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Synthesis and Properties of Chiral Dopants Synthesized on the Base of 2-methylbutanol and *l*–menthol

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Chiral dopants are optically active substances used in liquid crystal systems. We have investigated the helical twisting power and its temperature dependences for the systematic rows of optically active organic compounds synthesized on the base of 2-methylbutanol and *l*-menthol. The compounds differ by molecular, chemical and spatial structure. Correlation between the value of helical twisting power and molecular structure of chiral dopants is analyzed. The mesogenity of new chiral dopants is also discussed.

Keywords: chiral compounds, liquid crystals, *l*-menthol and 2-methylbutanol

INTRODUCTION

Induced chiral nematic (N*) mesophases obtained by dilution of some amount of non-steric chiral dopant (CD) in the nematic host have been exciting interest for a long time. Such mesophases possess the properties of cholesteric consisting of cholesterol derivatives[1,2]. The dilution of even a small amount of chiral organic compound in a nematic matrix results in the formation of supramolecular helical structure with helical pitch P[2]. Efficiency of the inducing helical ordering for a given nematic host is characterized by the value of helical twisting power β which is defined by the following expression:

$$\beta = (rPc)^{-1} \qquad (1)$$

where c is the concentration of optically active dopant in the nematic host and r is enantiomeric purity (taken for simplicity $r=1$).

The value of β of the CD as well as its twisting sense depends on a spatial structure, a type of chemical bonds and specific intermolecular interactions of CD with the nematic host. However the introduction of CD even in a small amount into nematic matrix not only induces the helical supramolecular structure, but more often results in a significant disordering of N* mesophase and as a consequence the depression of a clearing point occurs. This effect is practically inevitable because organic chiral compounds (especially those of the natural origin) have spatially distributed and branched structure with low molecular resemblance to the nematic molecules. This fact leads to the significant decrease of hidden mesogenity that indicates the influence of CD on temperature range of existing induced N* mesophase. In this connection the synthesis of effective CDs with high values of β and hidden mesogenity is always in the range of interest. However the correlation of molecular structure of chiral compounds and its helical twisting power has not yet studied well enough, though a big progress in studying this problem has been achieved due to the number of relevant papers and communications[2-5]. Here we investigate the correlation between molecular structure of CDs, helical twisting power and their influence on thermal stability of the induced N* phase for two systematic rows, i.e. derivatives of ℓ-menthol and 2-methylbutanol.

RESULTS AND DISCUSSION

One of the most accessible optically active substances of natural origin is ℓ-menthol. Due to this the investigations of its derivatives were carried out by the numerous scientists[1,6,7] and they were mainly connected with different modifications of ℓ-menthyl fragment. In this paper the system of bimenthyl

derivatives with non-modified l-menthyl fragment branched through a bridged construction (M) was chosen as the object of investigation. The chemical structure of such system is shown in Fig.1. After the modification of a bridge type by the variation of chemical bonds and the length of molecular fragments physical properties were then compared to those of menthyl derivatives.

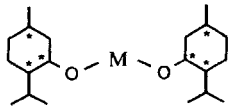
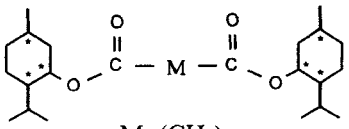
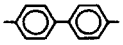
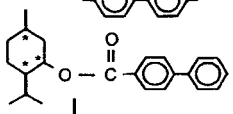
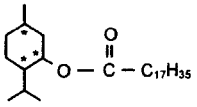


FIGURE 1 Chemical structure of bridged bimenthyl derivatives

The obtained results are displayed in Tab. I. Initially we synthesized the compounds with bridges of the aliphatic construction containing a different number n of $(CH_2)_n$ groups and varing in the range of n=1÷4. Elongation of a bridged aliphatic chain actually has led to a significant decrease of helical twisting power while thermal stability parameter A_{N^*} of N* mesophase has slightly improved. When the number of CH_2 groups reaches the value of n=4, the power of helical twisting for bimenthyl derivatives does not exceed the β of the analogous menthyl derivatives (see Tab I(g) (n=17)). Thus one can suppose the effect of flexibility in the bridged construction upon helical twisting. Indeed with the introduction of a rigid molecular fragment (see Tab.I(d),(e)), a significant growth of helical twisting power occurs. However the integrated effect on the values β for two substances (see Tab.I(e),(f)) doesn't differ so greatly as it was expected. For this reason we can think of the influence of specific intermolecular interactions between CD and nematic molecules. The investigations of helical twisting power for these two CDs in the nematic media LC807 (from NIOPIC) has shown somewhat stronger pronounced difference in twisting power and of the order of magnitude β=21,5±1,5 and β=12,2±0,7 for substances (e) and (f) respectively. One can also subtrace from Tab.I the increase of A_{N^*} parameter with anisometry growth of CD. From the curves of temperature dependences for the

TABLE I Helical twisting power (β) of *l*-menthol derivatives and their influence on thermal stability of the induced N^* mesophases in MBBA

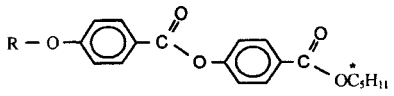
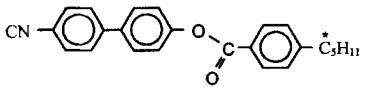
	Compound	β, $\mu m^{-1} \cdot wt\%^{-1}$	$T_{melt.}$ °C	A_{N^*}, degree/wt.%
	 M=$(CH_2)_n$			
a	n=1	-8.9±0.7	-	-3.35±0.08
b	n=3	-3.1±0.3	47	-2.85±0.07
c	n=4	-0.75±0.33	54	-2.98±0.07
d		-6.3±0.5	76	-5.78±0.09
e		-25.9±1.8	137	-2.5±0.07
f		-19.6±1.4	70	-2.88±0.07
g		<|0.64|	38	-2.03±0.07

helical pitch illustrated in Fig. 2(a) the behavior of low anisometry CDs is clearly observed in such substances the increase of a helical pitch with temperature is observed.

It is of importance to note that disordering of the induced N* mesophase in our experiments is accounted by parameter A_{N^*} that is defined as a slope of linear dependences of clearing temperature T_{cl} versus CD concentration in a nematic solvent[8]. As a nematic liquid crystals the 4-methoxybenzylidene-4'-(n-butylaniline) (MBBA) was used in our investigations. All helical twisting power measurements were carried out at room temperature in the stationary wedge cells using Cano-Granjean technique. The concentration of optically active additives was varied in the nematic host in the range of 0,5÷5 wt%.

One more systematic row studied belongs to the 2-methylbutanol derivatives. Because of sufficiently high molecular resemblance of synthesized chiral

TABLE II Helical twisting power (β) of 2-methylbuthanoles and their influence on thermal stability of the induced N^* mesophases in MBBA

	Compound	$\lvert\beta\rvert$, $\mu m^{-1}wt.\%^{-1}$	A_{N^*} degree/wt%
			
	$R=C_nH_{2n+1}$		
a	n=5	1.91±0.27	-0.44±0.04
b	n=6	2.12±0.27	-0.48±0.04
c	n=7	1.88±0.27	-0.48±0.04
d	n=8	2.26±0.28	-0.34±0.04
e	n=9	2.16±0.28	-0.18±0.04
f		0.72±0.36	+1.62±0.24

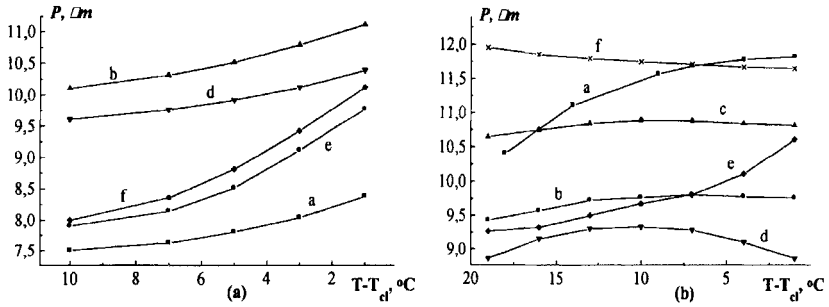


FIGURE 2 Temperature dependences of helical pitch of ℓ-menthol derivatives (a) and 2-methylbuthanoles (b)

compounds to the nematic molecules a significant improvement of a thermal stability due to a high value of hidden mesogenity was expected. For this reason five different substances of the same chemical structure but of different length of oxyalkyl chain were synthesized and subjected to testing. The basic physical data obtained with these substances are indicated in Tab. II. One can really observe the progress in the growth of the parameter A_{N^*} from the

obtained experimental results. However the column of β values indicates comparatively low magnitudes of helical twisting power for all substances. Moreover in this column one can also subtrace another interesting effect which lies in the oscillations of helical twisting power from one homologue to another within the homologous series. In the first approach we can note the influence of odd-even effects on inducing characteristics of optically active substances. The insignificant increase of helical twisting power magnitudes for even members in comparing to the odd members is detected. The experimental results obtained for the parameter A_{N^*} show that the elongation of oxyalkyl chain results in decreasing a disordering effect in the induced N* mesophase. When the anisometry of chiral molecules exceeds that of nematic molecules, the CD is even capable to impose the higher ordering than observed initially in a pure nematic state[8]. In this case the parameter of thermal stability becomes positive (see Tab. II(f)). The corresponding curves of temperature dependences for the helical pitch of the obtained CDs are shown in Fig. 2(b).

Acknowledgments

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