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High birefringence bistolane liquid crystals: synthesis and properties†

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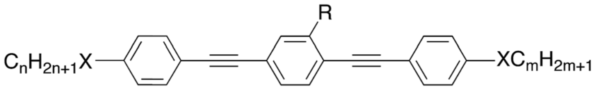
Twenty liquid crystals both symmetrical and non-symmetrical bistolanes with terminal alkyl, alkoxy and alkylsulfanyl chain and lateral methyl or ethyl group have been synthesized *via* Sonogashira cross-coupling and their mesomorphic properties have been studied. Most compounds exhibit an enantiotropic nematic phase in a broad temperature range (>40 °C). Optical properties of selected compounds have been investigated. They exhibit a high value of birefringence (>0.4).

1 Introduction

Liquid crystal materials that could be useful in applications should exhibit a low melting point, small melting enthalpy and broad temperature range for the liquid crystalline phase. Nematic liquid crystals having high birefringence (Δn) are especially attractive for various applications,[1] such as display devices[2–8] (*e.g.* scattering cholesteric[9] or scattering polymer-dispersed liquid crystals, PDLC systems[10,11]), devices working in the infrared range.[12–14] In recent years LCs have been found to be promising materials that can achieve high efficiency for microwave devices such as switchable phase shifters,[18–20] tunable filters,[21,22] metamaterials[23–26] and other applications. Therefore, there is a huge interest in studying high birefringence liquid crystal properties in the microwave region up to terahertz frequencies.[15–17] Working liquid crystal formula $d\Delta n$ should increase in order to achieve the required phase change in the long wavelength region. High birefringence help to reduce the cell gap, so that fast response time can still be maintained. Liquid crystalline molecule having rigid bistolane core exhibits the highest birefringence values.[1,27,28] Such system consisted of double tolane unit ensures large π-electron conjugation. The main disadvantage of such structures is very high melting point.[29–32] Short alkyl groups in the lateral position of bistolane core significantly reduce the temperature of crystalline–nematic transition.[33] The longer terminal alkyl chain the lower both melting and clearing point.[34,35] Asymmetric analogues of bistolanes generally show much lower melting temperatures than their symmetrical analogues.[36,37]

In this paper we describe newly improved synthetic routes, the mesomorphic and physical properties of two series of bistolanes (symmetrical and non-symmetrical) having lateral alkyl group in the central ring. The general structure of studied bistolane is:



wherein: X = single bond, O or S; R = CH_3 (Me) or C_2H_5 (Et); $n = 2–7$; $m = 2–7$.

These compounds are abbreviated by ***n*XRX*m***, where n and m are the numbers of carbon atoms in the terminal alkyl chain, X is a spacer unit between the terminal alkyl chain and phenyl ring (either single bond, S or O); R is the methyl (Me) or ethyl (Et) group in the lateral position of the central ring. Paper also describes the influence of the linking atom X between core and terminal chain on mesomorphic and optical properties.

2 Experimental

2.1 Synthesis

Symmetrically terminated final compounds have been obtained *via* Sonogashira cross-coupling reaction of 1,4-diiodo-2-methylbenzene (**1**) with 2 molar equivalents of proper 4-alkyl- or alkoxy- or alkylsulfanyl-1-ethynylbenzene (see Scheme 1a).

From the other side non-symmetric analogues have been obtained with improved synthetic method, in which we used a presence of steric hindrance of methyl or ethyl lateral group in Sonogashira reaction (see Scheme 1b). Originally reported method of bistolane core synthesis required the use of an amino-tolane derivative,[27,36] which was followed by the amine–iodine exchange reaction *via* diazonium salt. That additional synthetic step usually generated some difficult to remove impurities, what in consequence often made the isolation of the final liquid crystal extremely hard.

Later, more convenient method was given,[34] where the regioselectivity of Sonogashira cross-coupling toward iodine than to bromine atom had been used. Authors were able to

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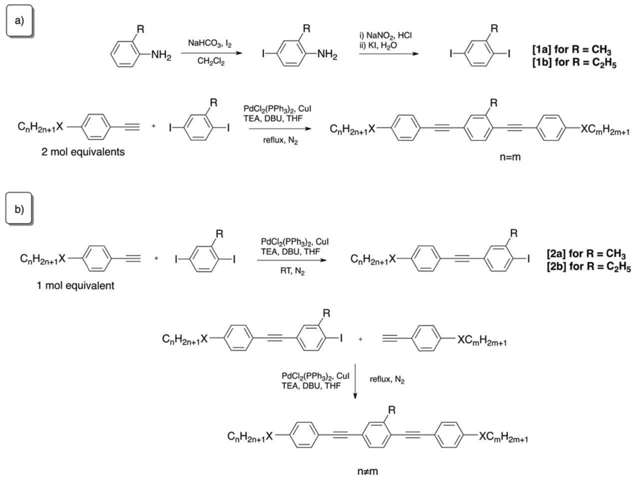
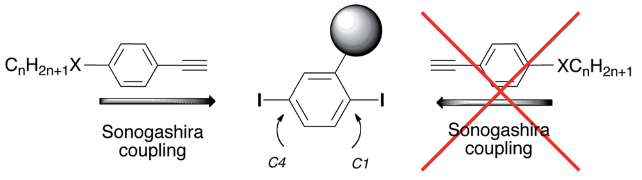


Scheme 1 The synthetic route of: (a) symmetrical and (b) unsymmetrical bistolanes.

obtain either non-substituted bistolane compounds, or substituted only with fluorine atoms in the lateral positions of the central benzene ring. In such case there is no steric hindrance, so the latter Sonogashira cross-coupling proceed with high yields also with bromine atom. Unfortunately this approach cannot be applied for compounds with by far bulkier substitution, such as methyl and ethyl group, which are the object of this work. Here, the activation energy of an palladium oxidative addition to aryl bromide Ar–Br is much higher than to analogous iodide Ar–I. Therefore, the catalytic cycle of Sonogashira reaction is considerably susceptible to any factor obstructing the access of bis(triphenylphosphine) palladium(0) complex to the carbon atom connected with bromine. This unfavourable factor was nothing else than the steric hindrance of lateral short alkyl chain. In this paper we demonstrate an improved method of bistolane core synthesis, in which we turn the steric hindrance of the lateral short alkyl chain from the unwanted obstacle in Sonogashira reaction into an advantage (see Scheme 2).

A proper choice of conditions during Sonogashira reaction allowed us to obtain high selectivity toward C4 than C1 carbon. Then the isolation and purification of a key semiproduct (**2**) in the synthesis did not bring any problems. And finally, the addition of the latter 4-alkyl-1-ethynylbenzene (where $m \neq n$) was carried out on the carbon C1 with high yields even in the presence of steric hindrance.



Scheme 2 The influence of steric hindrance on the Sonogashira coupling regioselectivity.

The preparative procedures and the characterization by GC chromatography (SHIMADZU GCMS-QP2010) with a quadrupole mass detector and by ^{1}H and ^{1}C NMR spectroscopy of the compounds of ***n*XRX*m*** are presented in the ESI.†

3 Results and discussion

3.1 Mesomorphic properties

The sequence of phase transitions and their temperatures were determined by polarizing optical microscopy with an "Olympus" BX51 polarising microscope (Shinjuku, Tokyo, Japan) equipped with a Linkam hot stage THMS-600 and by differential scanning calorimetry using the DSC SETARAM 141 instrument with the scanning rate 2 °C min^{-1} in both heating and cooling cycles. Table 1 lists the phase transitions temperatures and enthalpies of all compounds.

Compounds of series ***n*XRX*m***, where X = single bond exhibit enantiotropic nematic phase in broad temperature range. For symmetrical analogues the lengthening of terminal chain decreases both melting and clearing points. From the other side for asymmetrical compounds decrease of melting temperatures was observed only. Asymmetrical bistolanes with the alkyl terminal chain (where X = single bond) exhibit lower both melting temperature and enthalpy values comparing to their symmetrical analogues. Melting enthalpy values are rather at a moderate level (up to 27.3 kJ mol^{-1}). Compounds with the lateral ethyl group in the central ring exhibit much lower melting points that compounds with the lateral methyl group. The effect of the number of carbon atoms in the terminal alkyl chain on the melting and clearing point for symmetrical compounds ***n*XMeX*m***, where X = single bond is presented in Fig. 1.

Table 1 Melting temperatures (°C) (onset point) and enthalpies (kJ mol^{-1}) of all homologoues ***n*XRX*m*** from DSC measurements obtained during heating cycles

Acronym	R	*n*	*m*	Cr	T_{mp} [°C]	N	T_c [°C]	Δ*H* [kJ mol^{-1}]	Ref.
3Me3	CH_3	3	3	•	125.3	•	208.3	19.16	36 and 37
4Me4	CH_3	4	4	•	87.7	•	178.9	27.38	
5Me5	CH_3	5	5	•	80.5	•	176.1	20.60	
6Me6	CH_3	6	6	•	73.4	•	151.5	27.29	
7Me7	CH_3	7	7	•	72.7	•	147.4	26.94	
7Me4	CH_3	7	4	•	45.5	•	158.9	11.99	
7Me5	CH_3	7	5	•	53.3	•	160.7	15.90	
5OMeO5	CH_3	5	5	•	120.8	•	217.9	36.97	
2SMe5	CH_3	2	5	•	110.9	•	186.3	27.04	
5SMeS5	CH_3	5	5	•	120.0	•	126.4	50.32	
5SMe5	CH_3	5	5	•	94.1	•	150.2	34.57	
2Et2	C_2H_5	2	2	•	84.6	•	131.7	20.70	
3Et3	C_2H_5	3	3	•	48.2	•	151.9	14.48	
3Et5	C_2H_5	3	5	•	59.4	•	137.4	16.37	33
4Et4	C_2H_5	4	4	•	29.5	•	121.0	16.70	38
4Et2	C_2H_5	4	2	•	58.7	•	123.5	26.03	36
4Et3	C_2H_5	4	3	•	36.4	•	131.8	22.27	
5Et5	C_2H_5	5	5	•	3.9	•	120.7	5.88	
5Et3	C_2H_5	5	3	•	26.8	•	136.1	9.11	33
5SEtS5	C_2H_5	5	5	•	86.5	—		48.58	

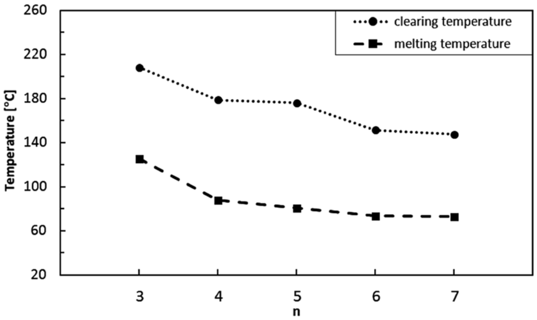


Fig. 1 The effect of the number of carbon atom in the terminal alkyl chain on the melting and clearing point for symmetrical compounds *n*Me*m*, where $n = m = 3$–7 and X = single bond.

Compounds with terminal alkylsulfanyl chains (X = S) exhibit much higher melting temperatures and lower clearing points than their corresponding analogues with alkyl chains (where X = single bond) in the terminal positions. It can be seen that systematic introduction of the sulphur atom into terminal chain of the liquid crystal molecule significantly decreases the clearing point together with systematical increase of their melting temperatures (see Fig. 2). Therefore the temperature range of liquid crystal phase is drastically shortened. Among these structures only compound **5SEtS5** shows no mesomorphism, as the clearing temperature drop is much below the melting point. And finally, compound **5OMeO5** with terminal alkoxy chains (X = O) shows the broadest range of mesophase, and exhibit higher both melting and clearing temperatures than its analogues with alkyl and alkylsulfanyl chains. Compounds with alkylsulfanyl and alkoxy chains have higher melting enthalpy values comparing to their alkyl analogues ($\Delta H = 35$–50 kJ mol^{-1}). The effect of the linking atom between the rigid core and the terminal pentyl chain on mesophase range for symmetrical compounds **5XMeX5** with fixed lateral group (Me) is presented in Fig. 2.

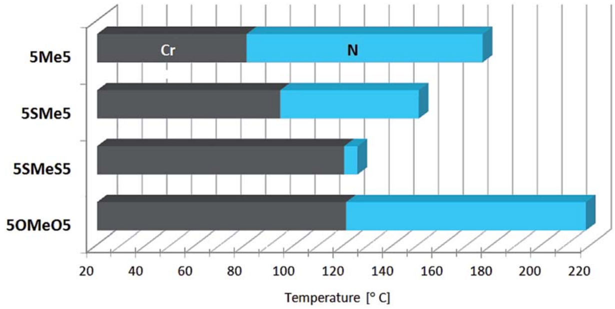
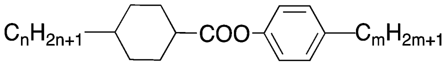


Fig. 2 The effect of the linking atom between the rigid core and the terminal pentyl chain on the mesophase range for symmetrical compounds 5XMeX5, where X = either single bond, S or O.

Table 2 Composition and properties of the host nematic mixture at 20 °C based on 4*n*-alkylphenyl *trans*-4*n*-cyclohexylcarbonates



n	*m*	mol%	Properties
4	1	33.3	$T_m < -20$ °C $T_{N\text{-}I} = 63.6$ °C
4	2	33.3	$\Delta n = 0.08$ (589 nm)
4	5	33.3	$\eta = 21.2$ mPa s

3.2 Birefringence measurements

All symmetrical final compounds with the lateral methyl group in the central ring have been evaluated for their optical properties. For the estimation of optical indices and birefringence values the guest–host system method was used. Three-component ester based nematic mixture[39] (4*n*-alkylphenyl *trans*-4*n*-alkylcyclohexanecarboxylates – Table 2) was doped with 5 wt%, 10 wt% and 15 wt% of each compound. Then, values of the ordinary (n_o) and extraordinary (n_e) refractive indices of all systems were measured by using multi-wavelength Abbe refractometer DR-M2 at the yellow doublet sodium D line. Nematic material was aligned with the polyimide parallel to the main prism surface. Both rays were selected using a polarization filter in front of the eyepiece of the instrument. All values for pure compounds were extrapolated from the eqn (1):

$$(n_{e,o})_{gh} = x(n_{e,o})_g + (1 - x)(n_{e,o})_h \tag{1}$$

where: $n_{e,o}$ is the refractive index, extraordinary and ordinary respectively; gh, g, h are guest–host system, guest and host respectively; x is the concentration (in mol%) of the guest compound.

Table 2 shows the composition and physical properties of host nematic material. Extrapolated values of refractive indices and the birefringence are given in Table 3. The effect of the carbon atom number in terminal alkyl chain on the value of birefringence for pure symmetrical compounds ***n*XMeX*m*** extrapolated at 20 °C is presented in Fig. 3.

Investigated compounds exhibit high values of the birefringence (Δn); from 0.38 to 0.61. The more carbon atoms in the terminal chain, the lower value of birefringence is observed, but also an odd–even effect is found.[40] Compounds with heteroatoms in terminal chain exhibit the highest values of the birefringence: 0.51 for compound **5OMeO5** and 0.61 for compound **5SMeS5** respectively. Heteroatom strongly amplifies the π-

Table 3 Refractive indices and the birefringence extrapolated at 20 °C ($\lambda = 589$ nm) of selected compounds

Acronym	n_e	n_o	Δn
3Me3	2.05	1.56	0.49
4Me4	2.01	1.59	0.42
5Me5	2.02	1.59	0.43
6Me6	1.92	1.55	0.37
7Me7	1.94	1.56	0.38
5Et5	1.92	1.55	0.37
5OMeO5	2.12	1.61	0.51
5SMeS5	2.21	1.60	0.61

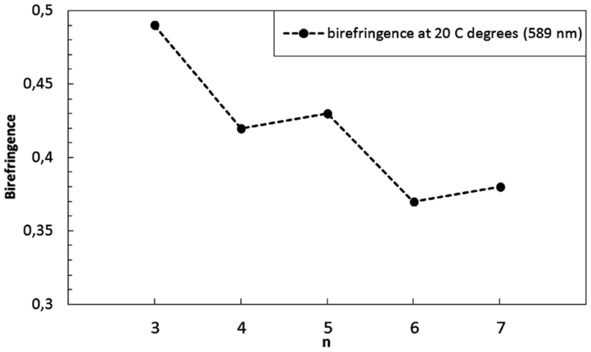


Fig. 3 The effect of the number of carbon atom in terminal alkyl chain on the value of birefringence for pure symmetrical compounds *n*XMeX*m*, where $n = m = 3$–7 and X = single bond.

electron conjugation of bistolane core. That is a consequence of increased polarizability of the sulphur and oxygen atom in comparison to carbon atom.[41] It finally leads to an increase of the molecular polarizability anisotropy $\Delta\alpha$. According to Vuks,[42] the magnitude of the birefringence strongly depends on the molecular polarizability anisotropy $\Delta\alpha$ for elongated molecules. Therefore structures **5OMeO5** and **5SMeS5** show much higher optical anisotropy than it is observed for compound **5Me5**. In other words lack of such structural unit leads to a significantly lower values of birefringence (compound **5Me5**). To confirm that relation we used molecular simulation program ADF[43–45] to calculate the molecular polarizabilities, then the total tensor of the polarizability and finally the molecular polarizability anisotropy $\Delta\alpha$ of investigated compounds. Polarizability was calculated "*in vacuo*" at the density functional theory (DFT) level on the optimized molecular structures using the combination of BLYP functional with the QZ4P basis set.

For our system we assumed that the principal molecular axis is along the *x*-axis and two shorter molecular axes are in the orthogonal directions[46] (see Fig. 4). We can also assume that the polarizability tensor with respect to the principal molecular axes has a following diagonal form:

$$\alpha = \begin{bmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{bmatrix}$$

Calculation data is listed in Table 4. It is clearly seen that the presence of more polarizable oxygen or sulphur atom in molecular system, enhances the molecular polarizability anisotropy and further brings an increase of the birefringence.

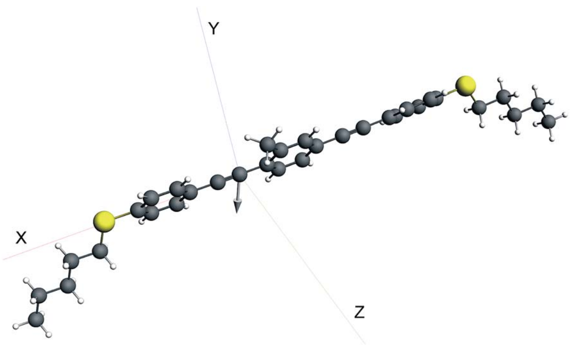


Fig. 4 The orientation of the **5SMeS5** molecule and principal axes.

Table 4 Calculation data for **5Me5**, **5OMeO5** and **5SMeS5** compounds

	Polarizability					
Acronym	α_{xx}	α_{yy}	α_{zz}	$\Delta\alpha$	Average α	Δn
5Me5	903.3	282.8	335.4	595.9	507.2	0.43
5OMeO5	926.4	305.2	338.0	605.5	523.2	0.51
5SMeS5	1096.8	370.0	327.8	748.8	598.2	0.61

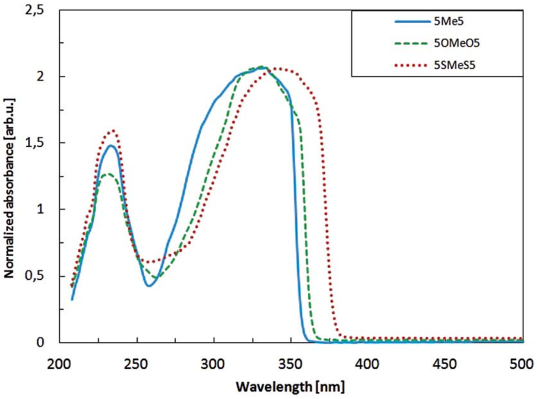


Fig. 5 The UV-vis absorption spectra of selected compounds *n*XRX*m*, where $n = m = 5$ and X = either single bond, S or O.

3.3 UV-vis absorption

The absorption spectra of several compounds in hexane solution (0.43 mg mL^{-1}) were investigated (180–1000 nm), using UV-VIS-NIR 3600 Shimadzu spectrophotometer (Nakagyo-ku, Kyoto, Japan). Measured compounds exhibit intense absorption band in ultra violet (UV) range and they all are photochemically stable above 380 nm of the visible light range (see Fig. 5).

4 Conclusions

High birefringence liquid crystal mixtures are necessary for applications in visible, infrared and recently also in GHz and THz ranges of electromagnetic radiation.[47–49] In this work, we have synthesized a set of both symmetrical and non-symmetrical bistolanes with terminal alkyl, alkoxy and alkylsulfanyl groups and the lateral both methyl and ethyl group, abbreviated ***n*XRX*m***. We have measured their mesomorphic and optical properties. Most of them exhibit broad nematic temperature range and the birefringence higher than 0.4, which makes them suitable dopants for high birefringence systems. It has been proven[50,51] and here confirmed that the sulphur atom generates the most significant increase of the polarisability of the liquid crystal system and hence the birefringence.

Additionally, we have demonstrated an improved method of the bistolane core synthesis. Here we used the presence of the steric hindrance generated by the lateral alkyl group. This allowed us to gain the regioselectivity of the Sonogashira cross-coupling reaction in the crucial stage of the bistolane synthesis.

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