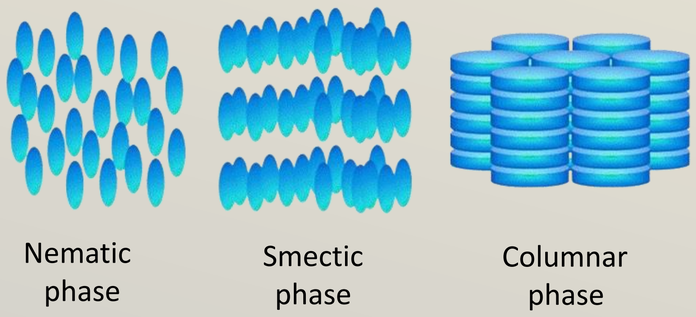
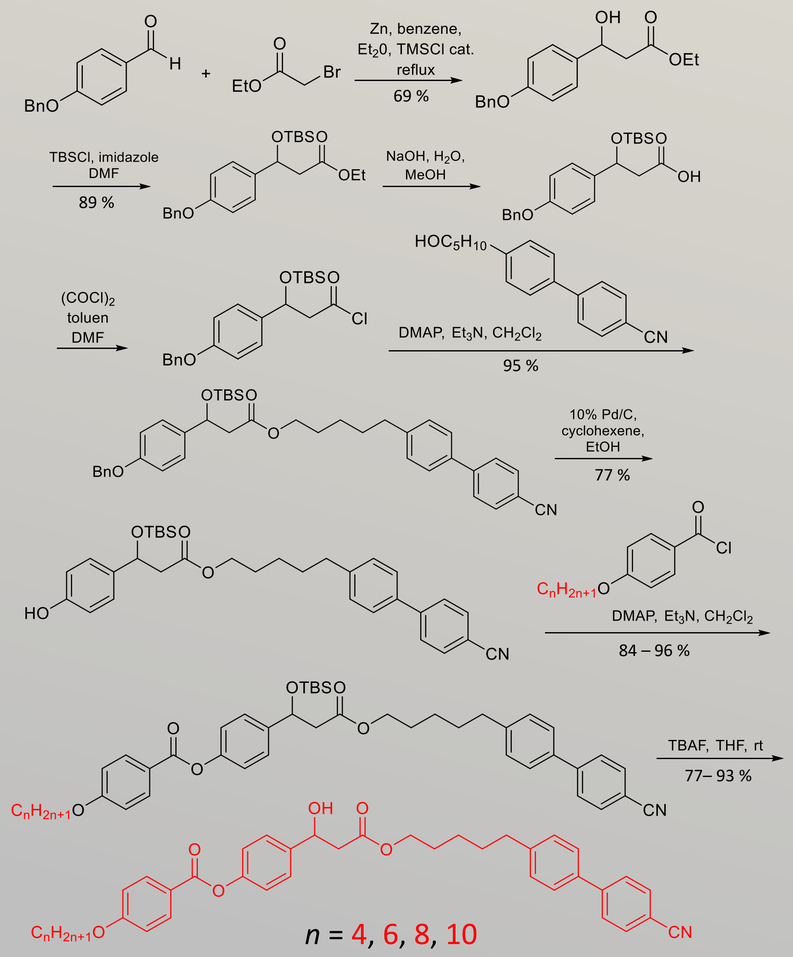
THE EFFECT OF TERMINAL CHAIN LENGTH ON MESOGENIC PROPERTIES OF BENT-SHAPED DIMERS

Aleksandra Šimanović,* Irena Dokli, Andreja Lesac
Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Bijenička cesta 54, Zagreb, Croatia
*asimanov@irb.hr

Liquid crystals are organic molecules with properties between solid crystal and conventional fluid: the fluidity of the liquid and some structural and optical properties of crystals. According to temperature and physical properties, the liquid-crystalline phase occurs between solid and liquid and therefore is called the mesophase and the compounds mesogenic compounds. Liquid crystal molecules can self-organize into different mesophases that exhibit characteristic textures visible under a polarizing microscope. Depending on the arrangement and orientation of molecules in space, smectic, nematic and columnar mesophases are most often distinguished [1]. The formation of mesophases is primarily governed by the shape of the molecule; bent-shaped dimers are particularly interesting because they can form helical structures without chirality at the molecular level [2]. In order to examine the structure-property relationship, bent-shaped dimers that consist of two mesogenic units connected by a flexible odd spacer and differ in the length of the terminal chain were synthesized. Increasing the length of the terminal chain can influence the formation of the smectic phase [3]. The mesogenic properties of the prepared dimers were investigated.



SYNTHESIS

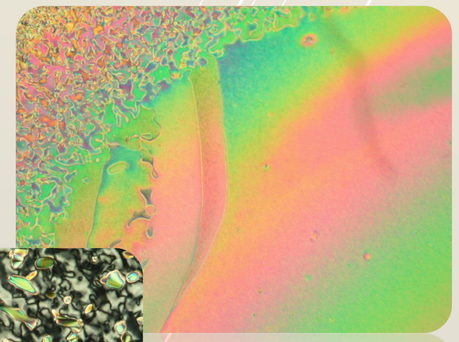


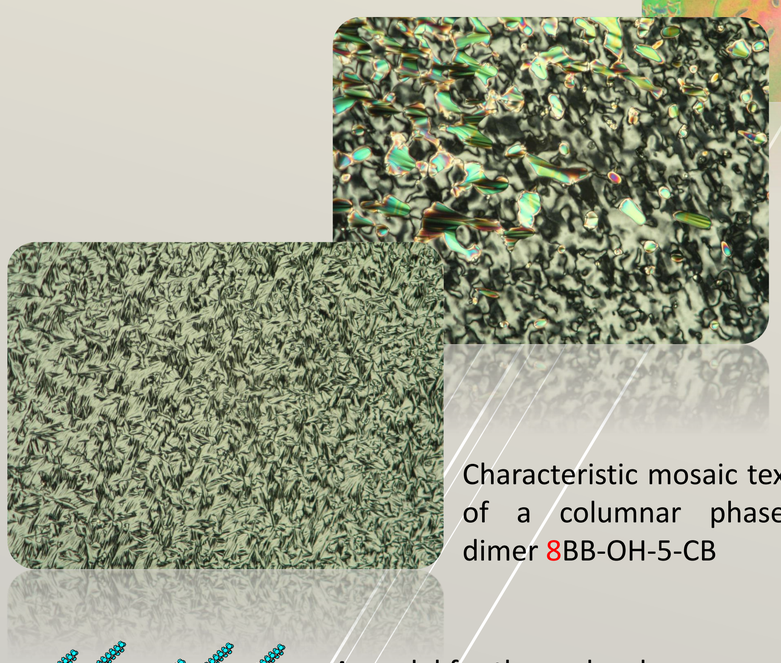
MESOMORPHIC BEHAVIOUR

Dimer	Transition temperatures (°C) and associated enthalpies (kJ mol^{-1})
n = 4; 4BB-OH-5-CB	Cr[a] • 73 (SmC_A • 34 • N • 49) • I 25,97 0,25 0,05
n = 6; 6BB-OH-5-CB	Cr • 65 (SmC_A • 35 • N • 49) • I 26,83[b] 1,86 0,05
n = 8; 8BB-OH-5-CB	Cr • 71 (Col_r • 36 • SmC_A • 46 • N • 55) • I 36,00 0,07 2,71 0,07
n = 10; 10BB-OH-5-CB	Cr • 72 (Col_r • 54 • N • 59) • I 35,34 4,72 0,10

Cr: crystalline phase; SmC_A: smectic C_A phase; N: nematic phase; Col_r: rectangular columnar phase; I: isotropic liquid; (): monotropic phase, obtained on cooling; [a]: crystalline phase obtained on cooling at 24 °C, [b]: combined enthalpies, Cr – Cr transition at 60 °C.

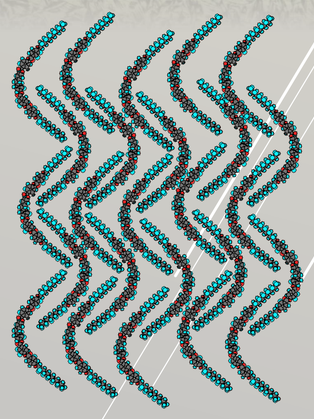
Characteristic marble texture of a nematic phase of dimer 4BB-OH-5-CB





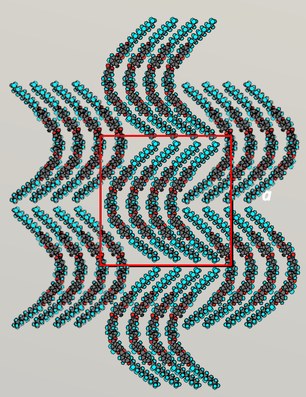
Characteristic fan-shaped and *schlieren* textures of a smectic C_A phase of dimer 8BB-OH-5-CB

Characteristic mosaic texture of a columnar phase of dimer 8BB-OH-5-CB



A model for the molecular packing in the anticlinic smectic C phase

A model for the molecular packing in the rectangular columnar phase



CONCLUSION

To study the structure-property relations, bent-shaped dimers with different lengths of the terminal chain (n = 4, 6, 8, 10) have been synthesized. All dimers exhibit mesomorphic behaviour.

The shorter homologues (*n* = 4, 6) display a monotropic nematic and intercalated SmC_A phase.

Higher homologues (*n* = 8, 10) additionally display a texture characteristic of a columnar phase.

If the terminal chains are significantly longer than the spacer chain (n = 8, 10), terminal chains and the spacer can segregate and form a more highly ordered columnar phase.

REFERENCES

[1] P. J. Collings, M. Hird, *Introduction to Liquid Crystals*, Taylor & Francais, London, 1997.
[2] J. W. Goodby, P. J. Collings, T. Kato, C. Tschierske, H. F. Gleeson, P. Raynes, *Handbook of Liquid Crystals: 8 volume set*, Wiley-VCH Verlag GmbH & Co. KGaA, 2014.
[3] C. T. Imrie, *Liq. Cryst*. **33** (2006) 1449–1454.

ACKNOWLEDGEMENT: The authors thank the Croatian Science Foundation [grant ref. IP- 2019-04-7978] for financial support.