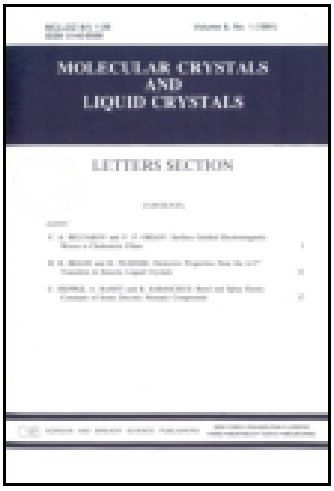

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Structural Analysis of Chiral Dopants in Nematic Systems by Example of Ether-Ester-Substituted 1,4:3,6-Dianhydrohexitols

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Structural Analysis of Chiral Dopants in Nematic Systems by Example of Ether-Ester-Substituted 1,4:3,6-Dianhydrohexitols

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Series of ether-ester-substituted 1,4:3,6-dianhydrohexitols were synthesized and studied as chiral dopants to nematics as compositions with 4′-pentyl-4-cyanobiphenyl. The most helical twisting power was found for bis-esters. Lesser values were found for mixed ether-esters with certain configuration. Other ethers and ether-esters revealed noticeably smaller values. Supramolecular peculiarities of such systems and their role in helical twisting are discussed.

Keywords Chiral dopant; helical twist; induced cholesterics; substituted 1,4:3,6-dianhydrohexitols

Introduction

Chiral nematic liquid crystals (N*-LC) possess properties of selective light reflection, high optical rotation, and circular dichroism, that is the base of their applications for different devices, first of all liquid crystalline displays [1, 2], holography [3, 4], LC lasers [5] and electro-active lenses [6]. Recently, new applications of N*-LC were proposed, such as a nematicon generation (nematicons are spatial solitons in a chiral nematic that lead to the formation of an optical waveguide by self-focusing of an optical beam) [7, 8], and UV-filters for medical applications and cosmetics [9]. Also, a new application area for liquid crystals arises – it is biomedical engineering for medical displays, sensors, actuators, and so on [10].

Chiral nematic mesophase (N*-LC) may be obtained by adding a chiral dopant (CD) to a nematic liquid crystal, which is achiral previously. CD induces helical supramolecular structure in a mesophase [11] that leads to the molecular chirality amplification [12].

The question of how molecular chirality is transferred into bulk chirality of the liquid crystalline phase is a fundamental problem. This phenomenon gives a unique potential to investigate the relationship between molecular structure, intermolecular interactions, and mesoscale organization [13].

The helical twisting power (HTP) defines the ability of a dopant to induce a helical submolecular structure in the LC host [14]. The HTP is the easiest of access characteristic

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of chirality transfer from single molecule to a macroscopic scale, both for measurements and modeling.

A collection of CDs that induce a great HTP (100 μm^{-1} and more) in nematics has been made [15–22]. Isosorbide (1,4:3,6-dianhydro-D-glucitol) esters refer to the most well-known chiral compounds with great HTP. Recently, a series of isosorbide esters with better solubility in LC hosts was synthesized [23, 24].

We have synthesized the new collection of 1,4:3,6-dianhydrohexitol ethers and mixed ether-esters, measured their HTP in 4,4′-pentylcyanobiphenyl (5CB), and revealed that only esters in this collection show a great twisting power (up to 176 μm^{-1}), not ethers. The HTP of mixed ether-esters varies from 0 μm^{-1} to 70 μm^{-1} depending on their structure.

In this paper, we undertook an attempt to interpret how molecular structure of CD had an effect on its HTP in nematics, and to reveal distinction in ester and ether groups in this aspect.

Theoretical Basis

The explicit connection between geometrical parameters of constituent molecules and HTP generated by them is absent in theoretical grounds. Theoretical physics [25, 26 and references therein] and molecular modeling of N*-LC [27–31] do not give a possibility to segregate fragments of molecules having influence on HTP. Whole shape of molecule and its surroundings define chirality transfer from chiral molecule to a mesophase.

Method of Wilson et al. [27, 28] uses the structure of CD molecule in molecular dynamics simulation. Surface chirality model (shape model earlier) [29–31] interprets a pitch of an induced cholesteric phase on the base of intermolecular interactions between a CD molecule and nematic solvent as an interplay between surface chirality and orientational order. In that model, HTP is proportional to the contraction of the two second-rank tensors $\mathbf{Q^{(2)}}$ and $\mathbf{S}$, where $\mathbf{Q^{(2)}}$ is the chirality tensor, and $\mathbf{S}$ is the ordering matrix for the solute molecule. With fundamental nature of this work, authors do not give a possibility to see what elements of molecular structure are the most responsible for the great HTP.

As shown in [30], macroscopic chirality is controlled by the difference in size of the substituents at the asymmetric carbon atom. However, the example of HTP difference in ester and ether derivatives of dianhydrohexitols shows that it is not enough.

We have made an attempt to understand the nature of difference in HTP for dianhydrohexitols in a nematic mesophase.

Experimental

Synthetic Procedure of Chiral Dopants

Procedures for synthesis of new CDs are given in Figure 1. Chemical shifts of protons (δ, ppm) in ^{1}H NMR spectra (DMSO-d_6) for newly synthesized compounds **3a-c, 4a-e, 5a-c, 6a-l, 7** are given in Table 1. Other analytical data are given in Table 2.

2-O-(aroyl)-5-O-(aryl)-1,4:3,6-dianhydro-D-sorbitol (3a, 3b)

I. 5-O-(4-cyanophenyl)-1,4:3,6-dianhydro-D-sorbitol
Sodium hydride (50%, 2 g; 41.6 mmol) was added to the solution of isosorbide (4.8 g; 33 mmol) in dry DMF (50 ml). The mixture was magnetically stirred at room temperature for 30 min, and 4-fluorobenzonitrile (4 g, 33 mmol) was added in small portions.

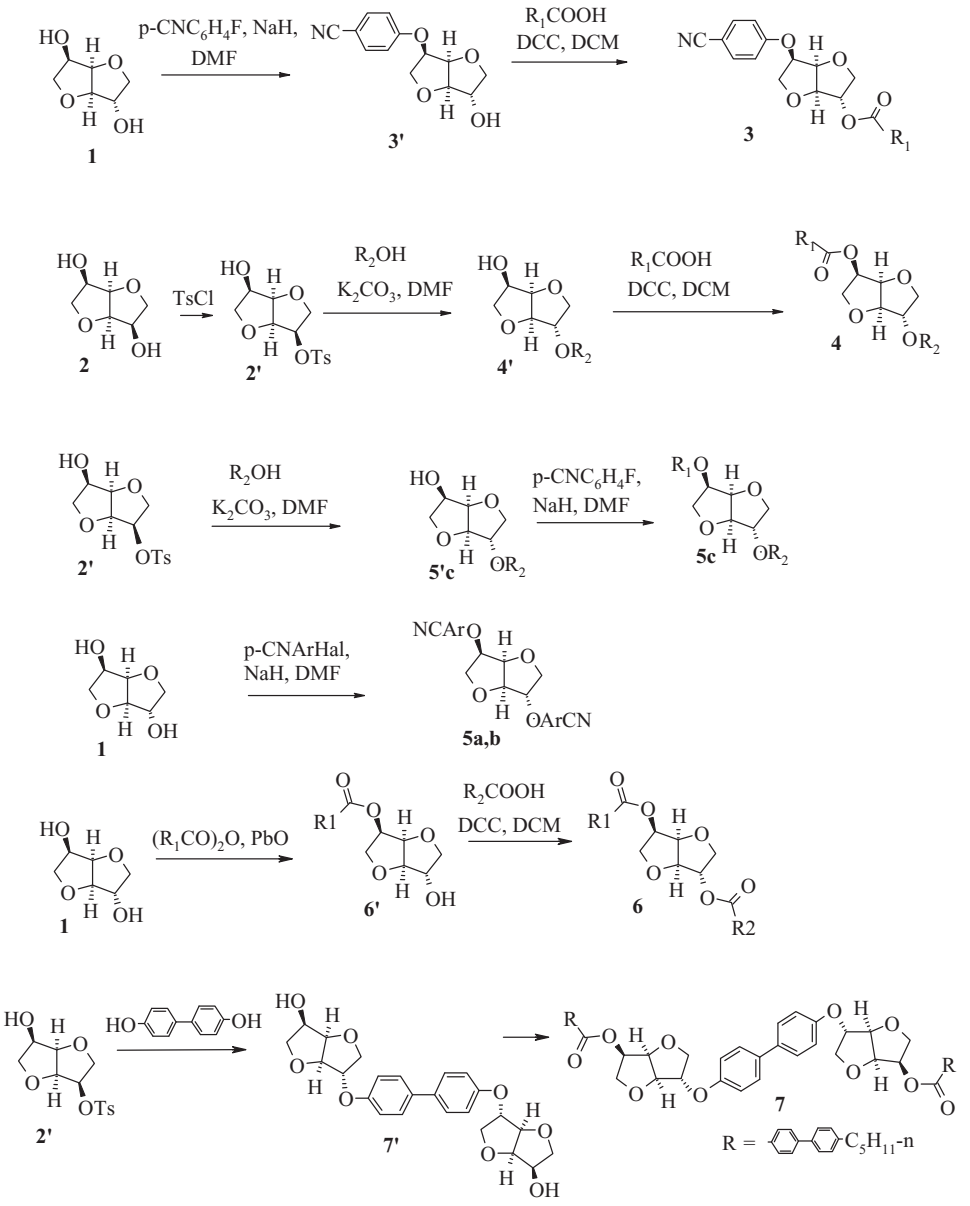

Figure 1. Synthetical methods for preparation of chiral dopants investigated.

Then the mixture was stirred at 55°C for 3 hr. After cooling, the reaction mixture was treated with a solution of ammonium chloride, and the product was extracted with ethylacetate. Then solvent was evaporated, and the residue was separated at silica gel (eluent DCM (dichloromethane) – ethylacetate). First fractions after crystallization from a cyclohexane–acetone mixture give 0.35 g of 2,5-*O,O*-Bis(4,4′-cyanophenyl)-1,4:3,6-dianhydro-D-sorbitol, that was identical to known product [32]. Fraction crystallization from more polar fractions gives 1.24 g of product with mp 138.5°C, $R_f = 0.18$ (toluene-ethanol), that differs from isomeric 2-O-(4-cyanophenyl)-1,4:3,6-dianhydro-D-sorbitol

Table 1. Chemical shifts of protons (δ, ppm) in ^{1}H NMR spectra (DMSO-d_6) for compounds **3–7**

Compounds	1-, 6-CH_2 (4H)	2-, 5-CH (2H)	3-CH	4-CH	Aryl	Alkyl
3a	3.98	5.37	4.66 (d)	4.98 (t)	8.24–7.34 (8H)	2.37 (s, 3H, Me)
3b	3.95	5.34; 5.09	4.65	5.09	7.99–7.20 (12H)	2.60 (t, 1H), 1.57 (1H), 1.25 (d, 10H), 0.83 (t, 3H)
3c	3.93(2H); 3.82–3.66(1H); 3.37(1H)	5.11(d); 4.11; 4.93 (d, J = 6.4 Hz, 1H, OH)	4.44 (br.s)	4.44 (br.s)	7.67 (2H); 6.95 (2H) 7.61 (d, 1H, −CH=) 6.48 (d, 1H, = CH−)	3.82–3.66 (3H)
4a	4.16 (d, 2H, H-6) 4.15–4.03 (2H, H-1)	5.46 (H-5); 4.90 (H-2)	4.71(d)	5.07	8.16–7.0 (16H)	3.86 (s, 3H, OMe), 2.34 (s, 3H, Me)
4b	4.14	5.39	4.76	4.96	7.82–7.0 (16H)	3.99 (2H, CH_2); 1.63 (6H, CH_2−CH_2); 1.32 (8H, CH_2−CH_2); 0.87 (6H, CH_3)
4c	4.35–3.97	5.38	4.35–3.97	4.55	8.04–6.91 (16H)	4.35–3.97 (2H); 2.56 (2H), 1.17 (22H)
4d	4.45 (2H); 4.00 (2H)	5.39 (d)	4.82	5.11	8.21–7.09 (16H)	2.78–2.50 (2H); 1.58 (3H); 1.27 (3H); 0.84 (t, 3H)
4e	4.56 (2H); 4.00 (2H)	5.38	4.99	4.99	7.80–7.09 (16H)	2.34 (s, 3H)
5c	4.53 (2H); 4.13–3.76 (2H)	5.02	4.92	4.92	7.83–6.84 (12H)	4.13–3.76 (2H); 1.82–1.53 (1H); 1.42 (1H); 1.28–1.04 (1H); 1.02–0.79 (4H)
6c	4.03–3.95	5.33 (dd), 5.29 (br.s)	4.58 (d)	4.95 (t)	7.90 (4H); 7.04 (4H)	3.82 (3H); 1.78–1.60 (2H); 1.50–1.12 (10H); 0.85 (t, 3H)
6d	3.96	5.36	4.62 (d)	4.98 (dd)	7.99 (d, 2H); 7.84 (4H); 7.63 (d, 2H); 7.32 (4H)	2.37 (s, 3H, Me); 2.34–2.27 (3H, Me)
6e	4.04–3.94	5.40–5.28 (1H); 4.98 (1H)	4.63	4.98 (t)	8.00–7.06 (12H)	3.83 (s, 3H, MeO); 2.36 (d, 3H, Me)
6g	4.01	5.56–5.28	4.63	5.02	8.19–7.30 (12H)	2.37 (s, 3H, Me)
6i	4.05–3.8	5.27 (br.s, 1H); 5.21 (t, 1H)	4.57	4.89	7.83–6.96 (8H);7.62 (d,−CH =); 6.53 (d, = CH-)	3.78 (s, 3H, MeO); 2.36 (s, 3H, Me)
6j	3.95	5.04	4.33	4.70	7.87–6.99 (16H)	3.84–3.62 (4H, CH_2CO); 2.28 (4H, CH_2-Ar); 1.75–1.25 (12H, CH_2)
6k	3.86	5.17	4.44 (br.s)	4.87	7.82–7.06 (16H)	4.87 (4H, OCH_2CO)
6l	4.21 (2H); 4.05 (2H)	5.56	4.85	5.18	8.59–7.57 (20H)	—
7	3.99 (8H)	5.40 (2H); 5.02–4.91(2H)	4.55 (2H)	5.02–4.91 (2H)	8.02–6.98 (24H)	1.68–1.47 (4H); 1.28 (s, 12H); 0.85 (m, 6H)

Note. Population is 1H, and multiplicity is m, unless it is marked otherwise.

Table 2. Analytical data for newly synthesized compounds

	Yield, %	Molecular formula	MW calculated	EIMS (m/z, M+)	Elemental analysis					
					Calculated, %			Found, %		
					C	H	Other	C	H	Other
3a	43	$C_{21}H_{19}F_3O_5$	408.38	408	61.76	4.69	F 13.96	61.63	4.51	F 13.60
3b	37	$C_{33}H_{35}NO_5$	525.65	525	75.41	6.71	N 2.66	75.25	6.64	N 2.48
3c	41	$C_{16}H_{18}O_6$	306.32	306	62.74	5.92	—	62.56	6.01	—
4a	46	$C_{33}H_{30}O_6$	522.60	522	75.84	5.79	—	75.90	5.59	—
4b	52	$C_{41}H_{46}O_6$	634.82	634	77.57	7.30	—	77.61	7.51	—
4c	41	$C_{43}H_{50}O_6$	662.87	662	77.92	7.60	—	77.73	7.79	—
4d	33	$C_{37}H_{35}NO_5$	573.70	573	77.46	6.15	N 2.44	77.28	6.39	N 2.27
4e	43	$C_{33}H_{27}NO_5$	517.59	517	76.58	5.26	N 2.71	76.49	5.31	N 2.90
5c	56	$C_{30}H_{29}NO_6$	499.57	499	72.13	5.85	N 2.80	72.25	5.91	N 2.59
6c	34	$C_{28}H_{34}O_8$	574.68	574	71.06	6.67	—	71.23	6.81	—
6d	67	$C_{28}H_{26}O_6$	458.52	458	73.35	5.72	—	73.24	5.57	—
6e	68	$C_{28}H_{26}O_7$	474.52	474	70.87	5.52	—	70.65	5.70	—
6f	56	$C_{31}H_{32}O_7$	516.60	516	72.08	6.24	—	72.20	6.07	—
6g	55	$C_{28}H_{23}F_3O_6$	512.49	512	65.62	4.52	F 11.12	65.46	4.66	F 10.89
6i	56	$C_{24}H_{24}O_7$	424.45	424	67.91	5.70	—	67.89	5.55	—
6j	63	$C_{42}H_{40}N_2O_6$	668.80	668						
6k	61	$C_{36}H_{28}N_2O_8$	616.63	616	70.12	4.58	N 4.54	70.23	4.44	N 4.30
6l	45	$C_{38}H_{28}N_2O_6$	608.66	608	74.99	4.64	N 4.60	75.05	4.56	N 4.37
7	47	$C_{60}H_{62}O_{10}$	943.16	943	76.41	6.63	—	76.58	6.79	—

[32], and which was identified by its spectroscopic data as *5-O-(4-cyanophenyl)-1,4:3,6-dianhydro-D-sorbitol*. Its characteristics are: ^{1}H NMR (500 MHz, DMSO) δ 7.73 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 5.16 (d, J 3.4 Hz, 1H, OH), 4.99 (m, 1H, H-5), 4.90 (m, 1H, H-4), 4.30 (d, J = 4.0 Hz, 1H, H-3), 4.09 (m, 1H, H-2), 3.90 (dd, J = 9.6, 5.7 Hz, 1H, H-6), 3.77 (dd, J = 9.5, 4.6 Hz, 1H, H-6), 3.67 (m, 1H, H-1), 3.61 (m, 1H, H-1).^{13}C NMR (126 MHz, DMSO) δ 162.00 (s), 134.48 (s), 119.60 (s), 116.46 (s), 103.34 (s), 89.14 (s), 80.48 (s), 77.98 (s), 75.69 (s), 75.32 (s), 70.74 (s). MW calculated 246.9, $C_{13}H_{13}NO_4$, EIMS (m/z, M+) 247.

II. The next stage (esterification with DCC and DMAP, Fig. 1) was carried out in known way with proper carboxylic acid [for example, 33]. The purification of the product was carried out by column chromatography on silica gel (eluent DCM). Yields 37%–43%. Product **3c** was obtained by esterification of isosorbide with 4-methoxycinnamic acid as above. Yield 41%.

2-O-(4-aryloxy)-5-O-(4-aryloyl)-1,4:3,6-dianhydro-D-sorbitol (4)

I. *Isomannide monotosylate* ***2′*** *was obtained like in [34].*

II. *Isosorbide monoether* ***4′***.

4-Alkoxy-4′-hydroxybiphenyl (AHB, 0.74 mmol) and 132 mg of potassium carbonate were added to 0.67 mmol of isomannide monotosylate **2′** in 10 ml of DMF. The mixture was stirred and boiled with reflux for 6–14 hr until AHB convert (control by TLC (silica gel, eluent dichloroethane)). Then the mixture was poured into an aqueous solution of hydrochloric acid with pH near 2, and the precipitate was filtered and washed with

an aqueous solution of Na_2CO_3. Product **4′**, which was identified by its spectroscopic data, was dried in air. Yields 70%–80%.

III. *Isosorbide ether-esters* were obtained by means of isosorbide monoether **4′** acylation with proper carboxylic acid, DCC and DMAP like the protocol used in [33]. The crude products were washed with propanol-2 and dried, and then they were purified by column chromatography on silica gel, eluent DCM.

1,4:3,6-Dianhydro-D-sorbityl-2,5-diether (5)

Bis-ethers of 1,4:3,6- dianhydro-D-sorbitol **5a** and **5b** were obtained like in [32]. The synthesis of product **5c** differs from above.

Intermediate 2-O-(4′-butoxydiphenyl)-1,4:3,6-dianhydro-D-sorbitol 5′c

4-Hydroxy-4′-butoxydiphenyl (250 mg, 1.1 mmol), isomannide monotosylate (330 mg, 1.1 mmol) were dissolved in DMF (10 ml) in 50 ml round-bottomed flask, and potash (260 mg, 2 mmol) was added. The resulting mixture was boiled at reflux for about 6 hr (control by TLC). Then the reaction mixture was diluted with water (100 ml), and obtained precipitate was filtered and washed three times with water. Yield 92%. mp 160°C. ^{1}H NMR (200 MHz, DMSO) δ 7.52 (dd, $J = 8.6$, 4.8 Hz, 4H), 6.98 (dd, $J = 8.6$, 6.4 Hz, 4H), 4.95 (d, $J = 6.2$ Hz, 1H, OH), 4.84 (s, 4H), 4.48 (d, $J = 2.5$ Hz, 2H), 4.23–3.84 (m, 4H), 3.85–3.66 (m, 1H), 3.40 (dd, $J = 15.4$, 7.8 Hz, 1H), 1.82–1.56 (m, 1H), 1.43 (dd, $J = 14.8$, 7.0 Hz, 1H), 0.92 (t, $J = 7.3$ Hz, 3H).

2-O-(4′-butoxydiphenyl-4-yl)-5-O-(4-cyanophenyl)-1,4:3,6-dianhydro-D-sorbitol (5c)

Compound **5′c** (0.32 mmol) was dissolved in dry DMF in round-bottomed flask at room temperature. Sodium hydride (50%, 1.3 mmol) was added to the stirred solution. When evolution of hydrogen finished, p-fluorobenzonitrile (0.35 mmol) was added slowly. The resulting mixture was heated at 75°C till reaction was finished (control by TLC). Then the reaction mixture was diluted with water, and obtained precipitate was filtered, washed with water and recrystallized from ethyl acetate. Yield 72%.

2-O-aroyl-5-O-aroyl′-1,4:3,6-dianhydro-D-sorbitol (6a-h)

I. *D-isosorbide monoester.*
DCM (25 ml) and PbO (0.01 g) were added to the mixture of D-isosorbide (0.29 g; 2 mmol) and substituted benzoic acid anhydride (3 mmol) (like in [35]). Then the mixture was stirred at room temperature up to full utilization of isosorbide (TLC control). Then resulting suspension was filtered, and the solvent was removed from the filtrate under reduced pressure. The residue was recrystallized from ethanol or ethylacetate. Products were identified by their spectroscopic data. Yields 27%–70%.

II. *Isosorbide bis-esters* were obtained by means of D-isosorbide monoesters acylation with proper carboxylic acid, DCC and DMAP like in [33]. Yields of **6** were 41%–78%.

bis-(5-(4′-n-pentylbiphenyl-4-oyl)-1,4:3,6-dianhydro-D-sorbit-2-yl)-(biphenyl-4,4′-diylbis(oxy)) (7)

*I. Bis-(1,4:3,6-dianhydro-D-sorbit-2-yl)-biphenyl-4,4′-diylbis(oxy) (**7′**)*
4,4′-Dihydroxydiphenyl (150 mg, 0.806 mmol) and isomannide monotosylate (510 mg, 1.7 mmol) were dissolved in DMF (25 ml). Then potash (270 mg, 1.96 mmol) was added, and the resulting mixture was heated at reflux for about 10 hr to 4,4′-dihydroxydiphenyl conversion (control by TLC). The reaction mixture was diluted with water (100 ml), and the precipitate obtained was filtered. Yield 84%.

*II. Bis-ester **7*** was obtained from **7′** by means of acylation with 4′-n-pentyldiphenyl-4-carboxylic acid, DCC and DMAP like the protocol used in [33].

Physical Measurements

Structures of newly synthesized compounds have been proved by nuclear magnetic resonance (^{1}H NMR) and mass spectrometry (MS). ^{1}H NMR spectra were measured in $CDCl_3$ and DMSO-d_6 using a Varian Mercury VX-200 NMR and Bruker AVANCE DRX 500 spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR spectra were measured using a Bruker AVANCE DRX 500 spectrometer at 125 MHz with $CDCl_3$ both as a solvent and the internal standard. Mass spectra were recorded on Varian 1200 L GS-MS. Elemental analyses were carried out using Element Analyzer EA-3000 (Eurovector, Italy). Measurements of melting points were carried in an open capillary with PTP(M) device (PO Khimlaborpribor, Klin, Russia).

Fabrication of CLC Cells and Measurements of HTP

Glass substrates were cleaned with a detergent solution and then rinsed with isopropyl alcohol and acetone. One percent water solution of polyvinyl alcohol was used for LC alignment layer formation (for a planar orientation of LC molecules) by spin-coating with postheating at 120°C–130°C for 30 min. After cooling to room temperature, its surface was rubbed with a velvet cloth perpendicular to wedge gradient and coated with LC composition between two glasses.

Values of the induced helical pitch, p, were measured by the conventional Grandjean–Cano wedge method as described in [36] using a PZO polarizing microscope (Warszawa, Poland) equipped with a heating stage with an accuracy of temperature measurement of 0.5°C. For all CD, the enantiomeric purity r was about 1 (0.98 ± 0.01). The CD concentration in N* systems on the base of 5CB was taken at about 0.25 mol%–5 mol%. The Adams–Haas equation [37] was used for the identification of the helix handedness in N* systems under study.

Computations

Quantum-chemical computations of equilibrium geometry of CD have been made with AM1 and PM6 [38] MOPAC2009 Package by James J. P. Stewart [39].

Results and Discussion

Helical Twisting Power of New Chiral Dopants and Its Connection with Peculiarities of Their Molecular Structure

The HTP of N*-LCs, HTP, and a temperature gradient of a helical pitch, *dP*/*dT* values, obtained for systems on the base of 5CB and CDs **3–7** are listed in Table 3.

As can be seen from Table 3, the highest HTP values of 70 μm^{-1}–176 μm^{-1} were obtained for CD **6** with two ester groups except **6j** and **6k** (HTP of 22 μm^{-1}–24 μm^{-1}) with four-methylene spacers that separate two rigid fragments. Thereby, non-rigid fragment (spacer) introduction in a CD structure considerably decreases HTP value. Chirality is connected with a rigid core unit in the structures of CDs that induce a great HTP in nematics (binaphthyl derivatives [16], (α,α,α',α'-tetraaryl-1,3-dioxolan-4,5-dimethanol derivatives (Taddols) [17], 2,6,9-trioxabicyclo[3.3.1]nonanes [18], esters of 1,4:3,6-dianhydrohexitols [19–21]). Mesogenic functionalization provides a considerable increase in HTP [40], probably, due to the extension of CD's rigid part and essential increase in interaction of a CD molecule with host.

Interestingly, though ester groups COO separate rigid fragments in isosorbide esters **6a-i**, it does not inhibit obtaining a great HTP. Ester group seems to be non-rigid because of probable rotation about an ordinary C–O bond.

A connection of rigid fragments by means of ester group produces quite tough immobilization of the propeller-shaped dianhydrohexitol core, as can be seen from potential energy

Table 3. Comparison of helical twisting power (HTP, μm^{-1}) between several types of CD **3–7** in nematic 4-pentyl-4′-cyanobiphenyl (5CB)

CC	R1	R2	HTP, μm^{-1} (C in mol%)	dP/dT, μm/degree
3a	4-$CF_3C_6H_4$	4-NC-C_6H_4	+35.21 ± 1.33	0.016 ± 0.004
3b	4-(4-n-$C_7H_{15}C_6H_4$)C_6H_4	4-NC-C_6H_4	+70.11 ± 0.84	−0.006 ± 0.006
3c	4-$CH_3OC_6H_4CH{=}CH$	H	0.6 ± 0.30	7.62 ± 6.12
4a	4-(4-$CH_3C_6H_4$)C_6H_4	4-(4-$CH_3OC_6H_4$)C_6H_4	+8.38 ± 0.27	precipitate
4b	4-(4-n-$C_5H_{11}C_6H_4$)C_6H_4	4-(4-n-$C_5H_{11}OC_6H_4$)C_6H_4	−6.96 ± 0.25	−0.10 ± 0.03
4c	4-(4-n-$C_8H_{17}C_6H_4$)C_6H_4	4-(4-n-$C_4H_9OC_6H_4$)C_6H_4	−9.22 ± 0.27	−0.16 ± 0.05
4d	4-(4-n-$C_5H_{11}C_6H_4$)C_6H_4	4-(4-NCC_6H_4)C_6H_4	0.6 ± 1.33	—
4e	4-(4-n-$CH_3C_6H_4$)C_6H_4	4-(4-NCC_6H_4)C_6H_4	−4.24 ± 0.45	−0.12 ± 0.01
5a	4-NC-C_6H_4	4-NC-C_6H_4	+12.49 ± 0.33	−0.017 ± 0.003
5b	2-(5-NC-Pyridinyl)	2-(5-NC-Pyridinyl)	+9.99 ± 0.46	0.122 ± 0.001
5c	4-NC-C_6H_4	4-(4-n-$C_4H_9C_6H_4$)C_6H_4	+10.16 ± 0.40	−0.17 ± 0.01
6a	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	+70.03 ± 1.05	0.004 ± 0.002
6b	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	+72.94 ± 3.77	−0.010 ± 0.004
6c	4-$CH_3OC_6H_4$	4-n-$C_7H_{15}OC_6H_4$	+95.68 ± 2.03	−0.003 ± 0.001
6d	4-$CH_3C_6H_4$	4-(4-$CH_3C_6H_4$)C_6H_4	+119.22 ± 0.24	−0.01 ± 0.001
6e	4-$CH_3OC_6H_4$	4-(4-$CH_3C_6H_4$)C_6H_4	+112.05 ± 3.09	−0.014 ± 0.002
6f	4-$CH_3OC_6H_4$	4-(4-n-$C_4H_9C_6H_4$)C_6H_4	+110.23 ± 1.22	−0.012 ± 0.001
6g	4-$CF_3C_6H_4$	4-(4-$CH_3C_6H_4$)C_6H_4	+107.25 ± 0.61	−0.008 ± 0.001
6h	4-(4-$CH_3C_6H_4$)C_6H_4	4-(4-$CH_3C_6H_4$)C_6H_4	+176.56 ± 4.54	−0.01 ± 0.001
6i	4-$CH_3OC_6H_4CH{=}CH$	4-$CH_3C_6H_4$	+71.66 ± 1.04	−0.01 ± 0.003
6j	4-(4-NC-C_6H_4)C_6H_4-$(CH_2)_4$-n	4-(4-NC-C_6H_4)C_6H_4-$(CH_2)_4$-n	+24.22 ± 0.39	0.101 ± 0.007
6k	4-(4-NC-C_6H_4)C_6H_4-OCH_2	4-(4-NC-C_6H_4)C_6H_4-OCH_2	+21.67 ± 0.20	0.084 ± 0.005
6l	4-(2-Ph-Quinolinyl)	4-(2-Ph-Quinolinyl)	−3.92 ± 0.58	1.48 ± 0.14
7	—	—	−27.49 ± 0.79	−0.18 ± 0.03

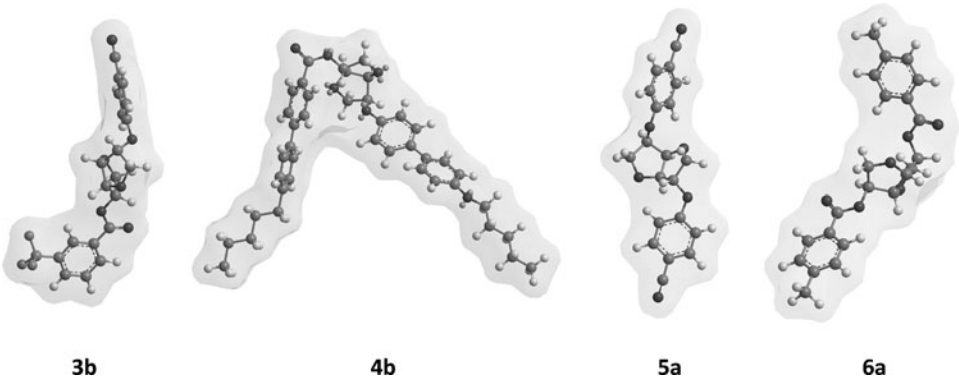

Figure 2. Molecular shape for ether-esters of 1,4:3,6-dianhydrohexitol **3b** and **4b,** ether **5a** and ester **6a** obtained by quantum-chemical energy minimization.

curve for rotation about CO group in those groups and adjacent to them. These curves have the narrowest minima as compared with rotation about CO bond in ethers, whether binding with dianhydrohexitol core or aryl substituent. Also, rotation about CO bond in esters changes little the shape of molecules while in ethers by rotation the shape of molecules changes considerably. Rigid fragment in a chiral molecule is a guide for nematic solvent molecules that transfer bend of the shape of chiral molecule to its molecular environment. Similar conception was proposed in modeling the interactions between a dichiral molecule and host one. A twist interaction between the binaphthyl group and a host molecule there was assumed to be organized by the core–core interaction [41].

As could be seen from Table 3, HTP of ethers of 1,4:3,6-dianhydrohexitols **5** is considerably less than esters **6** (absolute HTP 10 μm^{-1}–12 μm^{-1} for compounds **5a-c** and 70 μm^{-1}–176 μm^{-1} for compounds **6a-h**). In both cases, substituents in ethers and esters are rigid or have a lengthy rigid part adjacent with dianhydrohexitol core (4-NC-C_6H_4, 2-(5-NC-Pyridinyl), 4-RC_6H_4, 4-ROC_6H_4, 4-(4′-RC_6H_4)C_6H_4, where R is alkyl or CF_3 group). But according to quantum-chemical modeling (AM1, PM6), obtained shape is almost rod-like in the case of ethers **5** as opposed to esters **6** where shape is propeller-like (Figure 2).

It should be noted that quantum-chemical modeling describes the conformations of dianhydrohexitol core like the result of X-ray analysis [42].

The lowest HTP values were observed when CDs were mixed ether-esters (compounds **4a-e**), where substituent in 2 position is bound by the use of exocyclic ether group and substituent in 5 position by the use of endocyclic ester one (absolute HTP of 0.6 μm^{-1}–9.2 μm^{-1}). In this case, substituents in both cyclopentane rings are arranged in this way, so that chiral fragment (dianhydrohexitol core) appears almost completely shaded, and its influence on nematic solvent molecules is hindered. However, HTP values of compounds **3b-c** were rather great (35.2 μm^{-1}–70.1 μm^{-1}). In this case, substituent in 5 position is bound by the use of endocyclic ether group, and substituent in 2 position by the use of exocyclic ester one, and the shape of molecule is propeller-like as for compound **6** with the greatest HTP in examined case.

Low values of HTP for bis-esters of iditol [19] also may be accounted for their drawn rod-like shape.

The results observed speak in favor of surface chirality model [29–31] correctness with conformational mobility accounting [43].

Conclusion

We have synthesized series of 1,4:3,6-dianhydrohexitol ethers, esters, mixed ether-esters, and have investigated their HTP and thermal dependence of the helical pitch in a nematic solvent (4,4′-pentylcyanobiphenyl). The most HTP has been found for bis-esters **6**. Some less HTP values have been found for mixed ether-esters with certain configuration **3** with ester substituent in 2 positions and ether substituent in 5 positions. The lowest HTP values were observed when CDs were mixed ether-esters (compounds **4a-e**) with ether substituent in 2 positions and ester substituent in 5 positions. Bis-ethers **5** have some more values of HTP. The reason for preference of ester bridge group against ether one in molecular structures for HTP generation is lesser conformational mobility of structures with ester group.

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