A NOVEL PHENYL-3-HYDROXY PROPIONIC ACID BUILDING BLOCK FOR BENT-SHAPED LIQUID CRYSTALLINE DIMERS

Antonija Ožegović, Irena Dokli, Andreja Lesac

Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia.

The chiral LC structures were mainly achieved by connecting cholesterol mesogenic unit[1] or incorporating a methyl group.[2] The structural variations of materials with a cholesterol mesogenic unit are limited what diminishes detail investigation of structure-property relations and incorporation of the methyl group in the terminal chain or spacer resulted in branching and suppressed LC phase formation in dimers.[3] To investigate structure–property relations we focused on developing the synthetic pathway to dimers incorporating 3-hydroxy propionic ester moiety as a source of chirality. The chiral carbon atom is baring the hydroxy group which forms a hydrogen bond with the neighbouring carbonyl group and thus reduces the conformational freedom of the spacer. Furthermore, it is less spacious than the methly group, therefore allows for better intermolecular interactions.

Synthesis

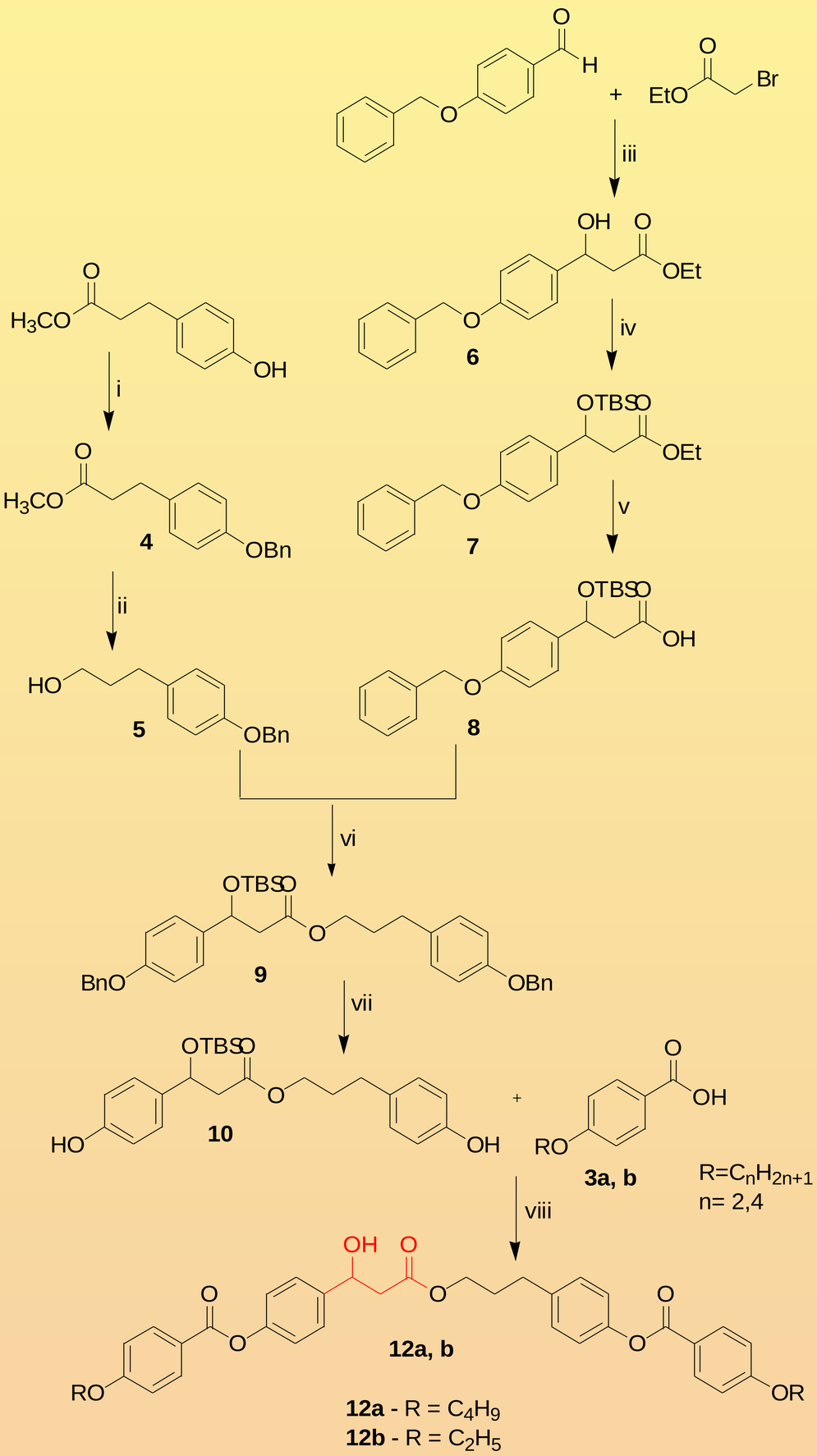


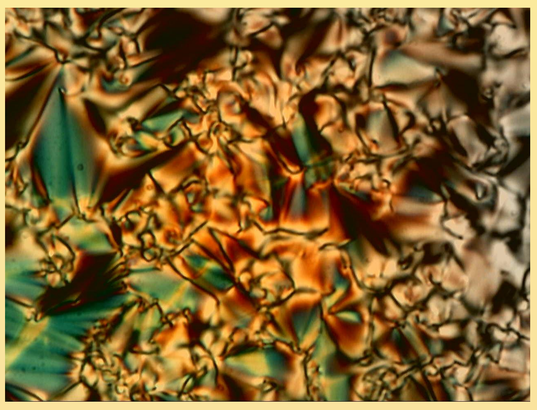
Figure 1. Synthesis of a racemic mixture of targeted molecules **12**; i) BnBr, K_2CO_3, acetone, 24h, 70°C; ii) $LiAlH_4$, Et_2O, 24h, r.t.; iii) Zn, TMSCl, benzene, Et_2O, 2h, r.t.; iv) TBSCl, imidazole, DMF, 24h, r.t.; v) NaOH, H_2O, MeOH, THF, 3h, r.t.; vi) 1. $(COCl)_2$, toluene, DMF, 1.5h, r.t., 2. DMAP, ET_3N, CH_2Cl_2, 2h, r.t.; vii) Pd/C, cyclohexene, EtOH, 24h, 100°C; viii) 1. $(COCl)_2$, toluene, DMF, 1.5h, r.t., 2. DMAP, ET_3N, CH_2Cl_2, 2h, r.t., 3. TBAF, THF, 3.5h, r.t.

Mesomorphic behaviour

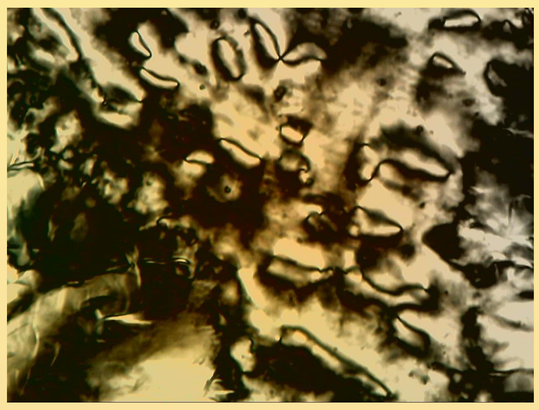
Table 1. Transition temperatures and enthalpies in italics for dimers **12**.

Dimer	Transition temperatures (°C) and enthalpies (kJ mol^{-1})
12a	Cr • 93 (SmC_A • 46) • I *31.46* *5.66*[a]
12b	Cr • 98 • I *44.75*

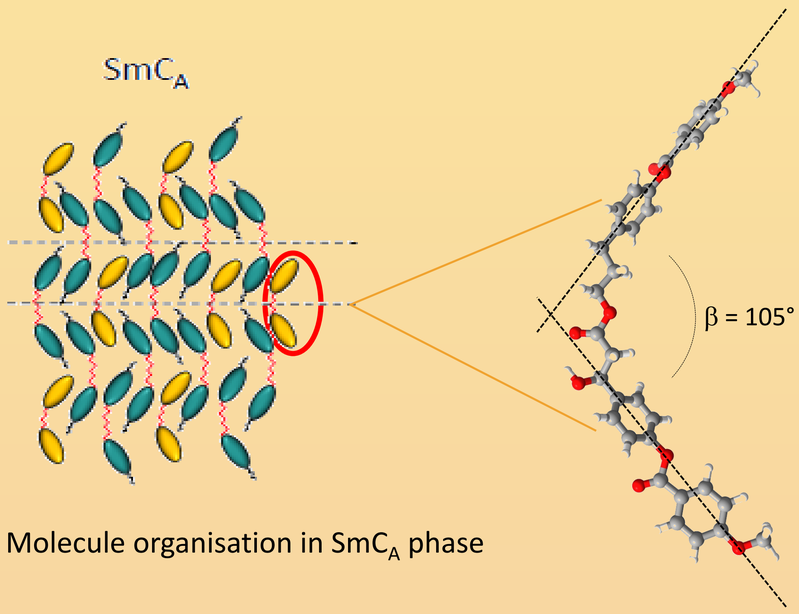
Cr: crystalline phase; SmC_A: anticlinic smectic C phase; I: isotropic liquid; (): monotropic phase; [a]: obtained on cooling.



Fan-shaped texture of the SmC_A phase



Schlieren texture of the SmC_A phase.



Molecule organisation in SmC_A phase

Geometry and bending angle

Conclusion

- The targeted molecules *rac*-**12a, b** were synthesized using a convergent approach
- The *rac*-**12a** exhibits a monotropic SmC_A phase, while **12b** shows only direct transition from crystal to isotropic liquid
- The targeted molecules are strongly bent-shaped
- The small bending angle in most extended form and low flexibility prevents the formation of the nematic (N) phase
- Further work includes modification of molecule structure in order to stabilize mesogenic properties and facilitate the formation of the N phase:
  - elongation of the spacer length in order to extend the bending angle and flexibility of the molecule
  - increasing the polarizability of the mesogenic unit introducing biphenyl group

References

[1] T. Donaldson, H. Staesche, Z. B. Lu, P. A. Henderson, M. F. Achard, C. T. Imrie, *Liquid Crystals* **2010**, *37*, 1097–1110.
[2] L. Dong, Z. Xu, H. Tao, X. Chen, J. Hu, D. Yao, M. Tian, *Liquid Crystals* **2018**, 1–12.
[3] R. J. Mandle, J. W. Goodby, *RSC Advances* **2018**, *8*, 18542–18548.

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