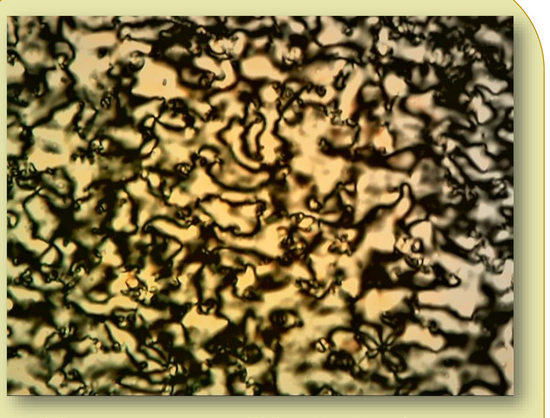
THE EFFECT OF SPACER LENGTH ON MESOGENIC PROPERTIES OF BENT-SHAPED DIMERS

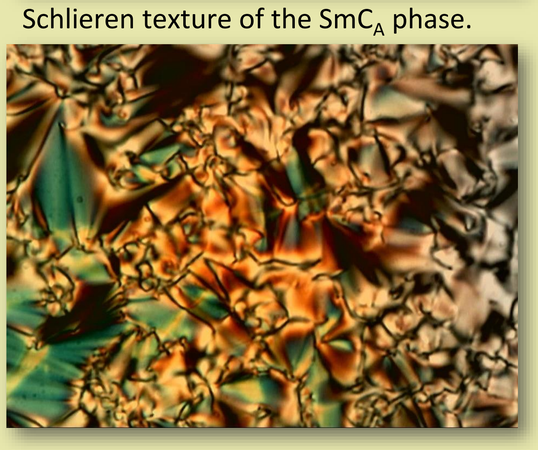
Antonija Ožegović, Irena Dokli, Andreja Lesac

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

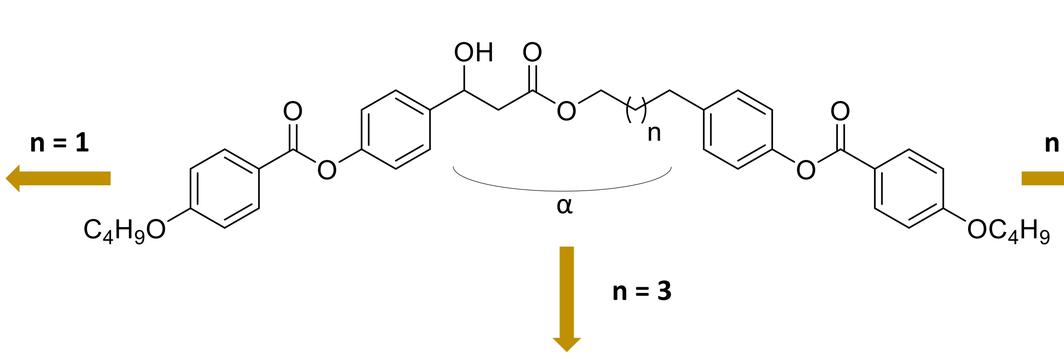
Liquid crystal (LC) dimers consist of molecules containing two mesogenic units connected by a flexible spacer. It is known that parity and the length of the spacer strongly affect the transitional behavior and molecular bending [1]. In dimers with an odd spacer length, mesogenic units are inclined to each other, resulting in a bent-shaped geometry of the molecule, and such dimers are particularly interesting because they can facilitate the formation of degenerate helices [2]. The first example of such behaviour is the twist-bend nematic phase (N_{TB}) [3]. Here we investigate the impact of the spacer length on the formation of the N_{TB} phase in 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.

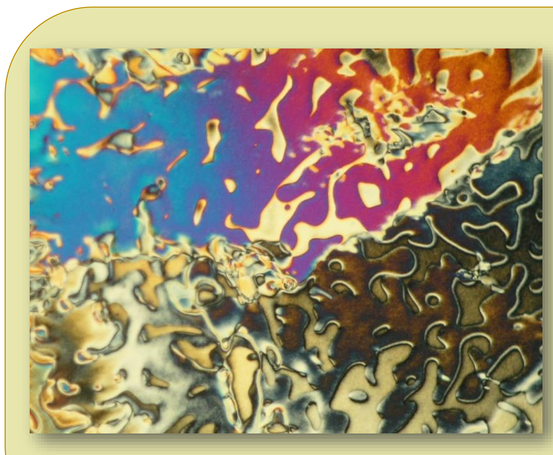


Schlieren texture of the SmC_A phase.

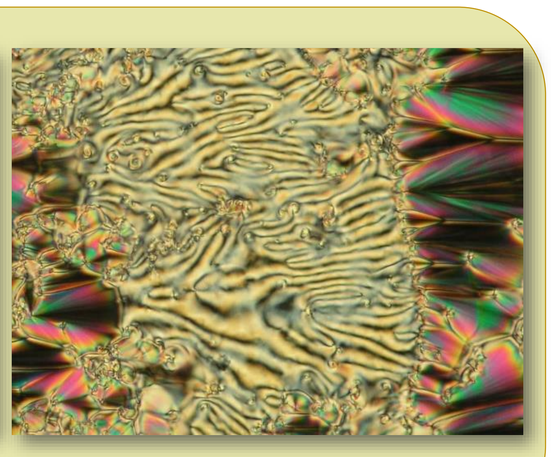


Fan-shaped texture of the SmC_A phase

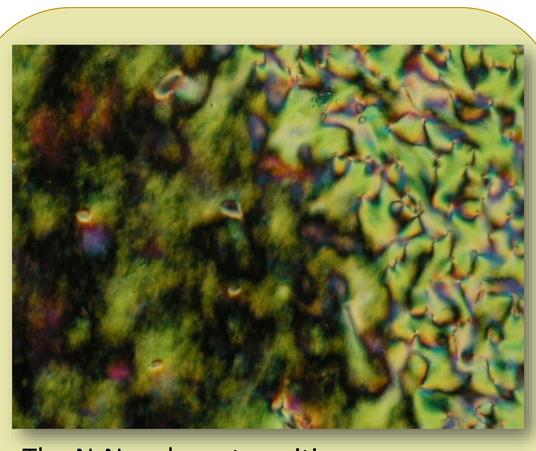




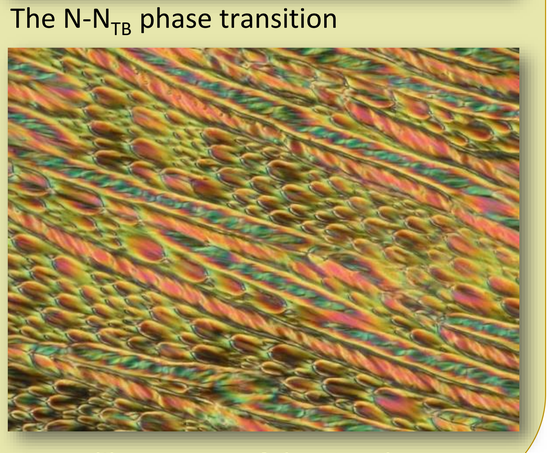
Marble texture of the N phase



Fan-shaped and schlieren texture of the SmC_A phase



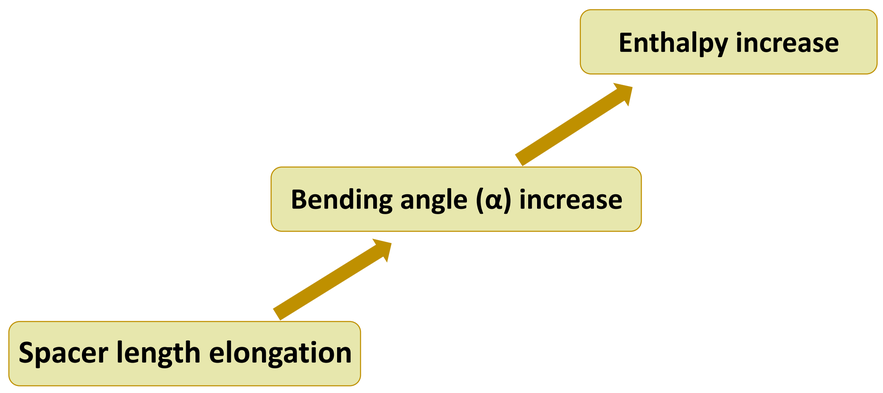
The N-N_{TB} phase transition



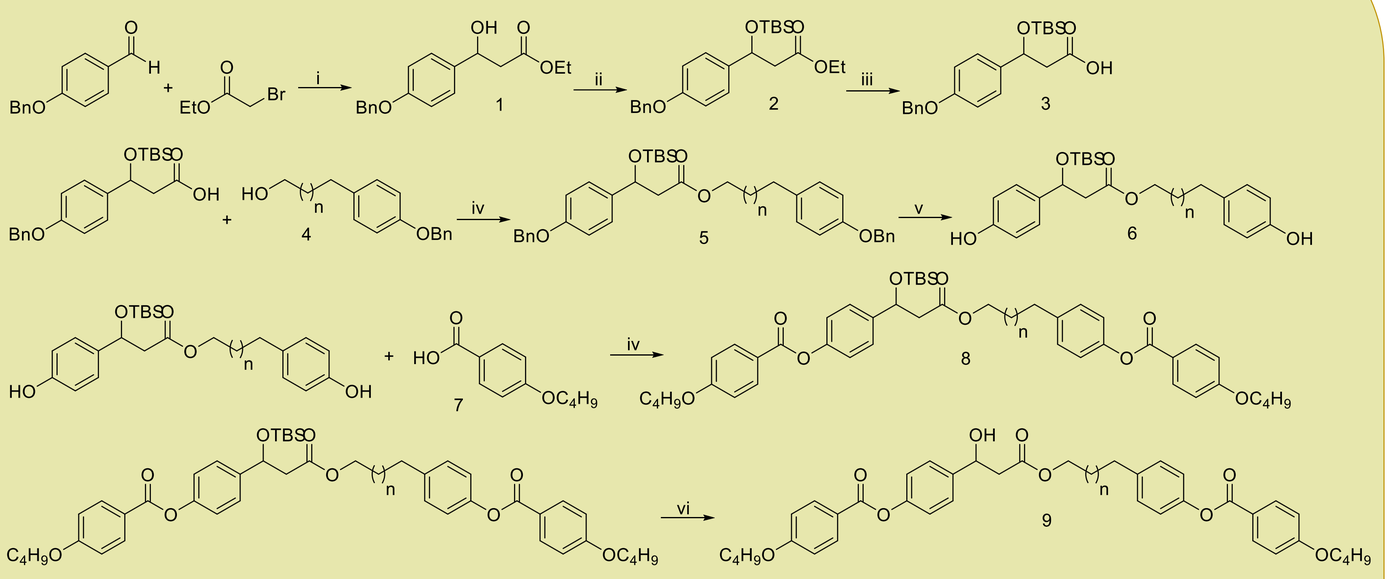
Rope-like texture of the N_{TB} phase

Table 1. Transition temperatures and enthalpies in italics for synthesized dimers

n	Transition temperatures (°C) and enthalpies (kJ mol^{-1})
1	Cr • 93 (SmC_A • 46) • I *31,46* *5,66*
3	Cr • 96 (SmC_A • 42 • N • 49) • I *48,10* *3,90* *0,03*
5	Cr • 72 (N_{TB} • 46 • N • 63) • I *58,60* *0,23* *0,23*



Synthesis



Synthetic pathway of racemic dimers: i) Zn, TMSCl, benzene, Et_2O, 2 h, r.t.; ii) TBSCl, imidazole, DMF, 24 h, r.t., iii) NaOH, H_2O, THF, MeOH, 3h, r.t. iv) 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, 80°C; vi) TBAF, THF, 3.5 h, r.t.

Conclusion

- The targeted molecules were synthesized using convergent approach.
- Elongation of the spacer length results in the change of mesogenic properties: smectic phase is destabilized and N_{TB} phase is formed.
- N_{TB} phase occurs when the bending angle is increased by elongating the spacer length.
- The N-I transition enthalpy increases with elongation of the spacer length (n =3, 4) pointing to the increase of the effective bending angle (α)
- Synthesis of modified dimers, in order to stabilize the N_{TB} phase, is in progress.

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

References

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

[2] M. Cestari, et. al., *J. Mater. Chem*., **21** (2011), 12303.

[3] M. Cestari, et al., *Phys. Rev. E*, **84**, 031704 (2011).