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Helical twisting power of laterally aryl substituted chiral mesogens

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The relationship between the helical twisting power (HTP) of cholesteric liquid crystals and the molecular structure of the chiral mesogens has been investigated. Rod-like mesogens are compared with analogues bearing a bulky lateral branch. Additionally, the HTP of induced cholesteric phases formed by chiral guest molecules in nematic host phases has been studied in terms of different molecular structures. The paper gives information on the influence of bulky lateral groups in mesogens on the HTP.

1. Introduction

Chiral guest compounds dissolved in a nematic host phase induce cholesteric phases. The strength of this chiral induction can be measured by the helical twisting power (HTP) [1]:

$$\delta = \left(\frac{dp^{-1}}{dx_G} \right)_{x_G \rightarrow 0} \quad (1)$$

where p is the pitch of the cholesteric phase in μm and x_G means the molar fraction of the solute. The HTP depends on the molecular structures of the guest as well as the host molecules [2-4]. However, knowledge of the relationship between twisting power and molecular structure is incomplete. In most cases, cholesteric phases have been induced in nematic host phases with rod-like mesogens consisting of chiral molecules of different structure [5, 6]. According to these results, larger values of the HTP can be observed if two-ring mesogens are mixed with chiral dopants of similar shape. The question arises as to what happens if the structure of the compounds deviates strongly from rod-like.

In this paper we investigate the effect of bulky lateral branches attached to the guest and/or the host molecules

on the magnitude of HTP. Substances of type I are rod-like mesogens, and in derivatives of type II, a substituted aromatic ring is connected by an odd-numbered spacer to the basic molecule. For this reason, many mixtures were prepared of compositions I + I, I + II and II + II. We also discuss the influence of the localization of the chiral centre that can be situated at both terminal positions of the basic mesogens, as well as in the lateral branch.

2. Experimental

The helical pitch of the cholesteric phase was measured using wedge-shaped samples, contained between a convex lens and a plane glass plate, by means of the resulting Cano lines [7]. With a polarizing microscope (Leitz) and a digital ocular micrometer (Leitz) the distance between concentric inclination lines was measured at different temperatures and different molar fractions of the chiral compounds in the nematic host phase. The screw sense of the cholesteric helix was determined by the shift of the interference lines in monochromatic light on the rotation of the analyser as described by Gerber [8].



Scheme 1

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The chemical structures and phase transitions of the nematic hosts and chiral guest molecules are listed in tables 1 and 2, respectively. The host compound HOAB (Eastman-Kodak) was carefully purified; the substance 8008 was synthesized accordingly to Deutscher *et al.* [9]. The nematic phase 3K was prepared accordingly to Ferguson [10]. The liquid crystals 3K1 [11] and 3K1-chi-1 [12] were synthesized by Weissflog. The synthesis of the other compounds will be published elsewhere. The purity of each compound was checked by thin-layer chromatography and ^1H NMR spectroscopy.

The transition temperatures were measured by differential scanning calorimetry (Perkin-Elmer DSC 7) and thermomicroscopy (polarizing optical microscope Nikon F-601M).

3. Results

In the following figures the reciprocal pitch p^{-1} of the induced cholesteric phases is given as a function of the molar fraction of the selected optically active compounds. The HTP was determined from the slope of the plots according to equation 1 at a temperature $T^* = T_{cl} - 5\text{ K}$, where T_{cl} is the clearing temperature.

The twisting effect of the chiral rod-like derivative 3K-chi (figure 1(a)) is comparable to that of the laterally branched mesogen 3K1-chi-5, containing the same basic mesogen 3K-chi (figure 1(b)). The influence of the chemical structure of the host substances (table 1) can be judged by the different slopes of the plots.

The HTPs of the compounds bearing the chiral centre in the lateral branch are illustrated in figure 2. Whereas

for the dopant 3K1-chi-1 the chiral centre is directly connected to the parent molecule, in 3K1-chi-1,4' the chiral centre is positioned at the end of the lateral branch. It should be emphasized that the same chiral amyl ester mesogens exhibit cholesteric structures with opposite helical screw sense.

The influence of two nematic host phases on the induced helical structure is shown in figure 3. Contrary to figures 1 and 2, in figure 3 the effect of different chiral substances (table 2) in nematic host phases consisting of the rod-like mesogen 3K (figure 3(a)) and the bulky branched mesogen 3K1 (figure 3(b)), is given.

The HTPs of all induced cholesteric phases under investigation are summarized in table 3, where the units of the HTP are μm^{-1} . The screw sense could be determined for the pure guest substances (d = right-handed, l = left-handed) and for the mixtures (no symbol means right-handed and minus denotes left-handed) in most cases. The helical screw senses of three chiral guest compounds are not given because no. 11 has a monotropic smectic A phase and no. 12 and no. 13 do not show liquid crystalline behaviour. Some mixtures could not be investigated because a perfect orientation of the samples could not be obtained.

4. Discussion

4.1. Structural effect of the cholesterogenic compounds

According to the theoretical treatment [1] based on the Goossens theory of cholesterics [3], the HTP can be given in terms of a molecular interaction parameter

Table 1. Host compounds.

| No. | Structure | Acronym | Transition temperature/ $^{\circ}\text{C}$ |
|-----|-----------|-----------|--|
| 1 | | HOAB | Cr 74.4 S _c 95.4 N 124.2 I |
| 2 | | 8008 | Cr 61.4 S _c 72.7 N 89.7 I |
| 3 | | 3K | Cr 123 S _c 129 N 195 I |
| 4 | | 3K1 | Cr 105 S _c 123 S _A 133 N 147 I |
| 5 | | 4K1 | Cr 133 S _c 165 N 194 I |
| 6 | | 4K1-rac-5 | Cr 118 S _c 140 N 159 I |

Table 2. Chiral guest molecules (the appropriate acronyms contain the abbreviation 'chi').

| No. | Structure | Acronym | Transition temperatures/ $^{\circ}$ C |
|-----|-----------|-------------|---------------------------------------|
| 7 | | 3K-chi | Cr 87 Ch 134 I |
| 8 | | 4K-chi | Cr 116 S _C 143 Ch 242 I |
| 9 | | 3KI-chi-1 | Cr 105 (Ch 81) I |
| 10 | | 3KI-chi-1,4 | Cr 84 S _C 91 Ch 111 I |
| 11 | | 3KI-chi-5 | Cr 121 (S _A 113) I |
| 12 | | 3KI-chi-2 | Cr 110 I |
| 13 | | 3KI-chi-2,5 | Cr 93 I |
| 14 | | 4KI-chi-5 | Cr 118 S _C 141 Ch 160 I |
| 15 | | CE2 | Cr 103 Ch 115.5 I |
| 16 | | CB | Cr 150.5 Ch 182 I |

as follows:

$$\delta = \left(\frac{dp^{-1}}{dx_G} \right)_{x_G \rightarrow 0} = \frac{1}{2\pi r_{ab}} \cdot \frac{B_{21}}{A_{22}} S_R(T) \quad (2)$$

B_{21} describes the dipole-quadrupole interaction of the chiral guest molecule (1) with its nematogenic neighbours (2), A_{22} is the anisotropy parameter of the polarizability of the nematic host phase and r_{ab} is the distance between two quasi-nematic layers. The rotational order parameter S_R has the expected value

$$S_R = \frac{3}{2} \langle \sin^2 \theta \cos 2\psi \rangle \quad (3)$$

as proposed by Vertogen and van der Meer [13] considering not only the rotational distribution around the molecular long axis by an angle ψ [1], but additionally

the fluctuations of the long axis with respect to the director (angle θ). Obviously, S_R is temperature dependent as it has been treated by introduction of an appropriate potential $U(\theta, \psi)$ [14]. Concerning the data for the guest molecules given in table 2, it is expected that their chemical structures, as well as the shapes of the molecules would play an important role in determining the HTP, especially by steric guest/host interaction. Surprisingly, the HTP values given in table 3 are rather low. Thus, some aspects of the relationship between the molecular structure and the HTP are discussed in the following text.

Rod-like chiral guest molecules such as 3K-chi and 4K-chi induce a rather small HTP in rod-like structured host phases such as HOAB, 8008 and 3K, as well as in host phases with laterally branched molecules (see figure 1(a) and table 3).

The twist effect of the rod-like chiral guest molecule

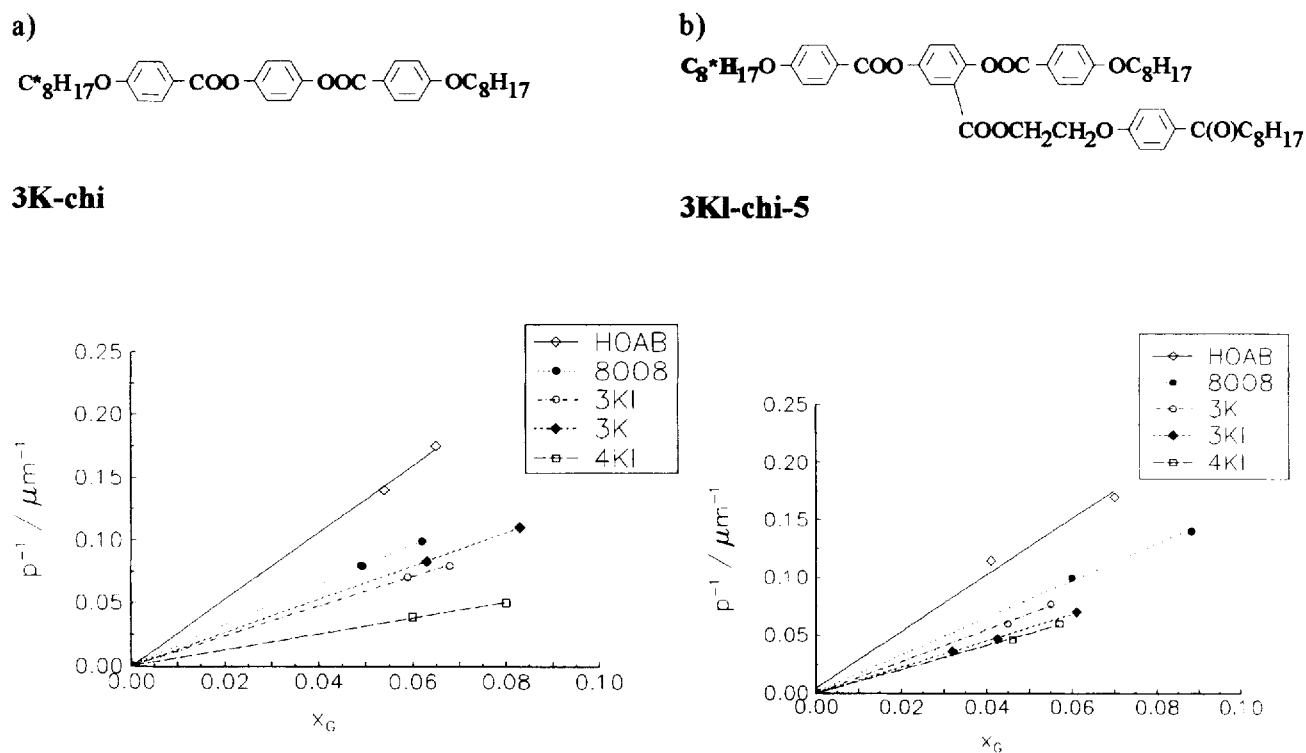


Figure 1. Reciprocal pitch vs. molar fraction of two chiral compounds: (a) 3K-chi; (b) 3KI-chi-5 in different host phases.

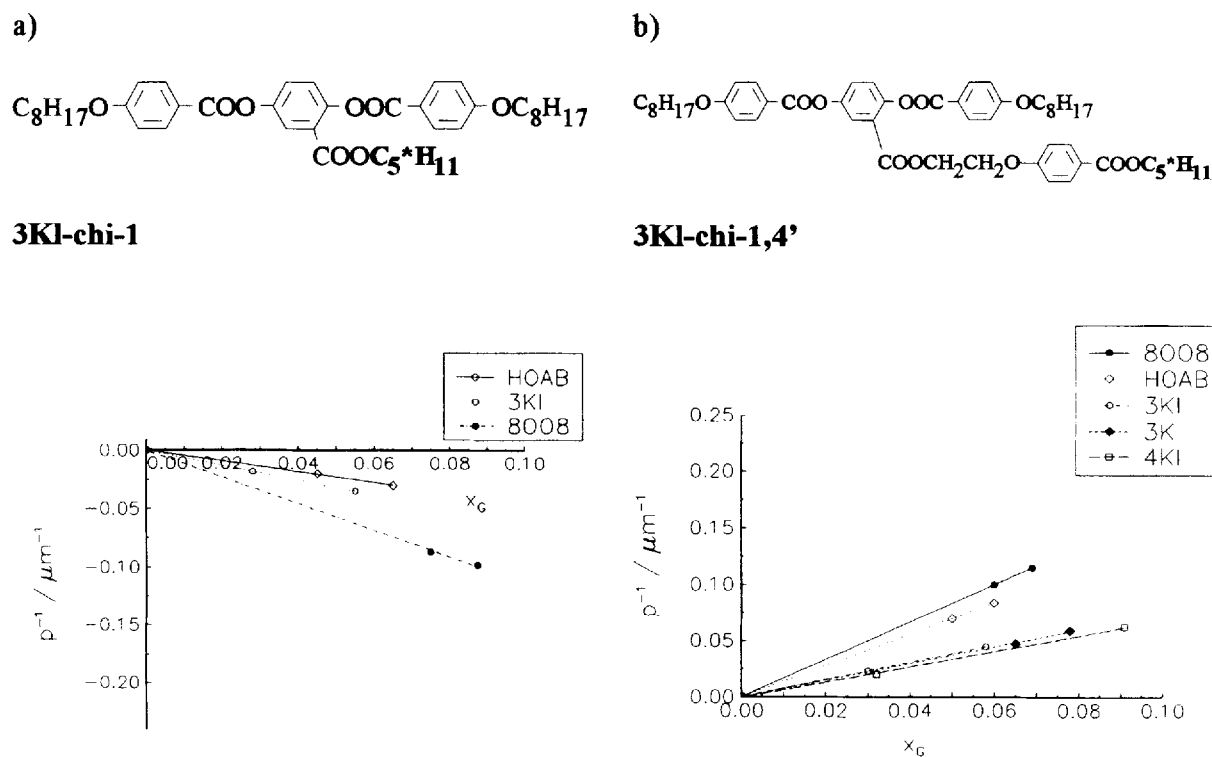
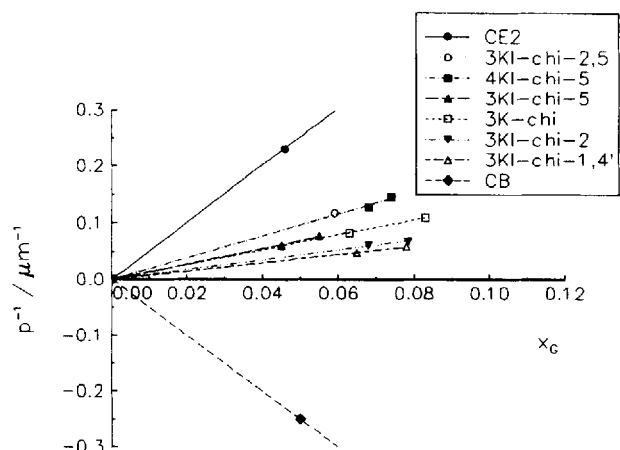
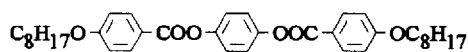


Figure 2. Reciprocal pitch vs. molar fraction of the chiral compounds bearing the same optically active centre in different host phases: (a) 3KI-chi-1; (b) 3KI-chi-1,4'.

a) 3K as nematic host phase



b) 3Kl as nematic host phase

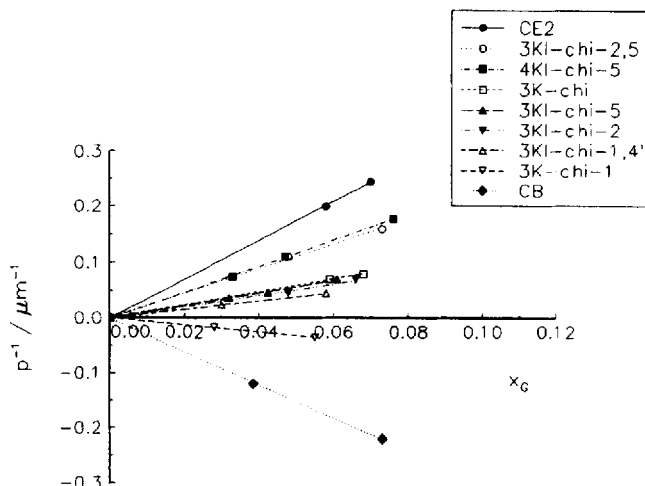
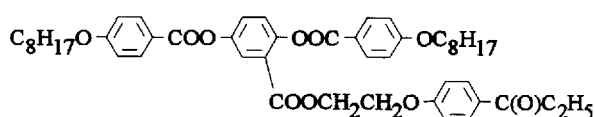


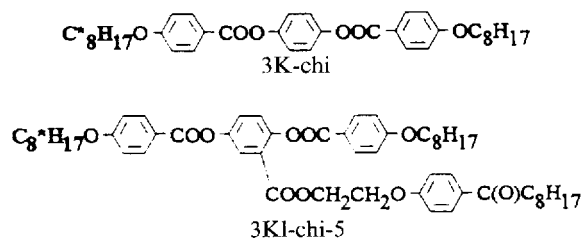
Figure 3. Influence of the chemical structure of chiral guest substances (table 2) on the induction of cholesteric structures in two nematic phases: (a) 3K; (b) 3Kl.

Table 3. Helical twisting power in μm^{-1} of chiral guest molecules nos 7–16 in different host phases.

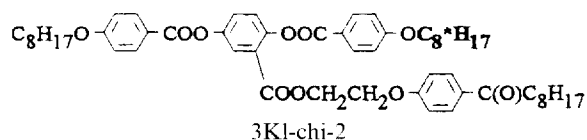
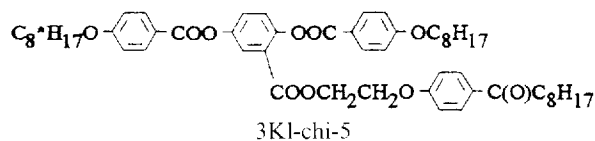
| No | Guest | Host | | | | | |
|----|------------------|------------|------|------|------|------|-----------|
| | | HOAB | 8008 | 3K | 3Kl | 4Kl | 4Kl-rac-5 |
| 7 | (d) 3K-chi | 2.7 | 1.6 | 1.2 | 1.3 | 0.6 | |
| 8 | (d) 4K-chi | 1.7 | 2.2 | — | 1.4 | 1.1 | |
| 9 | (l) 3Kl-chi-1 | −0.5 | −1.2 | — | −0.7 | — | |
| 10 | (d) 3Kl-chi-1,4' | 1.4 | 1.7 | 0.7 | 0.8 | 0.7 | |
| 11 | 3Kl-chi-5 | 2.3 | 1.6 | 1.4 | 1.1 | 1.0 | |
| 12 | 3Kl-chi-2 | 1.3 | — | 0.9 | 0.9 | — | |
| 13 | 3Kl-chi-2,5 | 2.9 | 2.2 | 2.0 | 2.0 | — | |
| 14 | (d) 4Kl-chi-5 | 2.2 | 2.8 | 1.9 | 2.0 | 1.1 | 1.37 |
| 15 | CE2 | — | — | 5.0 | 3.4 | — | |
| 16 | CB | −12.3 / 7/ | — | −5.1 | −2.9 | −1.8 | |

3K-chi (figure 1(a)) is surprisingly much the same as that of the laterally branched molecule 3Kl-chi-5 (figure 1(b)) which possesses the same basic mesogenic unit (cf. the HTP values in table 3, nos. 7 and 11). This result is quite unexpected, for it has been derived by a hard particle treatment [15] that the nematic orientational order parameter $\langle P_2 \rangle$ increases with the increasing molecular length-to-breadth ratio L_z/L_x . As has been demonstrated previously [1, 13, 14], a deviation from molecular cylindrical symmetry (as occurs in the laterally branched mesogens) by means of hard core interaction leads to a steeper rotational potential function $U(\theta, \psi)$, resulting in a higher value of the order parameter S_R .

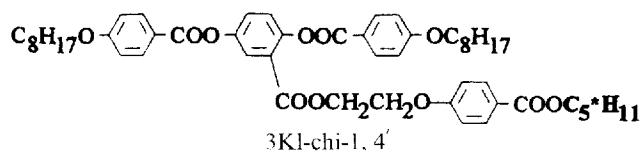
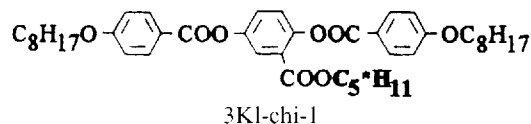
Consequently, laterally branched chiral dopants such as 3Kl-chi-5 have been expected to induce a higher HTP than unbranched dopants because of the larger sterical hindrance of rotation around their molecular long axes. Obviously, this is *not* the case (cf. table 3).



Another interesting result is that the position of the optically active centre in the laterally branched molecules influences the HTP (table 3). For example, the chiral substance 3Kl-chi-5 bearing the asymmetric carbon atom in the group in the 5-position of gentisic acid, shows a higher HTP than the isomeric compound 3Kl-chi-2 with the chiral octyloxybenzoate group in the 2-position.



This effect might be due to sterical factors. Comparison of molecular shapes with space filling models verified that 3Kl-chi-5 can interact more strongly with the nematic molecules. Probably, the intermolecular chirality transfer [16] in 3Kl-chi-2 is reduced compared with 3Kl-chi-5 because, in the former molecule, the chirality centre is shielded by the lateral group.



In the next step we compare the HTP of the guest compounds 3Kl-chi-1 and 3Kl-chi-1,4' (figures 2(a) and 2(b)) in which the chiral centres are both located within the lateral branch (see table 3, nos. 9 and 10). The HTP of 3Kl-chi-1 is somewhat smaller than that of 3Kl-chi-1,4' in the host phases 8008 and HOAB. The location of the chiral centre at the middle part of the basic mesogen in the former guest molecule prevents an optimal intermolecular chirality transfer [16] resulting in small HTP values. On the other hand, as the chiral centre at the end of the elongated lateral branch in 3Kl-chi-1,4' is not sterically shielded by the basic mesogen, the intermolecular chirality transfer is facilitated leading to a higher HTP. This situation is comparable with 3Kl-chi-5 with the chiral centre also located at a molecular end position, enabling an unshielded interaction with

the host molecules. Consequently, their HTP values are comparable.

A non-trivial result is the opposite helical screw sense of the pure compounds 3Kl-chi-1 and 3Kl-chi-1,4', despite the fact that their chiral centres are 2-methylbutyl ester groups of the same absolute configuration. This result demonstrates the role of molecular structure in determining intramolecular chirality transfer which in the very end governs the intermolecular chirality transfer [16]. Although Gray and McDonnell [17] have shown a relation between the absolute configuration and the screw sense in a certain class of biphenyl derivatives, the problem of the helical screw sense remains a theoretically open question. We also note that in the cholesteric phases induced by both compounds as guest molecules in different host phases (cf. table 3), the screw sense remains the same as in the pure compounds and no host phase induced helix inversion was observed.

Another interesting result is the additivity of the HTP values due to different chiral groups. In 3Kl-chi-2,5, two chiral centres are located at the two ends of the basic mesogen. The HTP value is approximately the sum of the HTP values of 3Kl-chi-2 and 3Kl-chi-5 bearing only one chiral centre at the opposite ends of the basic mesogen. An exception has been found in the host phase HOAB whose different behaviour is also noted in the following section. However, it has been demonstrated [18] for cholesterogenic molecules with more than one chiral centre that the twisting powers of individual chiral elements can be summed up to a macroscopic HTP if the chiral centres can be regarded as independent. This hypothesis is evidenced by the results given in table 3.

4.2. Influence of the host phases

According to equation (2), the nature of the nematic host phase is expected to influence the HTP by means of the parameter A_{22} which is proportional to the inverse value of δ . This relationship could be confirmed essentially by our results. As can be derived from the data in table 3, the following order of increasing HTP values of a given chiral guest has been observed for different nematic host phases:

$$8008 > \text{HOAB} > 3\text{K} > 3\text{Kl} > 4\text{Kl}.$$

Exceptions are the cholesteric phases induced by 3Kl-chi, 3Kl-chi, and 3Kl-chi-2,5 for which the sequences of 8008 and HOAB are interchanged. There is an increase in the polarizability anisotropy from 8008 and HOAB with only two phenyl groups to 4Kl with four. As the interaction parameter A_{22} of the host increases in the same order, the ranking of the HTP values given above follows straightforwardly from equation (2). HOAB with its strong NO dipole has a special position because of possible guest/host interactions of permanent dipoles.

We had expected that the influence of the length-to-breadth ratio L_z/L_x of the guest, as well as that of the host molecules on the HTP would be more pronounced as this ratio enhances the nematic order $\langle P_2 \rangle$ [15]. Although L_z/L_x of 3K is larger than that of 3Kl, the HTP values of the chiral laterally substituted guest molecules are approximately equal in these two host phases. Only for CE2 and for CB is the HTP larger in 3K than in 3Kl as expected. Solladie *et al.* [19] have pointed out that a more pronounced guest/host interaction takes place if guest and host molecules possess similar chemical structures which would lead to higher HTP values because of an improved intermolecular chirality transfer. This prediction is not verified by the present results, because the guest/host systems 3K-chi/3K, 3Kl-chi-5/4Kl and 4Kl-chi-5/4Kl-rac-5, respectively, do not exhibit remarkable HTP values. Generally, nematic host phases of laterally branched shape (type II) seem to be less twistable than rod-like ones (type I).

5. Summary

The helical pitch of rod-like (I) and laterally branched chiral mesogens (II) has been investigated for pure substances as well as for induced cholesteric phases. Generally, low values of the helical twisting power (HTP) have been found and the differences between the HTP of rod-like guest molecules and the branched derivatives are rather small. As the rotational distribution function with respect to the molecular long axis is expected to exhibit steeper minima in the case of the laterally branched molecules, our results lead to the conclusion that the rotational order parameter S_R does not play such an important role as predicted by the theory of Goossens [3, 13, 14].

However, it can be derived from our results that steric aspects influence the HTP in the laterally branched mesogens because the position of the chiral centre is of main importance. If the chiral centre is located in the middle part of the guest molecule, lower HTP values result than for molecules with a terminally located chiral centre. The reason for this result is a reduced intermolecular chirality transfer [16] because of steric shielding of the chiral centre by the branched group. The differences between the HTP of molecules with the chiral centre in the branch and at the terminal position of the basic mesogen can be understood in the same way.

Steric effects also govern the behaviour of the host

phases: those with laterally branched molecules are less twistable than those with rod-like ones. However, as expected from the theory of Goossens [3], a larger anisotropy of the host polarizability results in a higher parameter A_{22} , leading to smaller HTP values.

The prediction [19] that the guest/host interaction should be most effective if guest and host molecules are of similar structure cannot be verified by the present results: the HTP values do not exhibit large differences if both guest and host molecules are branched or rod-like or if branched (rod-like) guests interact with rod-like (branched) hosts.

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