INFLUENCE OF THE SPACER LENGTH ON MESOGENIC PROPERTIES OF CHIRAL LIQUID CRYSTAL DIMERS

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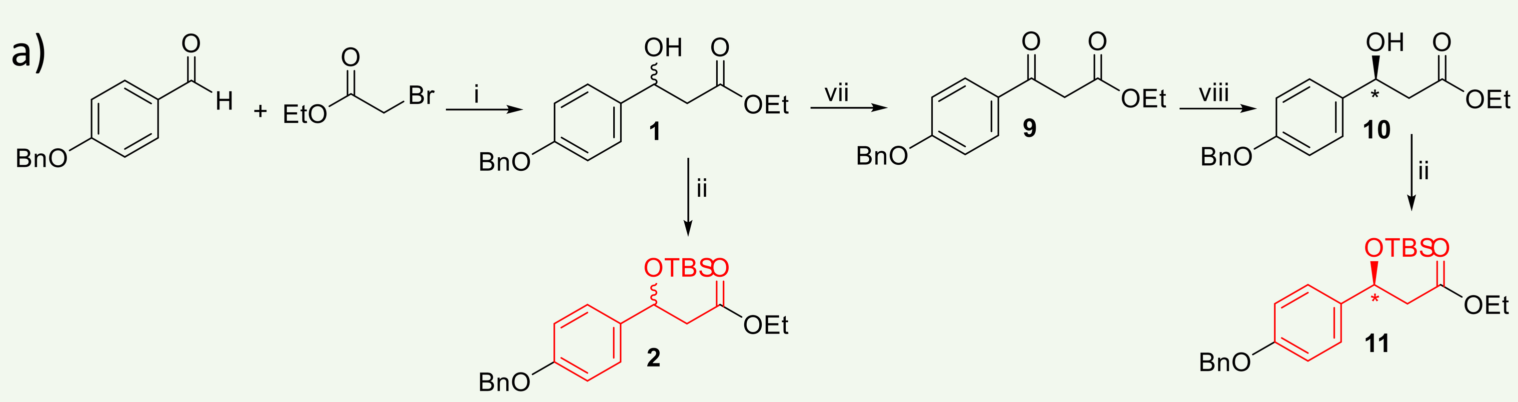
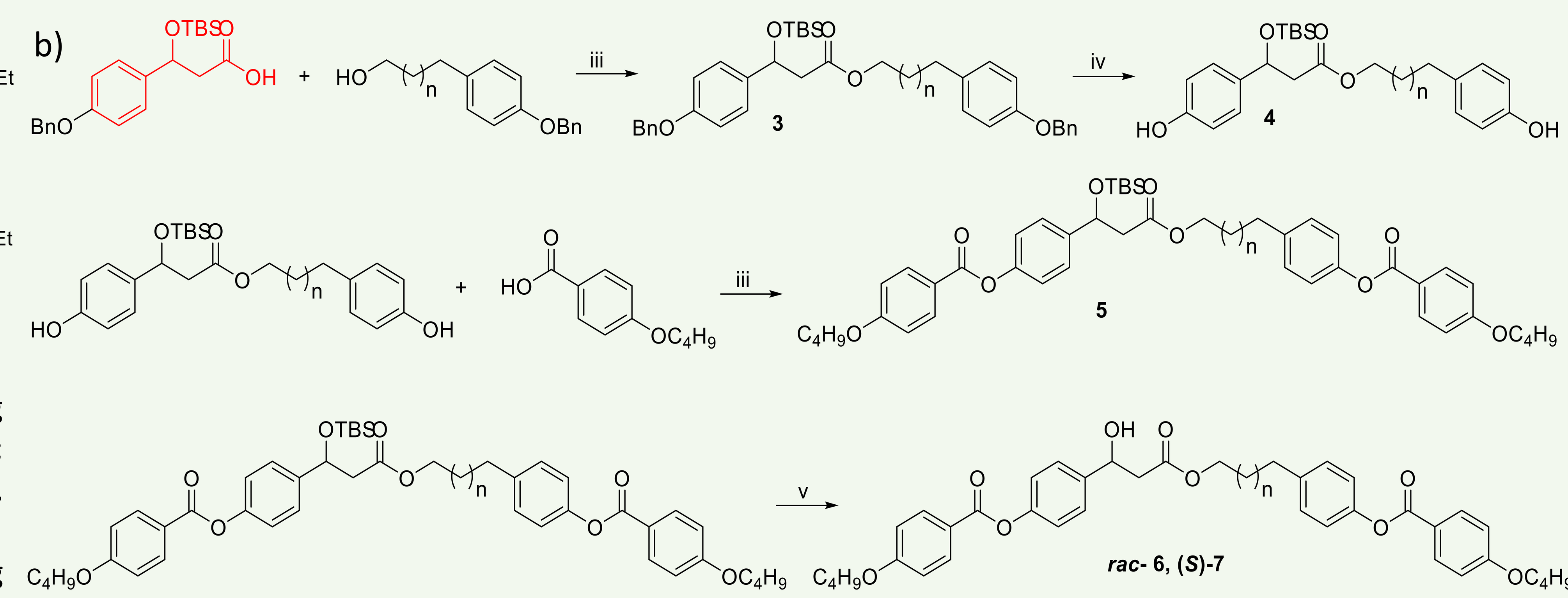
Liquid crystal (LC) dimers consist of molecules containing two mesogenic units connected by a flexible spacer. This class of materials exhibits interesting phase behavior as the shape of bent molecules can facilitate the formation of degenerate helices. Also, the presence of a chiral center in such dimers can have various consequences since chirality may cause a formation of an intrinsic helical structure. [1] It is known that parity and the length of the spacer strongly affect the transitional behavior and molecular bending. [2]. Here we describe the impact of molecular chirality and the influence of the spacer length on LC phases of the bent-shaped dimers. Characteristic textures are examined with polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) is used for determination of transition temperatures and accompanied enthalpy changes.

Synthesis





a) Synthetic pathway of racemic and chiral phenyl-3-hydroxy propanoate building block: i) Zn, TMSCl, benzene, Et_2O, 2 h, r.t.; ii) TBSCl, imidazole, DMF, 24 h, r.t.; vii) Jones reagent, acetone, 30 min, r.t.; viii) Ru cat, ligand, HCOOC/Et_3N=5/2, DMF, 40 °C, 20 h.

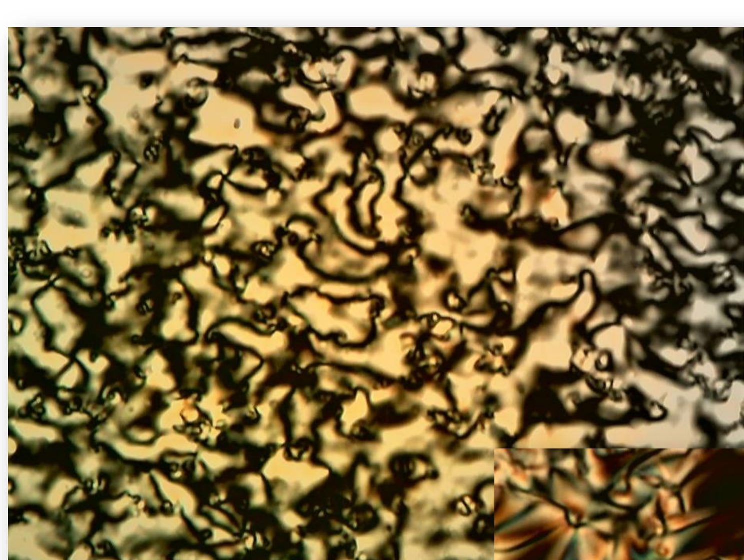
b) Synthesis of a racemic mixture, chiral molecule (*S*)-**7** is synthesized following the same synthetic route: iii) 1. $(COCl)_2$, toluene, DMF, 1.5 h, r.t., 2. DMAP, ET_3N, CH_2Cl_2, 2 h, r.t.; iv) Pd/C, cyclohexene, EtOH, 24 h, reflux; vi) TBAF, THF, 3.5 h, r.t.

Mesomorphic behaviour

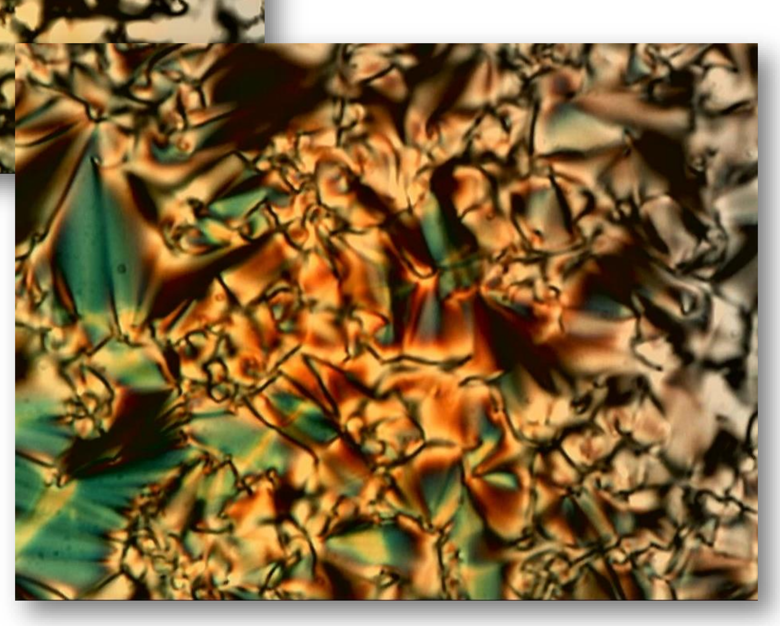
Table 1. Transition temperatures and enthalpies in italics for dimers **6** and **7**.

n	Dimer	Transition temperatures (°C) and enthalpies (kJ mol^{-1})
1	*rac*-6	Cr • 93 (SmC_A • 46) • I 31.46 5.66[a]
3	(*S*)-7	Cr[c] • 109 (SmA* • 40 • TGBA • 41 • BP • 49) • I 52.99 3.70[a], [b] 0.23[a],[b] 0.07[a]

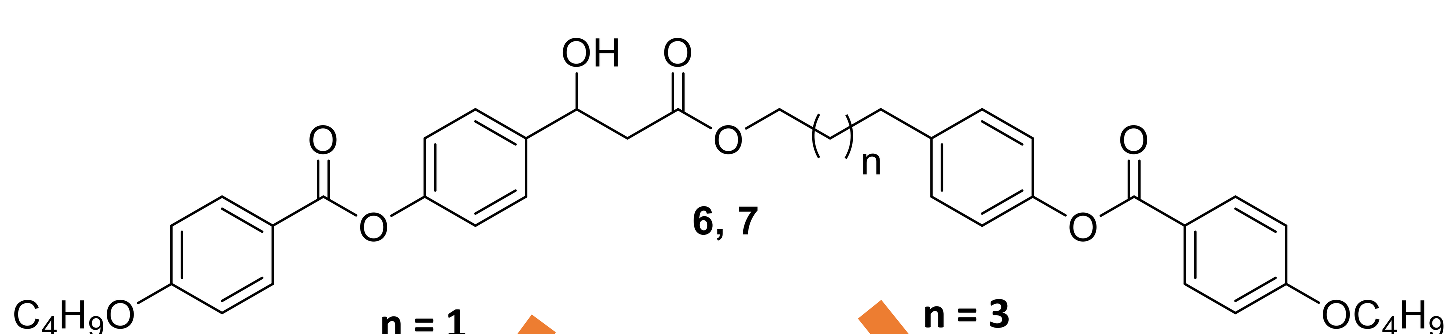
Cr: crystalline phase; SmC_A: anticlinic smectic C phase; SmA*: chiral smectic A phase; TGBA: twist grain boundary A phase; BP: blue phase; I: isotropic liquid; (): monotropic phase; [a]: obtained on cooling; [b]: combined enthalpies; [c]: glassy state obtained on cooling, Tg = 20 °C, *Cp* = 0.11 J/g °C.



Schlieren texture of the SmC_A phase.



Fan-shaped texture of the SmC_A phase



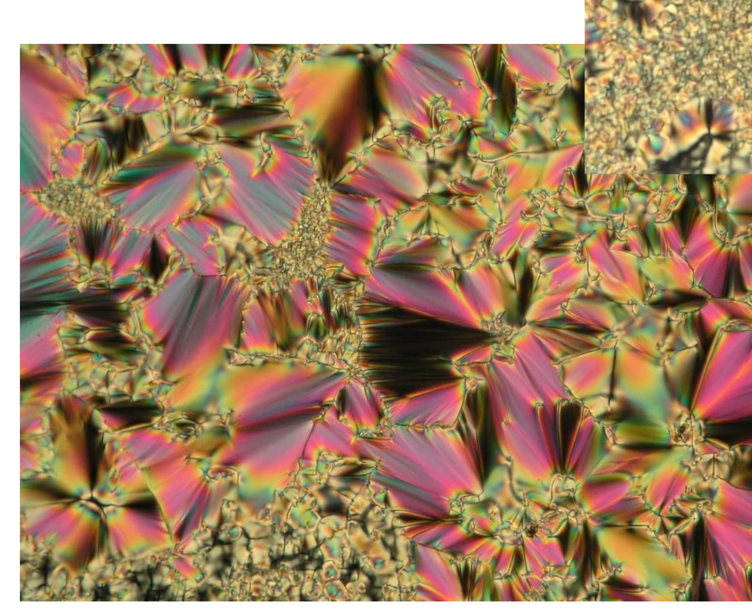
6, 7

n = 1

***rac*-6**

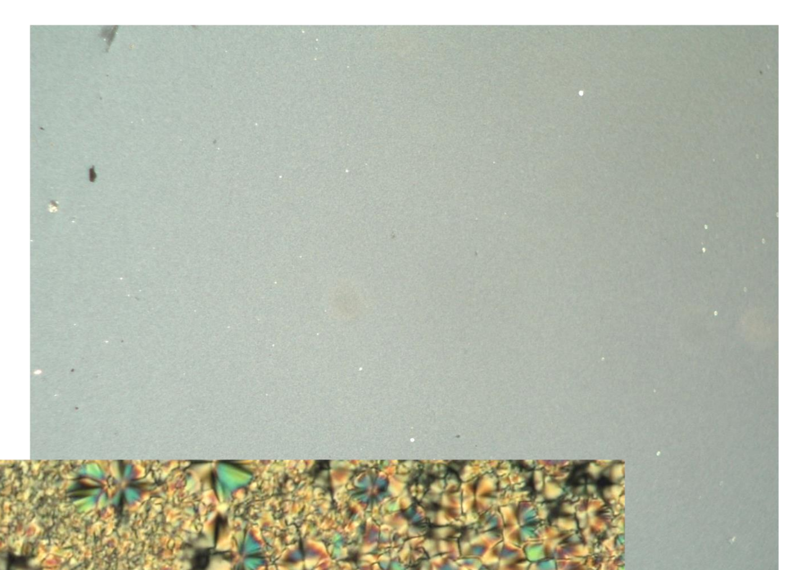
n = 3

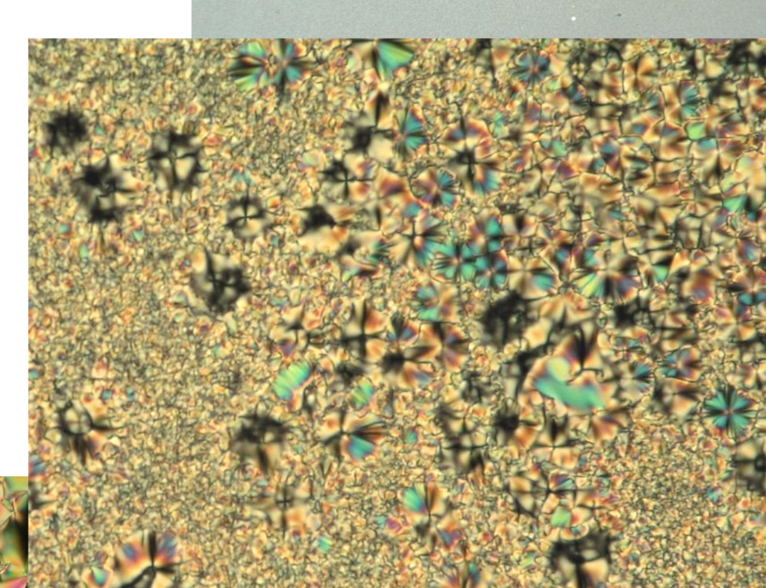
(*S*)-7



Fan-shaped texture of the SmA* phase

Texture of an unknown blue phase





Transition between possible TGBA phase and SmA* phase

Conclusion

- The targeted molecules *rac*-**6** and (*S*)-**7** were synthesized using the same convergent approach
- The *rac*-**6** exhibits a monotropic SmC_A phase with characteristic schlieren and fan-shaped texture
- The (*S*)-**7** exhibits chiral smectic A phase with characteristic fan-shaped texture, unkonwn BP and TGBA phase which is yet to be determined
- Extension of the spacer length results in destabilization of smectic phase
- Introducing a chiral center leads to polymorphism
- Synthesis of a chiral molecule with n = 5 is in progress

References

[1] H. S. Kitzerow, C. Bahr, Chirality in Liquid Crystals, Springer, New York, 2001.

[2] D. A: Paterson, et al. *Soft Matter* **12** (2016) 6827-6840.

Acknowledgement: The authors thank the Croatian Science Foundation [grant ref. IP- 2019-04-7978 and DOK-2020-01] for financial support