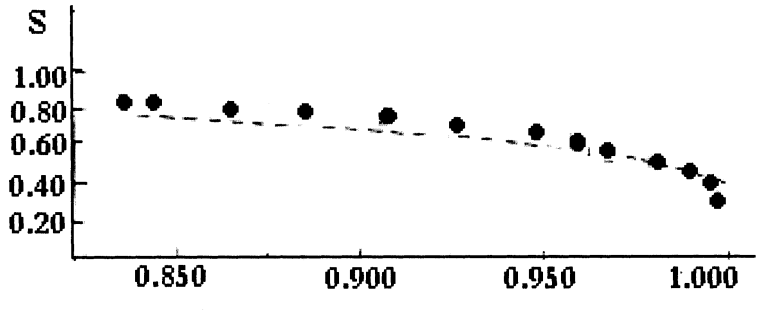

FIGURE 4 Order parameter S for BCH7CN as a function of reduced temperature; the broken line is calculated according to Maier-Saupe theory.

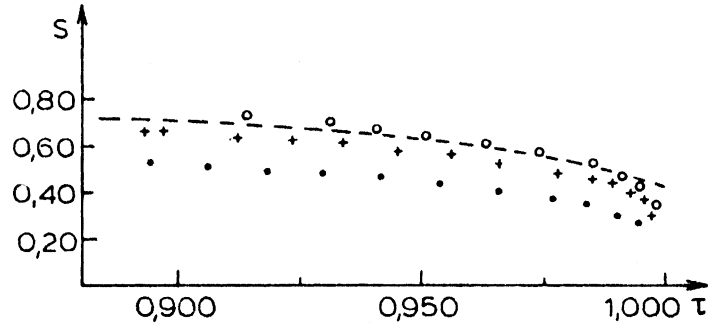

FIGURE 5 Order parameter S for BCH5F (●), BCH5Cl (+), and BCH5Br (°) as a function of the reduced temperature; the broken line is calculated according to Maier-Saupe theory.

containing LC compounds. It should be mentioned that because of the broad nematic range, the S-value reaches up to $S = 0.80$ at the phase transition to the SmA phase. The by this method obtained S data agree with the values obtained from magnetic anisotropies for the same compound BCH7CN [4]. In Figure 5 analogous data are presented for BCH5F, BCH5Cl, and BCH5Br. The order parameter for a given reduced temperature goes up in the series F < Cl < Br.

CONCLUSION

Densities and refractive indices were measured as function of temperature for the nematic and the isotropic state. It seems the expansion coefficient β

in nematic state reflect some degree of dipole interaction because there are smaller in the nematic state as in the isotropic state for compounds with a lateral dipole moment. The calculated order parameter based on refractive index data and the Vuks model on one side and bond and fragnent polarisabilities on the another side show some tendency to grow by increasing the anisotropic polarizabilities.

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