

BENT-CORE SYSTEMS BASED ON [1,3,4]OXADIAZOLE CORE WITH SHAPE BIAXIALITY

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The present paper is presenting the synthesis and characterization of new [1,3,4]oxadiazole derivatives obtained by attaching different mesogenic units to the central core. Liquid crystals properties analysis by POM and DSC techniques is presented and structure-properties correlations are discussed.

INTRODUCTION

Unconventional bent-core mesogenic systems received a great attention in the past years due to the interesting properties and mesophases (banana type mesophases, enantioselective segregation from achiral liquid crystals)^{1,2} and more recently due to the possibility of ordering in two directions in the nematic mesophase (biaxial liquid crystals) because of the shape biaxiality of these compounds.³⁻⁹

The bent-core systems analyzed in this paper are based on [1,3,4]oxadiazole central core and were obtained by esterification of the central core with different mesogenic units. Symmetric derivatives, which contain a bent central unit with

interesting mesophases and optically isotropic textures, were obtained.¹⁰ These dark conglomerate phases were observed for several other bent-core molecules with smectic phases in other reports.¹¹⁻¹⁵

RESULTS AND DISCUSSION

The purpose in using the oxadiazole unit was to obtain curved systems capable of inducing molecular ordering in two directions and an increase of the orthogonal polarity, with the formation of fast switching systems. The general structure of the synthesized derivatives is presented in Fig. 1:

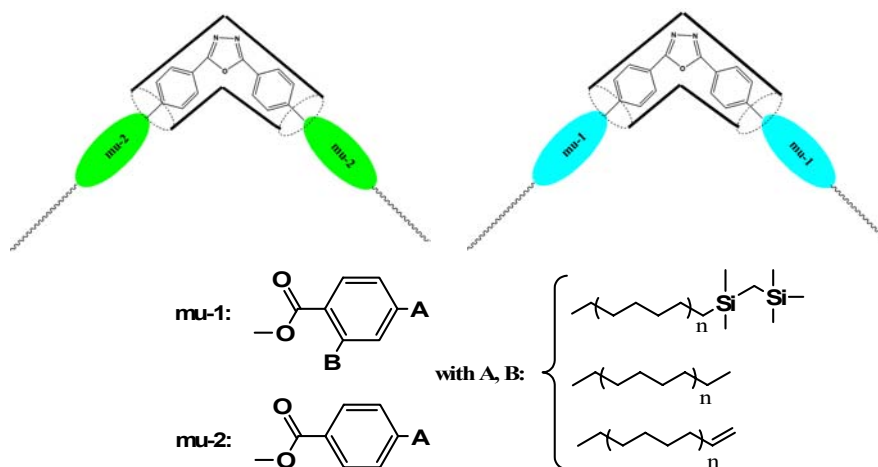


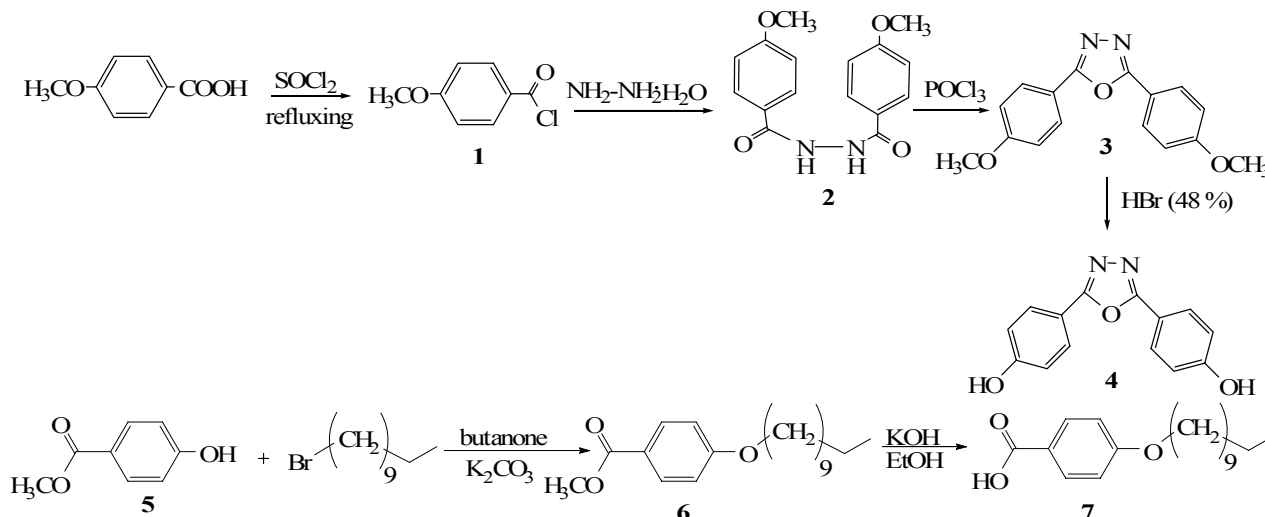
Fig. 1 – General structure of [1,3,4] oxadiazole derivatives.

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Synthesis of intermediates compounds

Oxadiazole derivatives were obtained in 3 stages, by synthesis of the oxadiazole core, synthesis of the mesogenic units and, finally, synthesis of the final derivatives by coupling the intermediates.

The [1,3,4]oxadiazole core is obtained from 4-Methoxy-benzoyl chloride as shown in Scheme 1.¹⁶ The mesogenic units used for the synthesis of the final compounds are acid derivatives obtained by Williamson reactions of the phenol groups of 4-hydroxy methyl benzoate followed by carboxyl group deprotection in KOH alcoholic solutions (Scheme 1).

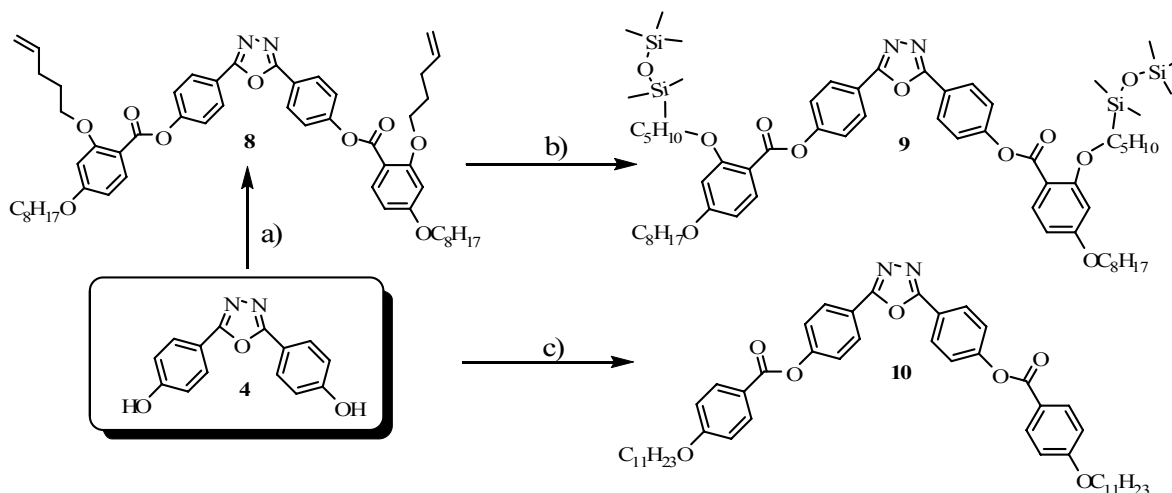


Scheme 1 – Synthesis of intermediates derivatives.

Synthesis of final compounds

The symmetric oxadiazole derivatives were obtained by esterification of the central core with

the mesogenic units and by hydrosilylation with 1,1,1,3,3-pentamethyldisiloxane, in the presence of Karstedt catalyst (Scheme 2).



a) 4-(octyloxy)-2-(pent-4-enyloxy)benzoic acid, dimethylaminopyridine (DMAP), diisopropylcarbodiimide (DIPC), CH_2Cl_2 , rt; b) Karstedt catalyst, toluene, 1,1,1,3,3-pentamethyldisiloxane; c) i. SOCl_2 ii. **8**, toluene, Py;

Scheme 2 – Synthesis of symmetric derivatives of [1,3,4]oxadiazole.

Mesomorphic properties

From all 3 symmetric [1,3,4]oxadiazole derivatives only 10 presents mesomorphic

properties with a strong polymorphism due to the laterally interactions between the oxadiazoles cores. The compounds show various smectic mesophases but also the nematic one, which were

studied by both POM and DSC techniques. For characterising the type of smectic mesophases, an XRD study of some samples has been made.

The POM and DSC study of **8** and **9** derivatives showed the lack of liquid crystal properties of

these compounds (Fig. 2). The compounds contain alkyl chains laterally connected to the oxadiazole core, which result in diminishing the molecule's interactions and as consequence the hindrance of the liquid crystal ordering.

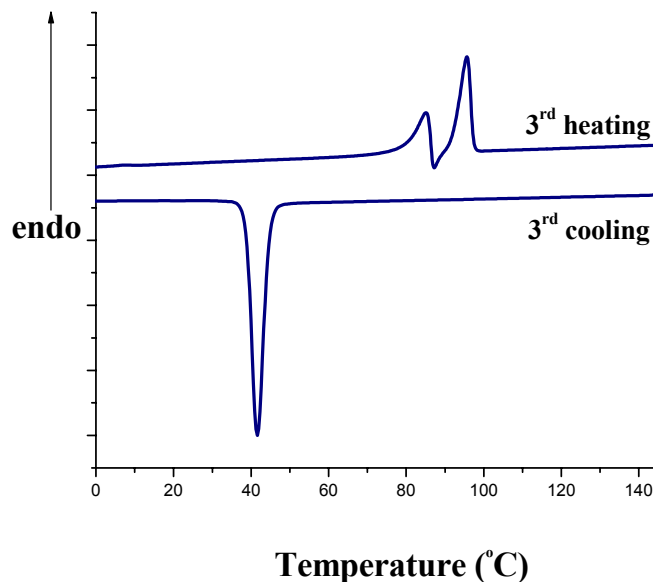


Fig. 2 – a) POM texture of sample **8** at rt (soft crystals) and b) DSC curves of derivative **9** at the third heating-cooling cycle for 10 °C/min.

The molecular modelling with HyperChem program showed the minimal energy molecular

geometry and proved the lack of ordering due to the sterically hindrance.

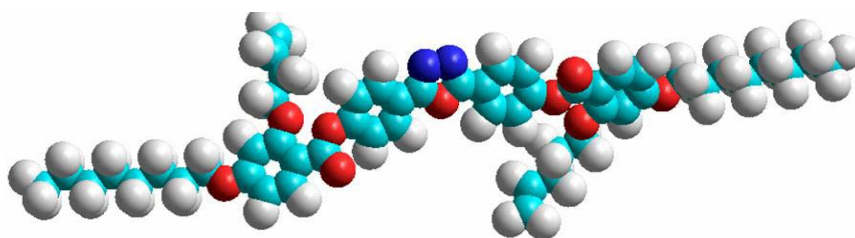


Fig. 3 – The geometry of minimal energy of derivative **8**, obtained by molecular modelling.

The molecular modelling of derivative **10** showed an elongated structure with a strong lateral dipole that can generate intense interactions

responsible of the mesomorphic behaviour and molecules ordering in multiple phases (Fig. 4).

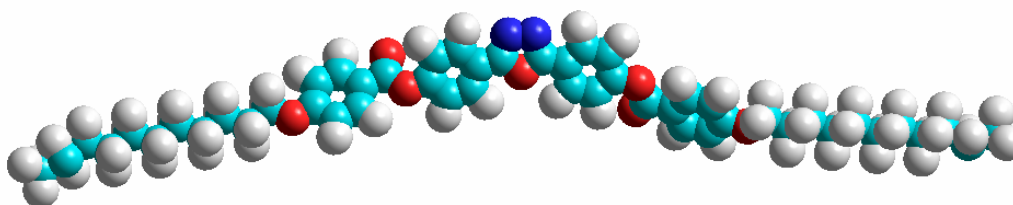


Fig. 4 – The geometry of minimal energy of derivative **10**, obtained by molecular modelling.

In principle, the attachment of the siloxane unit is expected to give rise to ordering in liquid crystal

structures at lower temperatures. Although the melting point was decreased with 67 degrees, the

sterically hindrance blocked the molecules approaching and as consequence their ordering in the liquid crystals phase. The analysis by POM of **8** and **9** compounds showed a very small scale texture of soft crystals and the DSC study didn't confirm the mesomorphic properties (Fig. 2). Compound **10** presents liquid crystals properties with ordering in polymorphic smectic and nematic structures.

The microscopy study showed the entrance in mesophase at 122 °C, and observance of one non specific smectic texture and one corresponding to smectic C mesophase followed by the transition to nematic at 176 °C, with typically Schlieren texture and the clearing at 197 °C. On cooling, the behaviour was more complex, starting from

nematic to smectic C (Fig. 5 a), with Schlieren textures, behaviour which was confirmed also by DSC study, followed by multiple transitions, with non specific textures, corresponding probably to smectic mesophases (Fig. 5 d-f).

Interesting, a completely dark mesophase (optically isotropic) has been observed at 132 °C, which is not typically to a highly birefringent smectic phase.

The DSC study of derivative **10** showed the presence of 4 phase transitions on heating (crystal – smectic 2, smectic 2 - smectic C, smectic C - nematic and nematic - isotropic), respectively 5 phase transitions on cooling with the appearance of a new smectic mesophase whose nature couldn't be established (Fig. 6.a).

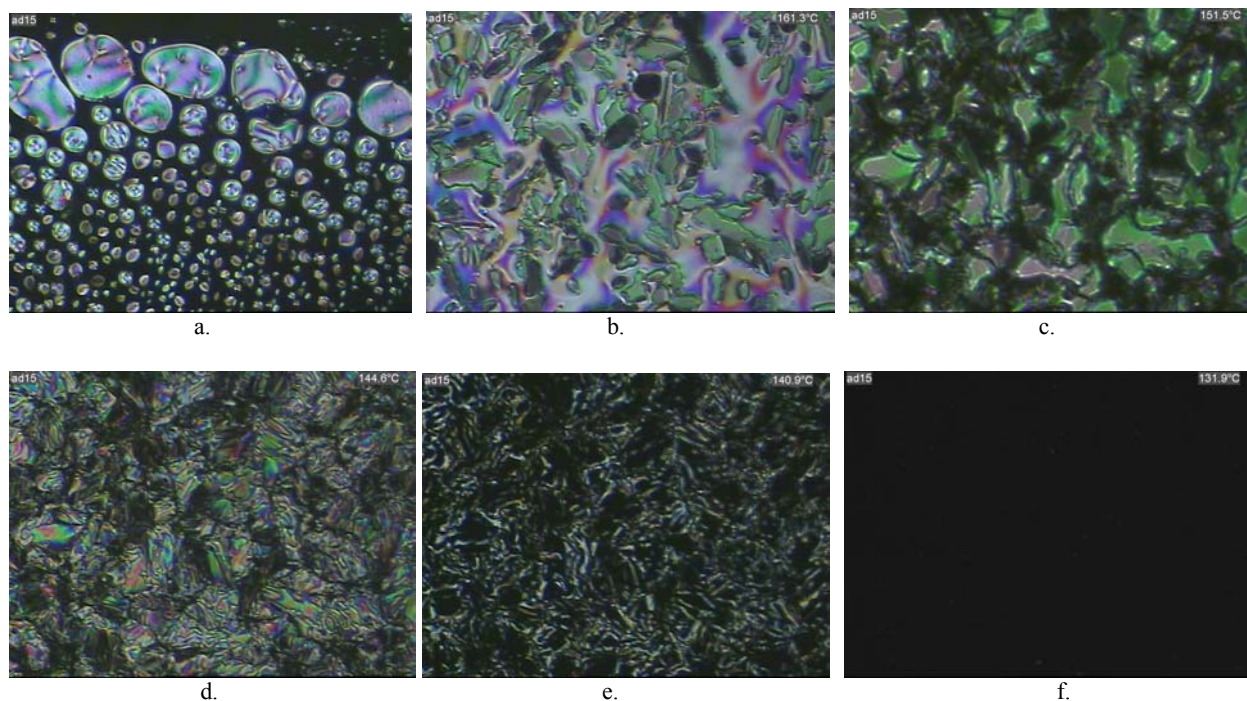


Fig. 5 – Textures of sample **10** at: a) 190 °C on the second cooling (nematic droplets), b) 161.3 °C on the third cooling, c) 151.5 °C cooling, d) 144.6 °C, e) 140.9 °C, f) 131.9 °C.

The ordering in specific textures (broken fan-shaped and Schlieren) suggests the occurrence of smectic C mesophase on the 165 - 203 °C temperature domain (on heating) and 203 °C - 169 °C (on cooling). The cooling on lower temperatures gives rise to successive changes of the textures for which the DSC study showed changes of the mesophase type. The textures are non specific and as consequence the identification of the smectic phase type couldn't be attributed (Fig. 5e). A dark

mesophase with grainy unspecific texture which is completely dark (optically isotropic) has been detected on cooling on the temperature domain 142 °C – 108 °C. In this case the highly birefringent textures usually observed for smectic phases are replaced by optically isotropic phases.

The liquid crystal properties of symmetric [1,3,4]oxadiazole derivatives are schematically presented in Table 1.

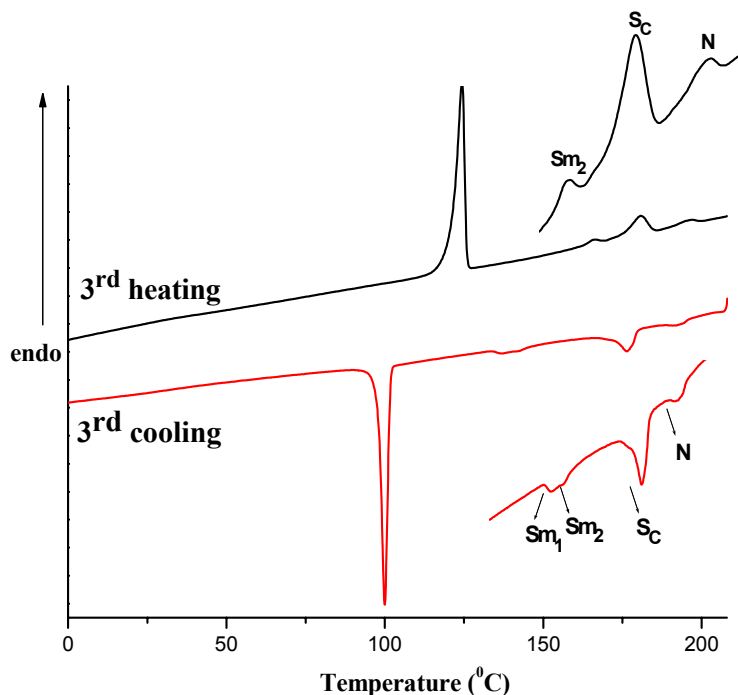


Fig. 6 – DSC curves of derivative **10** at the third heating-cooling cycle for 10 °C/min.

Table 1

Phase transitions of symmetric oxadiazole derivative

Sample	Phase transitions		Temperature (°C)		Enthalpy, ΔH (J/g)		
	3 rd heating	3 rd cooling	3 rd heating	3 rd cooling	3 rd heating	3 rd cooling	
10	K/Sm ₂	N/I	120.97	196.03	33.62	0.87	
	Sm ₂ /SmC	I/N	162.72	196.05	0.75	1.18	
		N/SmC		179.68			6.28
SmC/N	SmC/Sm ₂	Sm ₂ /Sm ₁	175.34	145.25	5.3	1.4	
				Sm ₁ /K		142.12	1.6
						101.63	30.89

EXPERIMENTAL

Materials. All materials were used as purchased unless mentioned otherwise. All reactions involving DCC and DMAP were performed under a dry atmosphere of nitrogen. Silica gel 60 (Merck) was used for column chromatography. TLC was performed on Silica gel plates (Merck, Silicagel F₂₅₄).

Instrumentation. Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol JNM-ECP 400 MHz FT-NMR spectrometer. Chemical shifts are reported in ppm relative to TMS. Thermal properties were investigated using a Mettler Toledo differential calorimeter (DSC 822⁵) in nitrogen against an indium standard. Transition temperatures were determined as the onset of the maximum in the endotherm or exotherm. The mesophases were studied on an Olympus BH-2 optical polarising microscope, equipped with a Mettler FP82 HT hot stage and a Mettler FP90 central processor. Pictures of the mesophases were taken using a JVC digital video camera connected to a PC. Software *Studio Capture*, supplied by Studio86Designs was used for image capturing. XRD study was performed on MAR345 diffractometer, equipped with 2D

images detector, CuK_α radiation source, graphite monochromator, λ = 1.54 Å.

4-Methoxy-benzoyl chloride (1) – 4-methoxybenzoic acid (10 g, 65.72 mmol) and 200 ml of thionyl chloride is refluxed for 1.5 h and then concentrated until dry on vacuum. The product is used immediately in the next stage without purification.

4-Methoxy-benzoic acid N'-(4-methoxy-benzoyl)-hydrazide (2) Acid chloride **1** was dissolved in 100ml of dry DCM and hydrazine hydrate (9.6 ml, 0.19 mol) was added drop wise. After 10 h of refluxing, the reaction mixture was concentrated and the product was purified by crystallization from methanol giving rise to a white-yellowish crystals, 5.89 g (yield 59.68 %). ¹H-NMR δ_H (DMSO): 10.29 (s, 2H, -NH-), 7.90 (d, 4H, Ar), 7.05 (d, 4H, Ar), 3.82 (s, 3H, -CH₃). ¹³C-NMR δ_C (DMSO): 165.39, 161.99, 129.3, 124.78, 113.7, 55.4.

2,5-Bis-(4-methoxy-phenyl)-[1,3,4]oxadiazole (3) Over a solution of **2** (3 g, 5 mmol) dissolved in 120 ml of dry toluene, and heated at 80 °C, POCl₃ (10.94 ml, 50 mmol) is added and leaved for stirring at temperature for 2 h. TLC checking of the reaction show the appearance of a highly fluorescent spot corresponding to the product. After cooling and concentration, the product is purified by column chromatography on silica

with DCM giving 2.59 of a white product, yield 73.82%; $^1\text{H-NMR } \delta_{\text{H}}$ (DMSO): 8.04 (d, 4H, Ar), 7.16 (d, 4H, Ar), 3.85 (s, 6H, $-\text{CH}_3$), $^{13}\text{C-NMR } \delta_{\text{C}}$ (DMSO): 163.46, 161.96, 128.40, 115.80, 114.83, 55.52.

2,5-Bis-(4-hydroxyphenyl)[1,3,4]oxadiazole (4) 120 ml of HBr (48%) was added to compound **3** (1 g, 3.54 mmol) and stirred at 120 °C for 24 h. The reaction mixture is cooled to room temperature, poured in 500 ml of water, filtered and then crystallized from ethanol giving 0.52 g of a white product (57.7%); $^1\text{H-NMR } \delta_{\text{H}}$ (DMSO): 10.28 (s, 2H, $-\text{OH}$), 7.91 (d, 4H, Ar), 6.95 (d, 4H, Ar), $^{13}\text{C-NMR } \delta_{\text{C}}$ (DMSO): 163.49, 160.64, 128.47, 116.15, 114.29.

4-Undec-10-enyloxy methyl benzoate (6) 4-hydroxy methyl benzoate (4 g, 26.28 mmol), 11-bromoundec-1-ene (5.23 g, 23.89 mmol), K_2CO_3 (4.94 g, 35.84 mmol), KI (1.98 g, 11.94 mmol) are dissolved in 200 ml of butanone and refluxed for 12h. After cooling the reaction mixture was filtrated and concentrated and the product was purified by column chromatography on silica with DCM : hexane (3: 1) giving 5.66 g of white product (yield 77.8 %), $^1\text{H-NMR } \delta_{\text{H}}$ (DMSO): 7.87 (d, 2H, Ar), 6.96 (d, 2H, Ar), 5.78 (m, 1H, $-\text{CH}=\text{}$), 4.97 (dd, 2H, $=\text{CH}_2$), 4.01 (t, 2H, $-\text{CH}_2-\text{O}$), 1.99 (q, 2H, $=\text{C}-\text{CH}_2-\text{C}$), 1.71 (qv, 2H, $\text{C}-\text{CH}_2-\text{C}$), 1.40-1.26 (m, 12H, aliphatic), $^{13}\text{C-NMR } \delta_{\text{C}}$ (DMSO): 168.22, 162.09, 139.41, 131.69, 125.92, 115.21, 114.37, 68.19, 55.49, 33.75, 29.51, 29.37, 29.30, 29.15, 29.07, 28.84, 26.02.

General method of hydrosilylation:

Over a mixture of double bond end derivative (1 equiv) and 5 equiv of 1,1,1,3,3-pentamethyldisiloxane, dissolved in dried DCM, Karstedt catalyst is added dropwise and the mixture is stirring at room temperature for 12 h. The reaction mixture is concentrated and the product is precipitated in hexane and than purified by column chromatography with an appropriate mixture of solvents.

General method of esterification:

A mixture of 1 equiv of phenol, 1.2 equiv of acid, DMAP dissolved in dry DCM is stirring for couple a minutes and 1.2 equiv of DIPC dissolved in dry DCM is added dropwise. The reaction mixture is left for stirring for 12-24 h at room temperature in inert atmosphere of nitrogen. The reaction conversion is checked by TLC. After the DIPU is filtered, the solvent is concentrated and the product is purified by column chromatography on silica with the appropriate mixture of solvents.

2,5-Bis-{4-[4-octyloxy-2-(pent-4-enyloxy)phenylcarbonyloxy]phenyl}[1,3,4]oxadiazole (8)

Quantities: derivative **4** (0.14 g, 0.56 mmol), **10** (0.40 g, 1.19 mmol), DIPC (0.15 g, 1.19 mmol), DMAP (catalytic), 40 ml DCM, purification on silica with (DCM : hexane – 7 : 2), white product, yield 0.34 g (68.2%), mp: = 91.76 °C, $^1\text{H-NMR } \delta_{\text{H}}$ (CDCl_3): 8.20 (d, 4H, Ar), 8.0 (d, 2H, Ar), 7.38 (d, 4H, Ar), 6.51 (dd, 4H, Ar), 5.81 (m, 2H, $-\text{CH}=\text{}$), 4.99 (dd, 4H, $=\text{CH}_2$), 2.28 (q, 4H, $-\text{CH}_2-$), 1.96 (qv, 4H, $-\text{CH}_2-$), 1.82 (qv, 4H, $-\text{CH}_2$), 1.29 (m, 20H, $-\text{CH}_2-$), 0.88 (t, 6H, $-\text{CH}_3$), $^{13}\text{C-NMR } \delta_{\text{C}}$ (CDCl_3): 164.86, 164.25, 163.52, 161.85, 154.08, 137.74, 134.70, 128.39, 122.95, 121.17, 115.43, 110.66, 105.53, 100.29, 68.50, 68.10, 31.89, 30.09, 29.42, 29.31, 29.21, 28.34, 26.08, 22.75, 14.20, m/z (MALDI): 888 $[\text{M}]^+$.

2,5-Bis-{4-[4-Octyloxy-2-(5-(1,1,3,3,3-pentamethylsilyloxanyl)pentyl)oxy]phenyl}carbonyloxy}

phenyl[1,3,4]oxadiazole (9) Quantities: derivatives **11** (0.12 g, 0.13 mmol), 1,1,1,3,3-pentamethyldisiloxane (0.26 ml, 1.3 mmol), 20 drops of Karstedt catalyst, purification on silica with DCM,

white grey product, yield 0.14g (93%), $^1\text{H-NMR } \delta_{\text{H}}$ (CDCl_3): 8.19 (d, 4H, Ar), 8.05 (d, 2H, Ar), 7.39 (d, 4H, Ar), 6.52 (ddd, 4H, Ar), 4.03 (q, 8H, $-\text{CH}_2-\text{O}$), 1.83 (m, 4H, $-\text{CH}_2-$), 1.46 (m, 4H, $-\text{CH}_2-$), 1.30(m, 24H, $-\text{CH}_2-$), 0.90 (t, 4H, $-\text{CH}_2-$), 0.50 (qv, 4H, $-\text{CH}_2-\text{Si}$), 0.03 (m, 30H, $-\text{Si}(\text{CH}_3)_2$ O-Si(CH₃)₃), $^{13}\text{C-NMR } \delta_{\text{C}}$ (CDCl_3): 164.86, 164.24, 163.50, 162.00, 154.1, 134.66, 128.35, 122.97, 121.13, 110.64, 105.47, 100.24, 69.02, 68.48, 31.90, 29.71, 29.42, 29.32, 29.22, 28.93, 26.08, 23.10, 22.75, 18.36, 14.20, 2.06, 0.41.

2,5-Bis-(4-undecyloxyphenylcarbonyloxyphenyl) [1,3,4]oxadiazole (10) Quantities: derivatives **4** (0.3 g, 1.1 mmol), 4-undecyloxybenzoic acid (0.7 g, 2.4 mmol), 100 ml SOCl_2 , toluene, 5 ml of pyridine, purification on silicagel (DCM : 10 % ethyl acetate), white product, yield 0.7 g (80.17%), $^1\text{H-NMR } \delta_{\text{H}}$ (CDCl_3): 8.21(d, 4H, Ar), 8.15 (d, 4H, Ar), 7.42 (d, 4H, Ar), 6.99 (d, 4H, Ar), 4.05 (t, 4H, CH_2-O), 1.82 (qv, 4H, $\text{OCO}-\text{CH}_2$), 1.48 (m, 32H, $-\text{CH}_2$), 0.88 (t, 6H, $-\text{CH}_3$), $^{13}\text{C-NMR } \delta_{\text{C}}$ (CDCl_3): 164.53, 164.20, 163.92, 153.92, 132.51, 128.44, 122.83, 121.40, 121.03, 114.51, 68.48, 32.00, 29.80, 29.69, 29.65, 29.55, 29.44, 29.35, 29.18, 26.07, 24.95, 22.78, 14.23.

CONCLUSIONS

The study of the biaxial nematic systems is of great importance not only from a theoretical point of view but also in the projection of materials with special properties for future technologies. New bent-core systems with shape biaxiality have been designed and synthesized. The mesomorphic properties analysis and the study of the molecular influence on mesomorphic properties have been performed. The molecular symmetry induces an increase of the ordering in the system and the appearance of different smectic mesophases for the symmetric oxadiazoles derivatives. The presence of smectic mesophases for the symmetric oxadiazole derivatives is due to the strong laterally dipole moment of the [1,3,4]oxadiazole unit according to the nitrogen heteroatoms with high electronegativity. The pentamethyldisiloxane unit in the terminal part of the flexible chain give rise to pronounced decrease of the melting point.

REFERENCES

1. V. Görtz and J. W. Goodby, *Chem. Commun.*, **2005**, 3262.
2. C. Keith, R. A. Reddy, A. Hauser, U. Baumeister and C. Tschierske, *J. Am. Chem. Soc.*, **2007**, *128*, 3051.
3. T. J. Dingemans and E. T. Samulski, *Liq. Cryst.*, **2000**, *27*, 131.
4. L. A. Madsen, T. J. Dingemans, M. Nakata and E. T. Samulski, *Phys. Rev. Lett.*, **2004**, *92*, 145505.
5. B. R. Acharya, A. Primak and S. Kumar S., *Phys. Rev. Lett.*, **2004**, *92*, 145506.
6. C. V. Yelamaggad, S. K. Prasad, G. G. Nair, I. S. Shashikala, S. S. Rao, C. V. Lobo and S. Chandrasekhar, *Angew.Chem.Int.Ed.*, **2004**, *26*, 3429.

7. J.L. Figueirinhas, C. Cruz, D. Filip, G. Feio, A.C. Ribeiro, Y. Frère, T. Meyer and G. H. Mehl, *Phys. Rev. Lett.*, **2005**, *94*, 107802.
8. G. R. Luckhurst, *Angew. Chem. Int. Ed.*, **2005**, *44*, 2834.
9. T. J. Dingemans, L.A. Madsen, N.A. Zafiroopoulos, WB Lin and E.T. Samulski, *Philosophical transactions of the Royal Society A-Mathematical physical and engineering sciences* **2006**, *364*, 2681.
10. D. Apreutesei and G. H. Mehl, Euroconference on dendrimer soft self assembly systems, Strassbourg, 17-21 May 2006, poster.
11. (a) J. Thisayukta, Y. Nakayama, S. Kawauchi, H. Takezoe and J. Watanabe, *J. Am. Chem. Soc.*, **2000**, *122*, 7441, (b) J. Thisayukta, H. Kamee, S. Kawauchi and J. Watanabe, *Mol. Cryst. Liq. Cryst.*, **2000**, *346*, 63.
12. H. N. Shreenivasa Murthy and B. K. Sadashiva, *Liq. Cryst.* **2002**, *29*, 1223.
13. J. Ortega, C. L. Folcia, J. Etxebarria, N. Gimeno and M. B. Ros, *Phys. Rev. E*, **2003**, *68*, 011707.
14. a) W. Weissflog, M. W. Schröder, S. Diele and G. Pelzl, *Adv. Mater.*, **2003**, *15*, 630. (b) A. Jakli, Y.-M. Huang, K. Fodor-Csorba, A. Vajda, G. Galli, S. Diele and G. Pelzl, *Adv. Mater.*, **2003**, *15*, 1606. (c) M. W. Schröder, S. Diele, G. Pelzl, U. Dunemann, H. Kresse and W. Weissflog, *J. Mater. Chem.*, **2003**, *13*, 1877. (d) M. W. Schröder, G. Pelzl, U. Dunemann and W. Weissflog, *Liq. Cryst.*, **2004**, *31*, 633. (e) W. Weissflog, S. Sokolowski, H. Dehne, B. Das, S. Grande, M. W. Schröder, A. Eremin, S. Diele, G. Pelzl and H. Kresse, *Liq. Cryst.*, **2004**, *31*, 923.
15. C. Keith, R. Amaranatha Reddy, A. Hauser, U. Baumeister and C. Tschierske, *J. Am. Chem. Soc.*, **2006**, *128*, 3051.
16. C.H. Lai, Y.-C. Ke, J.-C. Su, C. Shen and W.-R. Li, *Liq. Cryst.*, **2002**, *29*, 915.
17. D. Demus, J. Goodby, G. W. Gray, H. -W. Spiess and V. Vill, "Handbook of Liquid crystals, Fundamentals", 1998, vol. 1, p. 636.

