Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

The influence of molecular structure on helical twisting power of chiral azobenzene compounds

Md. Zahangir Alam[a]; Teppei Yoshioka[b]; Tomonari Ogata[b]; Takamasa Nonaka[b]; Seiji Kurihara[b]
[a] Department of Applied Chemistry and Chemical Technology, University of Dhaka, Dhaka 1000, Bangladesh [b] Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan

To cite this Article Alam, Md. Zahangir , Yoshioka, Teppei , Ogata, Tomonari , Nonaka, Takamasa and Kurihara, Seiji(2007) 'The influence of molecular structure on helical twisting power of chiral azobenzene compounds', Liquid Crystals, 34: 10, 1215 — 1219

To link to this Article: DOI: 10.1080/02678290701658241

URL: http://dx.doi.org/10.1080/02678290701658241

Liquid Crystals, Vol. 34, No. 10, October 2007, 1215–1219

The influence of molecular structure on helical twisting power of chiral azobenzene compounds

MD. ZAHANGIR ALAM*†, TEPPEI YOSHIOKA‡, TOMONARI OGATA‡, TAKAMASA NONAKA‡ and SEIJI KURIHARA‡

†Department of Applied Chemistry and Chemical Technology, University of Dhaka, Dhaka 1000, Bangladesh
‡Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

(*Received 2 June 2007; accepted in revised form 31 August 2007*)

Photochromic chiral azobenzene compounds with different molecular structures were synthesized, and a cholesteric phase was induced by mixing each chiral azobenzene compound with a non-photochromic chiral compound in a host nematic liquid crystal, E44. Helical pitch and, thus, helical twisting powers (HTP) of the chiral azobenzene compounds and the non-photochromic chiral compound were determined by Cano's wedge method. Molecular structures of the chiral azobenzene compounds were predicted by means of determining their molecular aspect ratio (*L*/*D*) with semiempirical molecular calculations (MOPAC at PM3 level). The effects of molecular structure on HTP of the chiral azobenzene compounds are studied in detail. Molecular structures of chiral azobenzene compounds significantly influence their HTPs.

1. Introduction

Chiral azobenzene compounds are of interest because they can induce the formation of cholesteric (Ch) phases in nematic hosts, and their helical pitch can be controlled by photoisomerization [1]. Ch phases are characterized by a helical packing of the mesogens with certain sign and pitch. Helical pitch, which is defined as the distance in a liquid crystal (LC) needed for the director of the individual mesogens to rotate through a full 360°, is a measure of chirality of the system. The optical properties of ChLCs depend, in part, on their pitch. Helical pitch can be altered by changing the structure of the LC itself or by admixing an auxiliary that changes the helical alignment of ChLC molecules [2–4]. When illuminated with white light, ChLCs reflect light of a certain wavelength dependent on helical pitch of the Ch phase [5]. According to well-established theories, the selective reflection wavelength (λ) of a Ch phase is governed by:

$$\lambda = nP, \tag{1}$$

where P is the helical pitch length and n is the refractive index of the LC.

Another important parameter of molecular design is the so-called helical twisting power (HTP), which is defined as the ability of a chiral compound to induce helical structure in a nematic host. HTP depends on the dipole–quadruple interactions of a chiral molecule with its nematogenic neighbours, on the anisotropy of the nematic host phase and on the order parameter [6]. HTP is related to helical pitch by [7]:

$$\mathrm{HTP} = 1/(Pc), \tag{2}$$

where c is the concentration of the chiral compound.

HTP is dependent on the molecular structure of a chiral compound. Therefore, when photochromic compounds, such as azobenzene, spiropyran, and so on, are dissolved in a Ch phase, photomodulation of macroscopic chirality can be induced by suitable light. Many studies have been reported on photochemical control of helical structures of ChLCs by means of photoisomerization of azobenzenes [8–11], menthone [12–15], spiropyrans [16], fulgides [17] and others [18]. In addition, there are some reports on the relationship between molecular structures and HTPs of chiral azobenzene compounds, and on the control of helical structures of chiral azobenzene compounds by *trans*→*cis* photoisomerization [19–21]. Photofatigue-resistance, the simplicity of the molecules and the ease of molecular structure modification makes azobenzene a very attractive phototrigger in cholesteric media. In this study, we discuss the influence of the structures of chiral azobenzene compounds on their HTPs.

---

*Corresponding author. Email: zahangir@univdhaka.edu

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701658241

2. Experimental

Photochromic chiral azobenzene compounds, **Azo-*n*** ($n=1$–8) and a non-photochromic chiral compound were synthesized according to the synthetic methods described elsewhere [22], and were characterized by IR, ^{1}H NMR and elemental analysis. A low molecular weight non-chiral nematic LC (E44) was purchased from Merck Co. Ltd. and was used as received. ChLCs were prepared by adding each chiral azobenzene compound, **Azo-*n***, and/or non-photochromic chiral compound to the host nematic LC, E44. The helical pitch of the ChLCs was determined by the Cano's wedge method with or without photoirradiation [23]. The HTPs of the chiral azobenzene compounds were calculated using equation (2).

3. Results and discussion

The structures of photochromic chiral azobenzene compounds (**Azo-n**) and the non-photochromic chiral compound are shown in figure 1. A Ch phase was induced by mixing each chiral azobenzene compound or non-photochromic chiral compound with E44. In such binary ChLC systems, consisting of a host nematic LC and a chiral compound, the HTP of the chiral compound can be evaluated by first determining the helical pitch by Cano's wedge method and then using equation (2). The azobenzene compounds are well known to show reversible photoisomerization by UV and visible light irradiation, respectively. It has been reported that the HTP of chiral azobenzene compounds can be changed by photoirradiation [19–21].

The UV–visible absorption spectra showed a strong absorption at 370 nm corresponding to the π–π* transition of the *trans*-azobenzene moiety and a weak absorption at 450 nm, which originates from the n–π* transition of the *cis*-azobenzene moiety. Upon UV irradiation, the absorbance at around 370 nm was decreased with an increase in the low-intensity band at around 450 nm due to *trans*→*cis* photoisomerization.

The photochromic chiral azobenzene compounds, **Azo-*n*** ($n=1$–6), differ only in their chiral substituents, as can be seen in figure 1. Their HTPs were decreased upon UV irradiation due to *trans*→*cis* photoisomerization of the chiral azobenzene molecules (table 1). *trans*-Azobenzene molecules are rod-like in their molecular structure, similar to that of LCs. Therefore, there is a strong interaction between the *trans*-chiral azobenzene molecule and constitutional LC, E44, and the influence of chirality becomes significant in yielding higher HTP. On the other hand, the *cis*-form of azobenzene molecule possesses bent molecular structure different from that of the LC, and the interaction between *cis*-chiral azobenzene molecules and rod-like LC, E44, becomes weak. Consequently, the HTP of the *cis*-form of chiral azobenzene molecule was lower than that of *trans*-form.

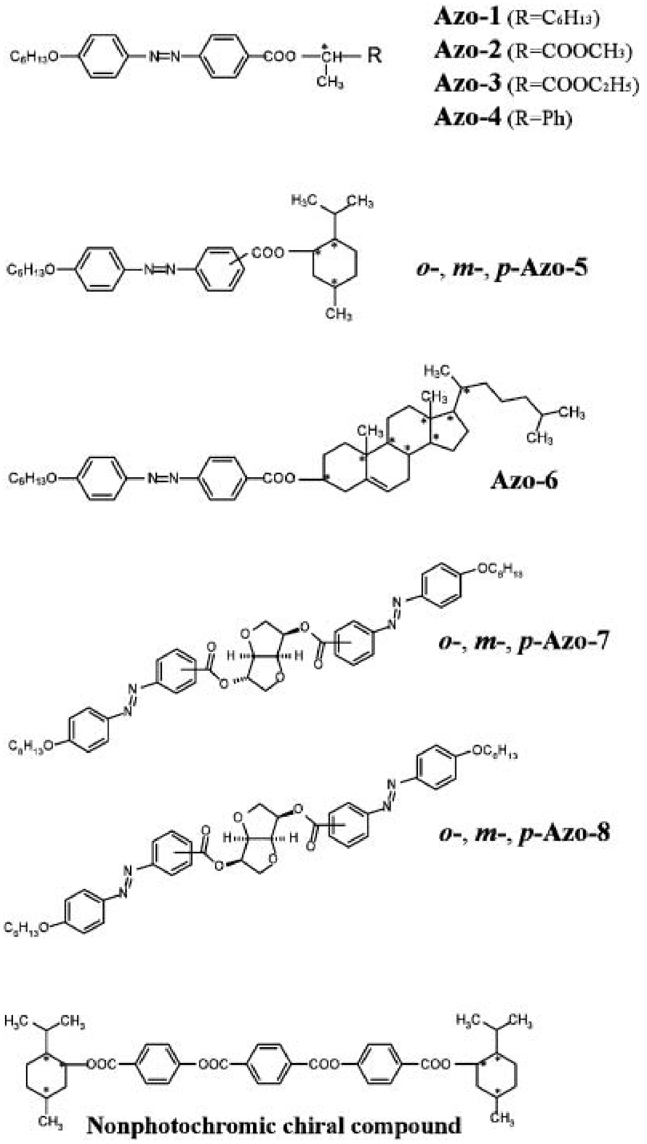

Figure 1. Structures of chiral azobenzene compounds and a non-photochromic compound used in this study.

Azo-7 and **Azo-8** contain two azobenzene moieties in a molecule. Three isomers, ***o***-, ***m***- and ***p*-Azo-7** and **Azo-8** were synthesized to investigate the influence of different combination position with an azobenzene group and a chiral group. The HTPs of **Azo-7** and **Azo-8** are also listed in table 1. Interestingly, ***m*-Azo-7** was found to show photochemical increase in HTP upon UV irradiation. The HTPs of the *trans*-form and the *cis*-form of ***m*-Azo-7** were $15.6\times10^2\,\mu\mathrm{m}^{-1}\,\mathrm{mol}^{-1}\,\mathrm{g(E44)}^{-1}$ and $79.4\times10^2\,\mu\mathrm{m}^{-1}\,\mathrm{mol}^{-1}\,\mathrm{g(E44)}^{-1}$, respectively.

Table 1. Helical twisting powers and molecular aspect ratio of chiral azobenzene compounds.

	HTP, $10^2 \mu m^{-1} mol^{-1}$ per g of-E44		Molecular aspect ratio, L/D	
Azo-n	HTP$_1$	HTP$_2$	*trans*-form	*cis*-form
Azo-1	32.0	20.9	5.0	1.3
Azo-2	28.9	12.6	5.1	1.2
Azo-3	36.6	19.9	5.4	1.2
Azo-4	68.7	36.3	4.5	1.3
o-Azo-5	44.3	12.7	2.6	1.7
m-Azo-5	48.4	11.1	3.3	1.1
p-Azo-5	49.0	10.8	3.9	1.1
Azo-6	10.7	10.5	5.2	1.4
o-Azo-7	4.6	4.5	2.1	3.3
m-Azo-7	15.6	79.4	2.5	4.5
p-Azo-7	202	48.9	5.4	1.4
o-Azo-8	59.9	34.5	3.0	2.2
m-Azo-8	129	20.5	4.3	1.8
p-Azo-8	141	16.5	4.4	1.6

HTP$_1$ – HTP of chiral azobenzene compounds before UV irradiation. HTP$_2$ – HTP of chiral azobenzene compounds after UV irradiation.

The molecular structures of the chiral azobenzene molecules, predicted by semiempirical molecular orbital calculation (MOPAC at PM3 level), help to explain the effects of molecular structure on photochemical changes to HTP. The models of **Azo-4**, **Azo-6**, **Azo-7** and **Azo-8** in the gaseous phase obtained by MOPAC calculation are shown in figures 2–4. As mentioned above, *cis*-forms of **Azo-4** and **Azo-6** with a single chiral substituent possess a bent shape. The *cis*-forms of ***p*-Azo-7** and ***p*-Azo-8** have a zigzag shape, rather than a bent shape, as shown in figure 3. On the other hand, ***m*-Azo-7** was found to show quite different molecular structures

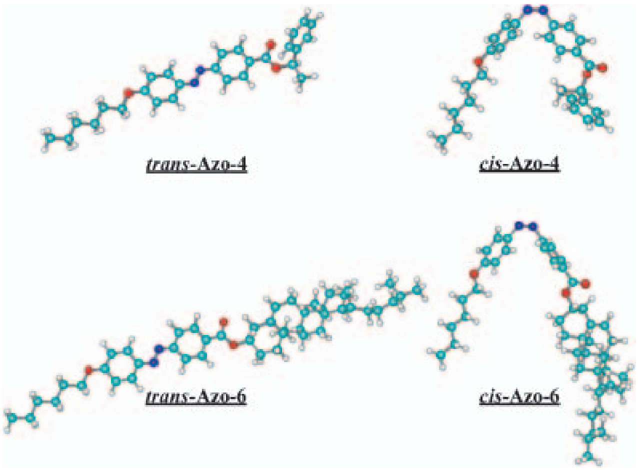

Figure 2. The most stable conformations for **Azo-4** and **Azo-6** predicted by semiempirical molecular orbital calculation (MOPAC at PM3 level (turquoise: C; grey: H; red: O; blue: N).

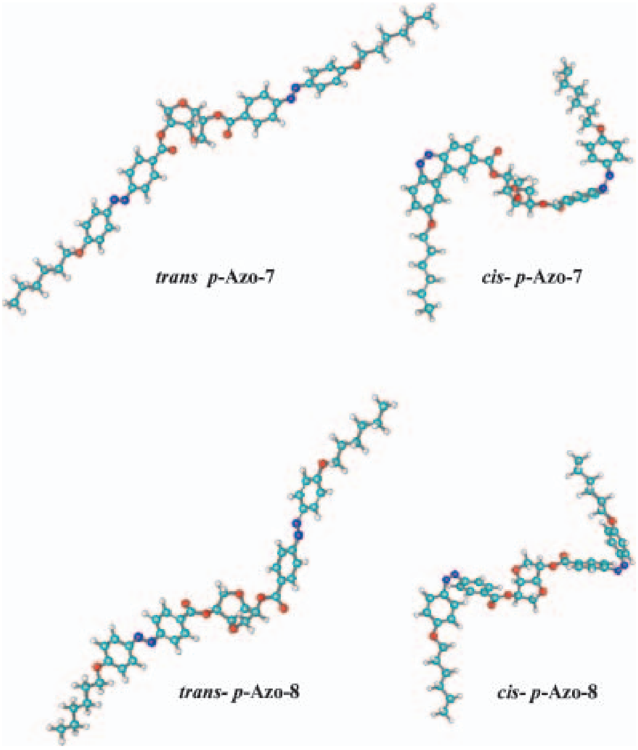

Figure 3. The most stable conformations for ***p*-Azo-7** and ***p*-Azo-8** predicted by semiempirical molecular orbital calculation (MOPAC at PM3 level (turquoise: C; grey: H; red: O; blue: N).

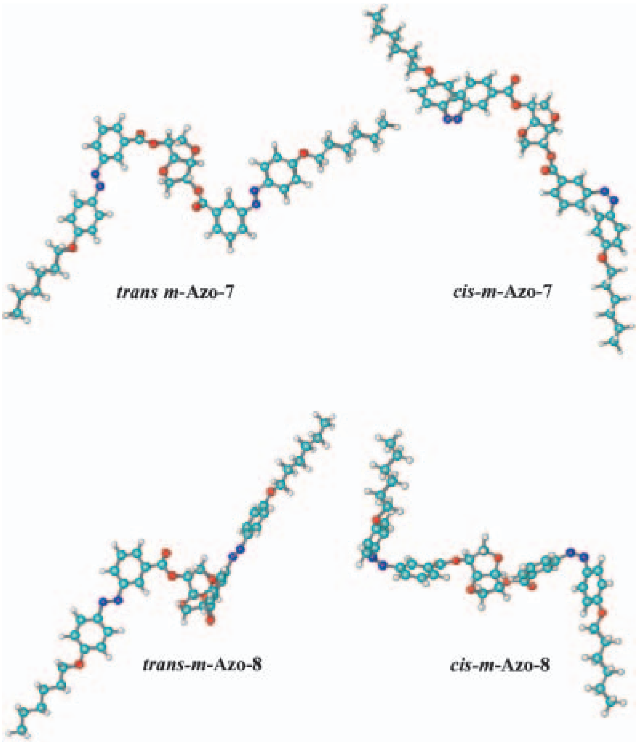

Figure 4. The most stable conformations for ***m*-Azo-7** and ***m*-Azo-8** predicted by semiempirical molecular orbital calculation (MOPAC at PM3 level (turquoise: C; grey: H; red: O; blue: N).

compared to others in its isomeric states. The *cis*-form of ***m*-Azo-7** was found to have a rod shape, whereas the *trans*-form has a bent shape. As a result, the HTP of ***cis*-*m*-Azo-7** is higher than that of ***trans*-*m*-Azo-7**.

It is well known that nematic and smectic phases are often observed for rod-like molecules [7]. In addition, it is reported that chiral compounds with LC-like structure show relatively higher twisting ability to induce helical structure [24]. Thus, in order to discuss the effects of structures on photochemical change in HTP of chiral azobenzene compounds in detail, the molecular length (L) and diameter (D) were estimated from the models obtained by MOPAC at PM3 level. The molecular aspect ratio, which is defined as the ratio of molecular length to molecular diameter, (L/D), of chiral azobenene molecules is a measure of anisotropy of molecular shapes, and reveals the structures of the molecules. A molecular aspect ratio equal to unity refers the molecule being spherical, whereas if $L/D>1$ for a chiral azobenzene molecule its structure is more rod-like.

The molecular aspect ratios of the chiral azobenzene compounds in their isomeric states are listed in table 1. The results reveal that the HTPs of chiral azobenzene compounds in both isomeric states depend on their molecular aspect ratio, with the exception of **Azo-6** and ***o*-Azo-7**. Molecules with larger L/D exhibited larger HTP, regardless of their isomeric states. However, the molecular aspect ratio as well as HTP of chiral azobenzene compounds is changed by *trans→cis* photoisomerization. Therefore, it is worthwhile to explore the effects of change in molecular shapes of chiral azobenzene molecules on their HTP in order to develop effective phototrigger for photomodulation of helical structure.

In figure 5, photochemical change in HTP, Δ(HTP) is plotted as a function of photochemical change in molecular aspect ratio, $\Delta(L/D)$; here $\Delta(\mathrm{HTP})=\mathrm{HTP}_{\mathrm{cis}}-\mathrm{HTP}_{\mathrm{trans}}$; $\Delta(L/D)=(L/D)_{\mathrm{cis}}-(L/D)_{\mathrm{trans}}$. It can be seen that the Δ(HTP) of a chiral azobenzene compound is dependent on its $\Delta(L/D)$. The relationship between Δ(HTP) and Δ(L/D) of the chiral azobenzene compounds can be classified into three groups: Group A (**Azo-1**, **Azo-2**, **Azo-3**, **Azo-5**); Group B (**Azo-4** and ***o*-**, ***m*-**, ***p*-Azo-5**); Group C (***o*-**, ***m*-**, ***p*-Azo-7**, ***o*-**, ***m*-**, ***p*-Azo-8**). Compounds with a single chiral group in the azobenzene core moiety fall in Groups A and B. Compounds in Group B have higher $\mathrm{HTP}_{\mathrm{trans}}$ as well as higher Δ(HTP) compared to the compounds in Group A. One of the reasons of the difference in Δ(HTP) of chiral azobenzene compounds may be due to the molecular size of the chiral groups. **Azo-6** with cholesterol group as chiral moiety showed much smaller Δ(HTP), although its $\Delta(L/D)$ was comparable to others.

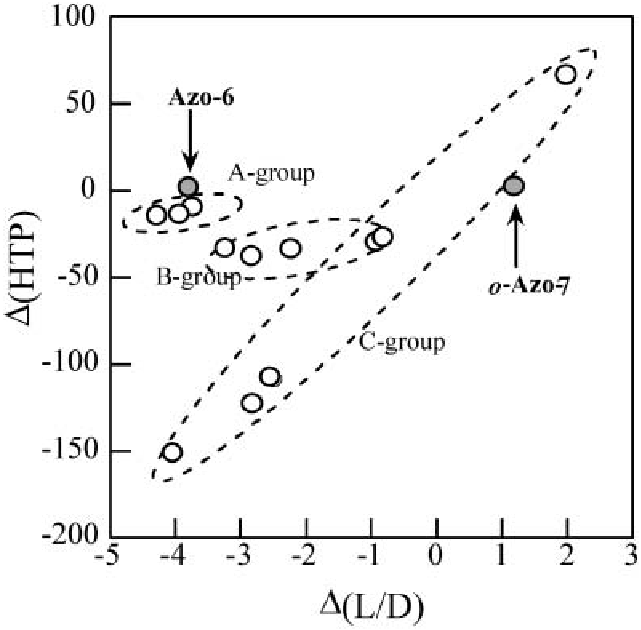

Figure 5. Δ(HTP) as a function of $\Delta(L/D)$ of chiral azobenzene compounds.

Figure 2 shows models of isomers of **Azo-4** and **Azo-6.** As can be seen in figure 2, their *trans*-forms are rod-like, whereas their *cis*-forms possess a bent structure. Comparison of the models reveals that the size of the bent part of **Azo-6** is much larger than that of **Azo-4,** because of the large molecular size of the cholesterol group. Therefore, it can be assumed that the *cis*-form of **Azo-6** can interact with nematogenic neighbours more efficiently than **Azo-4** and other azobenzene compounds having smaller chiral groups. Consequently, no significant difference between $\mathrm{HTP}_{\mathrm{trans}}$ and $\mathrm{HTP}_{\mathrm{cis}}$ of **Azo-6** was observed.

On the other hand, compounds in Group C showed the highest HTP and Δ(HTP), as shown in table 1 and figure 5. The introduction and isomerization of plural photochromic groups in a single chiral core is favourable for effective modulation of helical structure photochemically. The zigzag molecular shape of the compounds in Group C contributed to the larger photochemical change in HTP. However, ***o*-Azo-7** showed a little deviation from the plot of Group C. Figure 6 shows models of isomers of ***o*-Azo-7**. ***trans*-*o*-Azo-7**, which has a zigzag shape, yields a smaller HTP. In addition, the linearity of *cis*-form of ***o*-Azo-7** is much lower than that of ***m*-Azo-7** and other rod-shaped molecules, because of bonding at the ortho position. Consequently, ***o*-Azo-7** exhibits smaller HTP as well as smaller Δ(HTP) compared to the others. The results suggest that Δ(HTP) of chiral azobenzene compounds is related not only to the aspect ratio but also to the

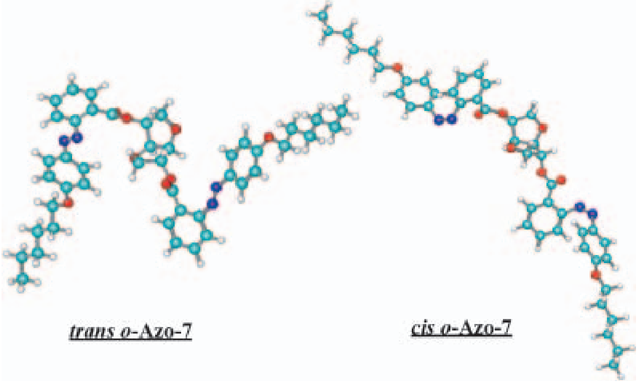

Figure 6. The most stable conformations for ***o*-Azo-7** predicted by semiempirical molecular orbital calculation (MOPAC at PM3 level (turquoise: C; grey: H; red: O; blue: N).

features of chiral groups, such as size, compactness, rigidity, linearity, planarity and so on.

3. Conclusion

A detailed investigation on effects of molecular structures on HTPs of chiral azobenzene compounds showed that HTPs and change in HTP by photoisomerization are acutely influenced by their molecular structures. The compactness of molecular structure of chiral azobenzene molecules plays a vital role on their HTP. MOPAC calculations demonstrated that ***m*-Azo-7** differed from other chiral azobenzene compounds in changing *L*/*D* through photoisomerization, contributing to the photochemical increase in HTP. The synthesized photochromic chiral azobenzene compounds and non-photochromic chiral compound may be used for the preparation of ChLC systems with reversibly controlled helical pitch. Thus, they may be useful in various high-performance optical devices.

References

[1] (a) D. Dunmar, K. Toniyama. *Handbook of Liquid Crystals*, **Vol. 1**, pp. 215–239, Wiley-VCS, Weinheim, (1998); (b) G. Meier. *Applications of Liquid Crystals*, pp. 1–21, Springer, Berlin (1975); (c) S. Chandrasekhar. *Liquid Crystals*, Cambridge University Press, Cambridge (1977).

[2] G. Gottarelli, M. Hibert, B. Samori, G. Solladie, G. Spada, R. Zimmermann. *J. Am. chem. Soc.*, **105**, 7318 (1983).

[3] G. Gottarelli, G. Spada. *Mol. Cryst. liq. Cryst.*, **123**, 377 (1985).

[4] G. Gottarelli, B. Samorei. *Tetrahedron*, **37**, 395 (1981).

[5] D.-K. Yang, X.-Y. Huang, Y.-M. Zhu. *Annu. Rev. Mater.*, **27** (1997).

[6] H. Finkelmann, H. Stegemeyer. *Bunsengs. Ber. Phys. Chem.*, **82**, 1302 (1978).

[7] P. de Gennes, J. Prost. *The Physics of Liquid Crystals*. Oxford Science Publications, Oxford (1993).

[8] E. Sackmann. *J. Am. chem. Soc*, **93**, 7088 (1971).

[9] H.-K. Lee, K. Doi, H. Harada, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda. *J. phys. Chem. B*, **104**, 7023 (2000).

[10] A.Y. Bobrovsky, N.I. Boiko, V.P. Shibaev, J. Springer. *Adv. Mater.*, **12**, 1180 (2000).

[11] M. Moriyama, S. Song, H. Matsuda, N. Tamaoki. *J. Mater. Chem.*, **4**, 1003 (2001).

[12] A.Y. Bobrovsky, N.I. Boiko, V.P. Shibaev. *Liq. Cryst.*, **25**, 679 (1998).

[13] A.Y. Bobrovsky, N.I. Boiko, V.P. Shibaev. *Liq. Cryst.*, **26**, 1749 (1999).

[14] M. Brehmer, J. Lub, P. van de Witte. *Adv. Mater.*, **10**, 1438 (1998).

[15] P. van de Witte, M. Brehmer, J. Lub. *J. Mater. Chem.*, **9**, 2087 (1999).

[16] A.Y. Bobrovsky, N.I. Boiko, V.P. Shibaev. *Adv. Mater.*, **11**, 1025 (1999).

[17] T. Sagisaka, Y. Yokoyama. *Bull. chem. Soc. Japan*, **73**, 191 (2000).

[18] B.L. Feringa, N.P.M. Huck, H.A. van Doren. *J. Am. chem. Soc.*, **117**, 9929 (1995).

[19] C. Ruslim, K. Ichimura. *Adv. Mater.*, **13**, 37 (2001).

[20] C. Ruslim, K. Ichimura. *Adv. Mater.*, **13**, 641 (2001).

[21] S. Kurihara, T. Yoshioka, T. Oagata, M.Z. Alam, T. Nonaka. *Liq. Cryst.*, **30**, 1219 (2003).

[22] T. Yoshioka, T. Ogata, T. Nonaka, M. Moritsugu, S.-N. Kim, S. Kurihara. *Adv. Mater.*, **17**, 1226 (2005).

[23] G. Solladie, R.G. Zimmermann. *Angew. Chem. Int. Ed.*, **23**, 348 (1984).

[24] G. Gottarelli, B. Samori, C. Fuganti, C. Graselli. *J. Am. chem. Soc.*, **103**, 471 (1981).