THE HENRYK NIEWODNICZAŃSKI
INSTITUTE OF NUCLEAR PHYSICS
POLISH ACADEMY OF SCIENCES

LIQUID CRYSTALS AS SURFACE TEMPERATURE INDICATORS

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FCB PhD Studies

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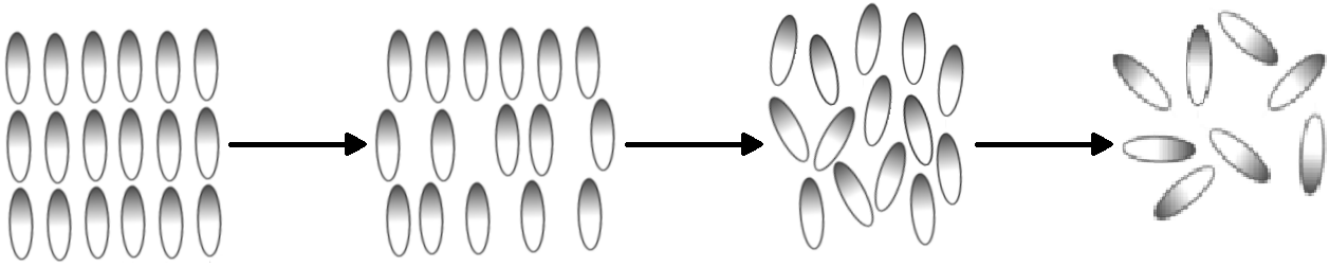
Outline

- Liquid-crystalline state
- LC applications
- (E)-4-((4-alkyloxyphenyl)diazenyl)phenyl alkanoates (*n*OABOOC*m*)
  - Synthesis
  - Phase situation
  - Basic research
- Mixtures (*n*OABOOC*m* + chiral LC)

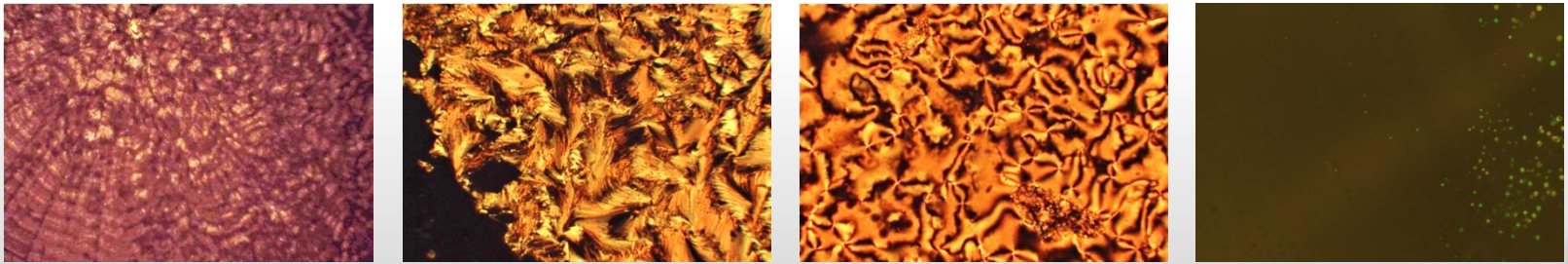
PART I: LIQUID-CRYSTALLINE STATE

Liquid crystals

- The intermediate state between crystal and isotropic liquid phases (i.e. mesophase);
- The ability to flow like liquids (only in a nematic phase);
- Arrangement of molecules (but only partial) and anisotropy of physical properties as in crystals;
- Shape of molecules: rod-like, disk-like, banana-like, etc.



Crystal | Smectic A (SmA) | Nematic (N) | Isotropic Liquid (Iso)

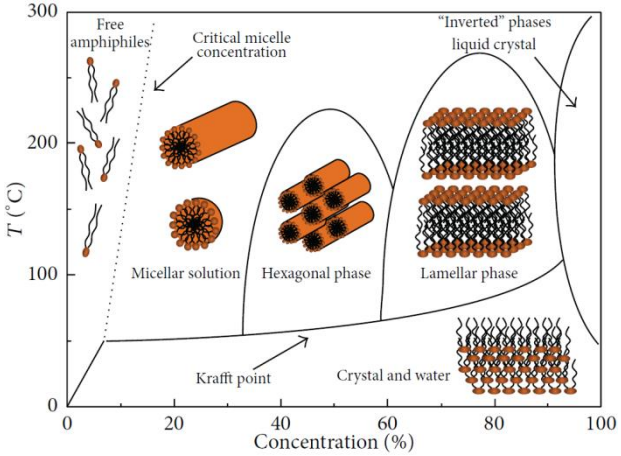


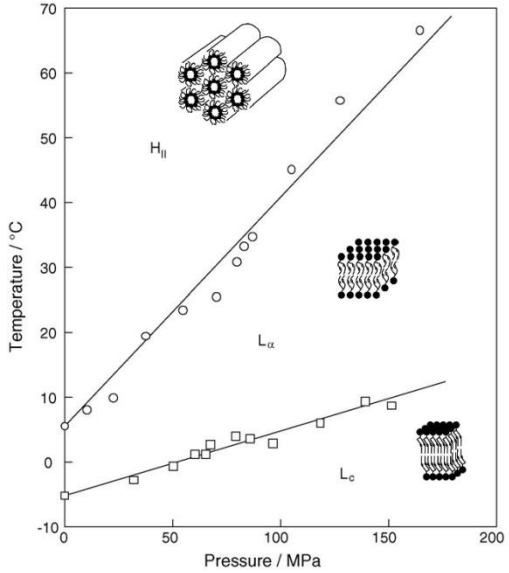
Example of possible phase sequence of liquid crystal compound.

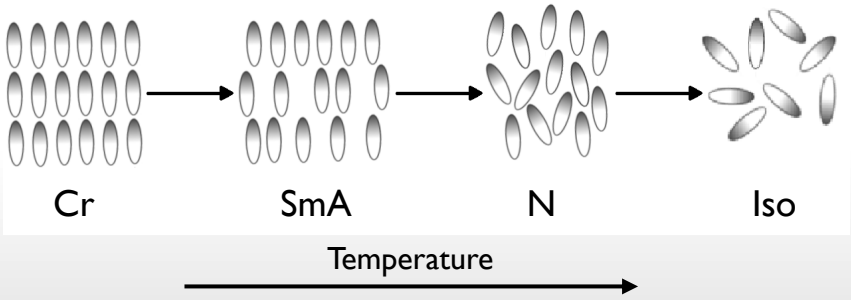
Liquid crystals

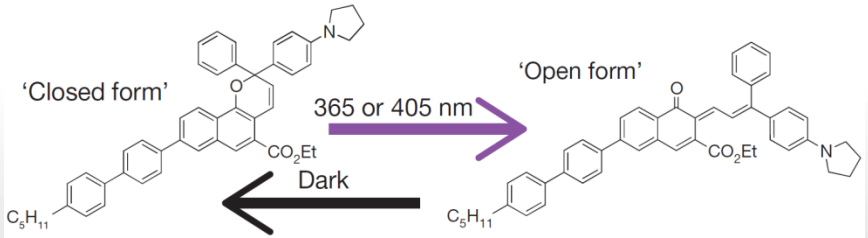
Factors inducing occurrence of LC phases:

- Temperature (thermotropic);
- Solvent (lyotropic);
- Pressure (barotropic);
- UV light (phototropic).





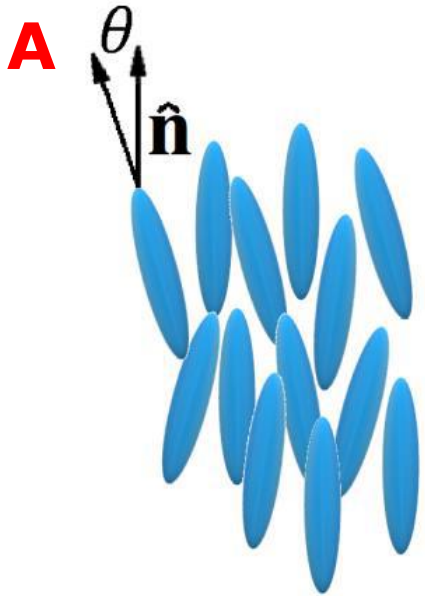


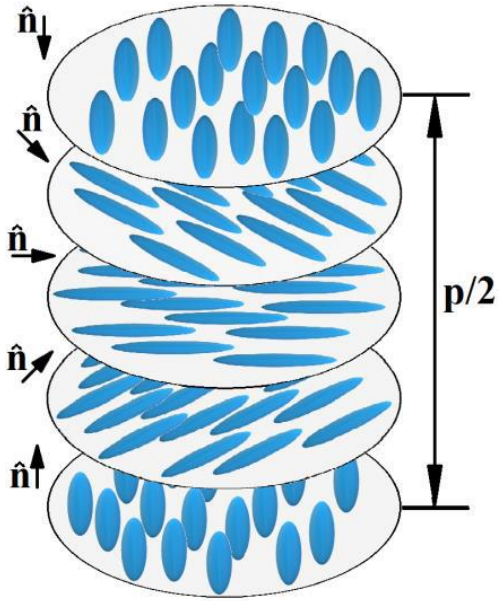


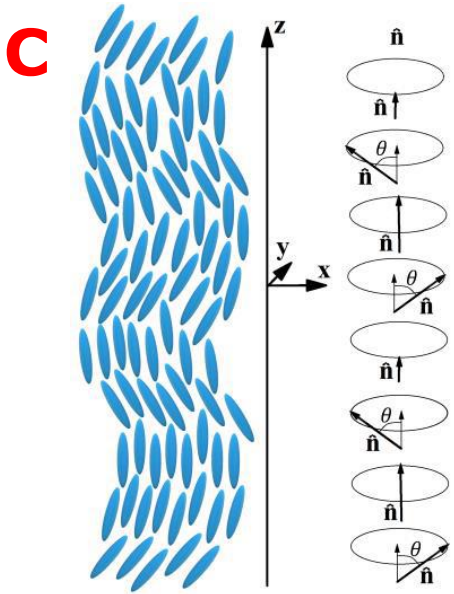
Examples of various mesophase inducing factors.

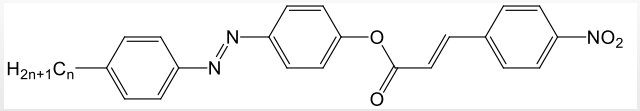
R. Sueyoshi, et al., Colloids and Surfaces B: Biointerfaces, ***50****, 85-88 (2006);*
D. Lombardo, et al., Advances in Condensed Matter Physics, ***2015****, 151683 (2015);*
T. Kosa, et al., Nature, ***485****, 347-349 (2012).*

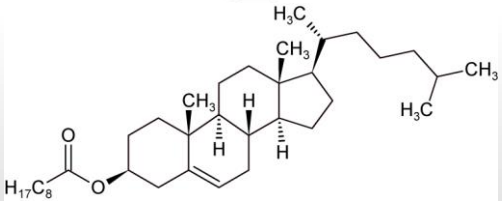
Nematic phases

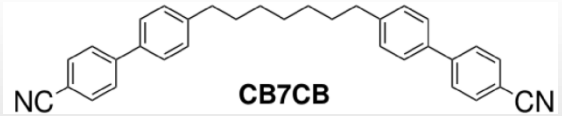






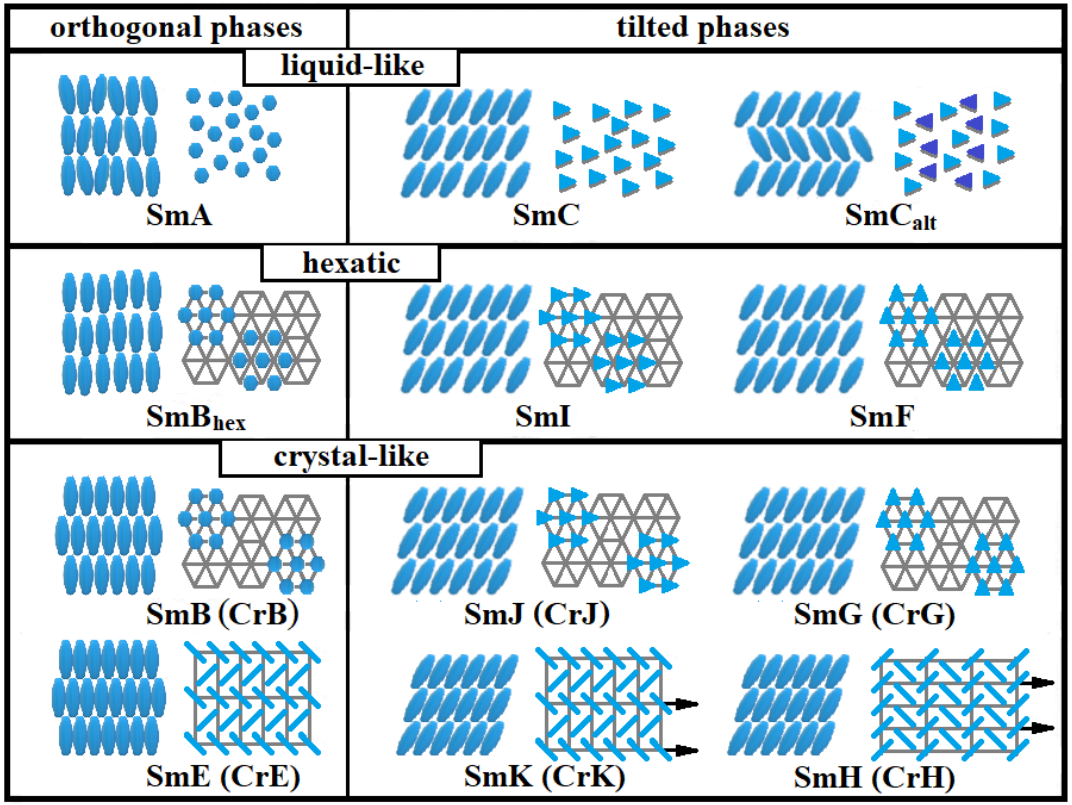






*Nematic phase: (**A**) uniaxial, (**B**) chiral, (**C**) „twist-bend". θ is angle between the long axis of the molecule and the director $\hat{\boldsymbol{n}}$, $\boldsymbol{p}$ – helix pitch.*

Smectic phases



Structures of smectic phases.

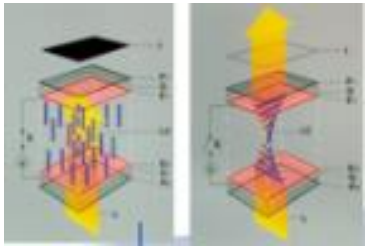
Ordering within single layer:

orientational order

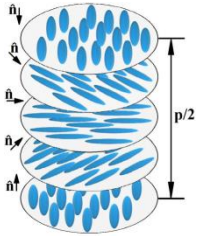
orientational order
a short-range positional order

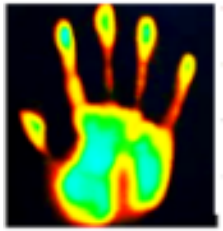
orientational order
a long-range positional order

LC Displays



LC Thermography

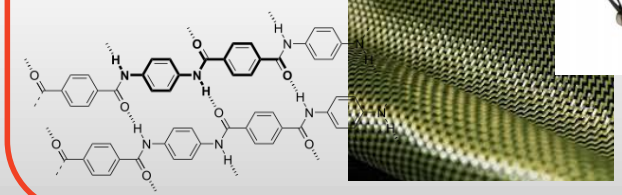




PART II: LIQUID CRYSTAL APPLICATIONS

LC Opto-electronic

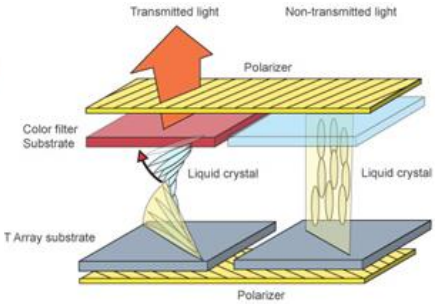
LC Polymer fibers



LC Displays

1968

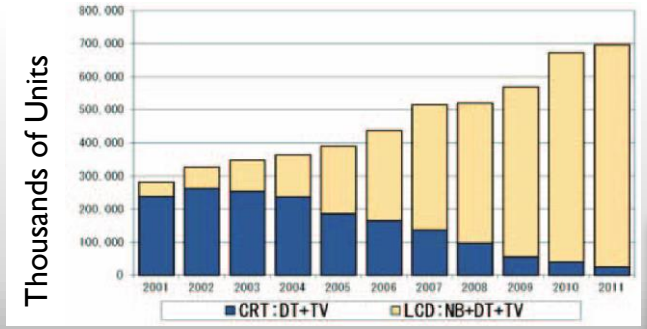
1973



1988

2000s – 2010s

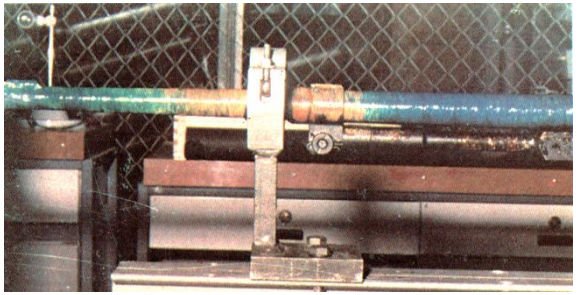
2020s

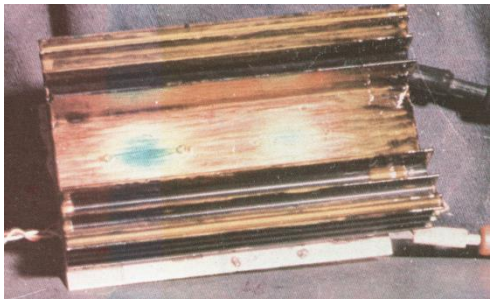


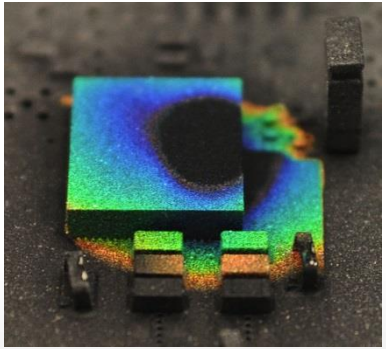
*G. H. Heilmeier, et. al, Proceedings of the IEEE, **56**, 1162 – 1171 (1968);*
https://tftcentral.co.uk/articles/panel_technologies;
H. Kawamoto, The history of liquid crystal display and its industry, IEEE (2012).

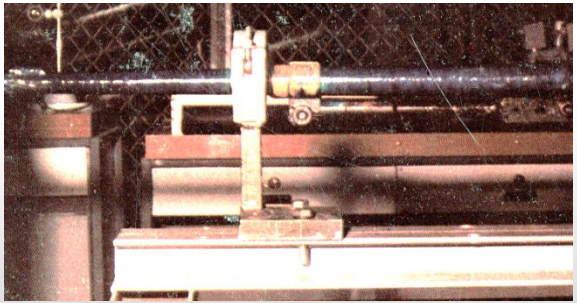
LC Thermography

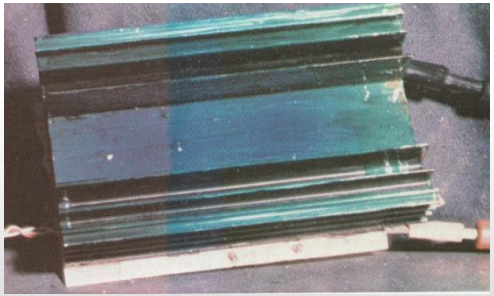
Thermography is a method of imaging temperature. It allows measurement of physical objects temperature and record it in the form of coloured images.





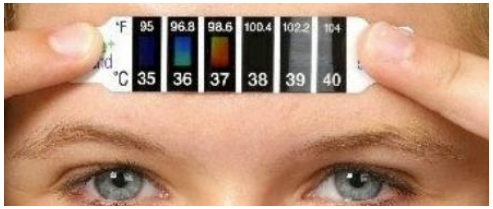


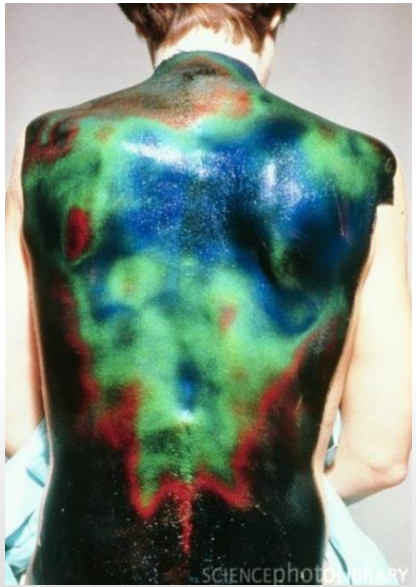




J. Żmija, et. al., Cholesteryczne ciekłe kryształy w detekcji promieniowania, WNT, Warszawa, 1989;
https://www.led-professional.com/products/

LC Thermography



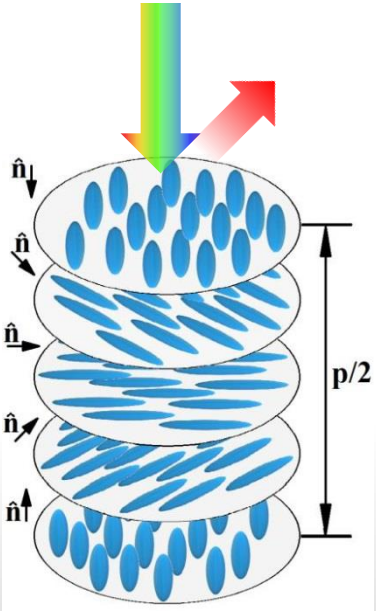


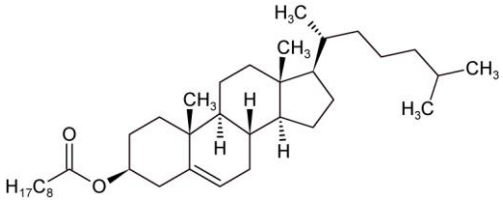
- Detection of any type of cancer is reliable, safe, and does not require ionizing radiation (as in mammography and Breast CT Scanning) or additional contrast agents (as in Magnetic Resonance Imaging).
- This method can be used on patients of all ages.
- Can be used in an early stages of cancer growth, in so-called neoangiogenesis process (the pathologically changing area has to become vascularized). In the area of the lesion, increased tissue temperature is observed. One can prevent of forming a much bigger cancer!
- It can be used as "safe" (without any fluids, etc.), cheap, small and light thermometers.

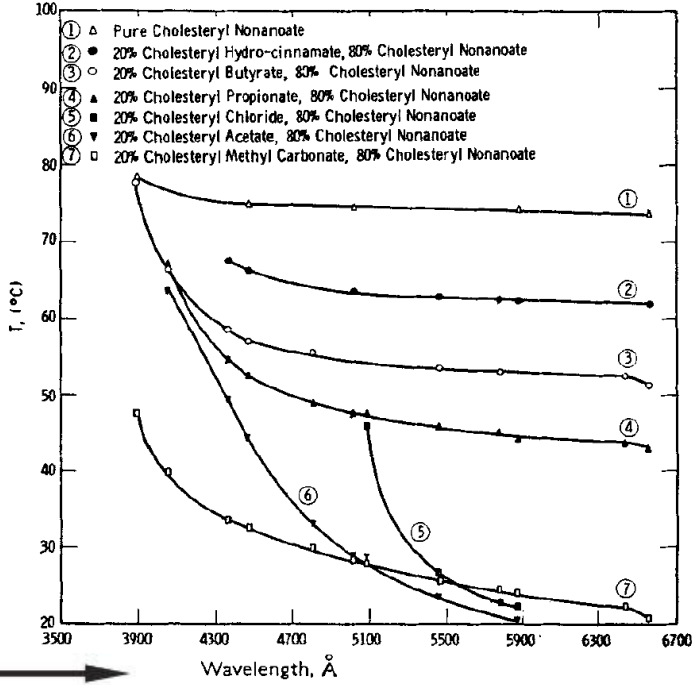
https://www.sciencephoto.com/; https://www.braster.eu/pl

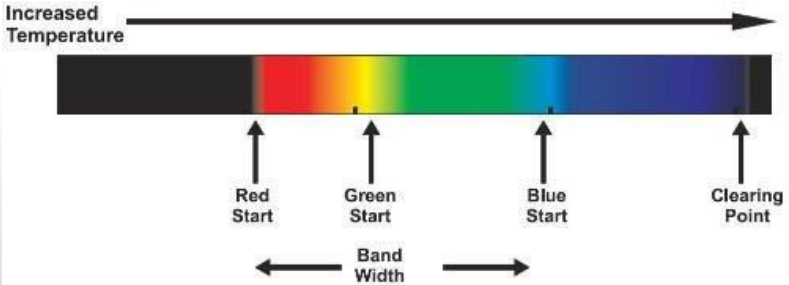
Thermochromic response

Chiral LCs are able to selectively reflect certain wavelengths (as function of temperature) when illuminated by white light. It is connected with change of the pitch.





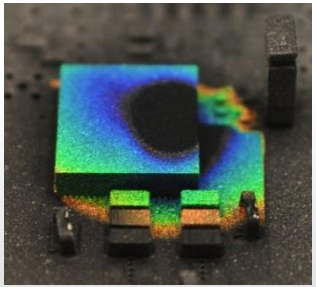




Thermochromic response phenomenon.

*J.L. Fergason, et. al, Molecular Crystals, **1**, 309 – 323 (1966)*

Contact Thermography (LC) vs. Non-Contact Thermography (IR camera)

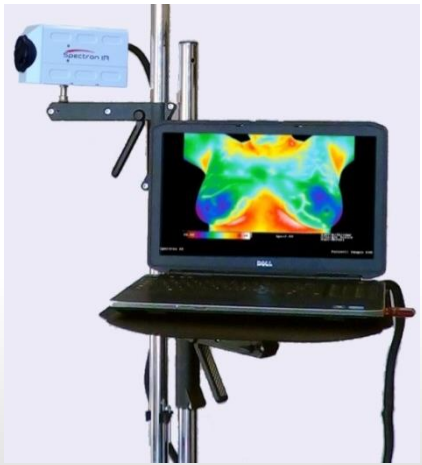


Advantages of LC Thermography:

- Several times cheaper;
- Temperature resolution down to 0.1°C;
- High spatial resolution down to 1 micron;
- Uses visible light;
- Fast response time- around 100ms;
- Can be used to exam/check temperature of:
  - Small objects, such as microchips, processors;
  - Surfaces with various shapes;
  - Objects standing close to heater.

Disadvantages of LC Thermography:

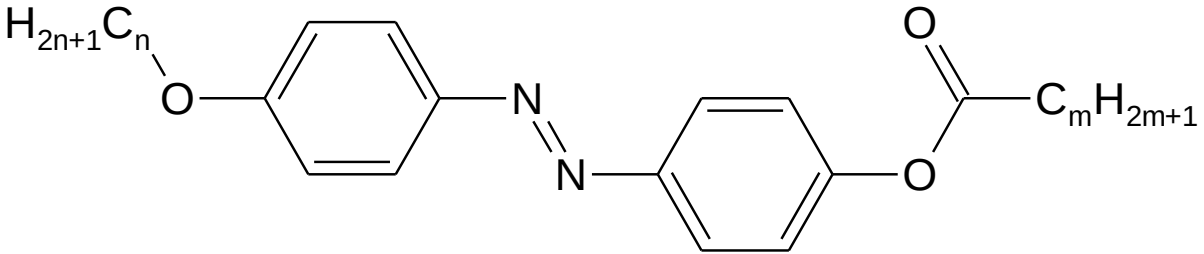
- Has to be spread over the whole surface;
- Layer of black primer is needed;
- Cannot be used to large surfaces, such as houses, windows, etc;
- Requires a stable uniform white light source with no IR or UV components;
- Can be intrusive due to changes in the heat conduction properties
- Works in limited ranges of object's temperature.



https://www.irdistributions.com/medical-infrared-imaging-equipment/; https://jwelectricalltd.co.uk/electrical-services/thermal-imaging/

PART III: *nOABOOCm* COMPOUNDS

*n*OABOOC*m* compounds



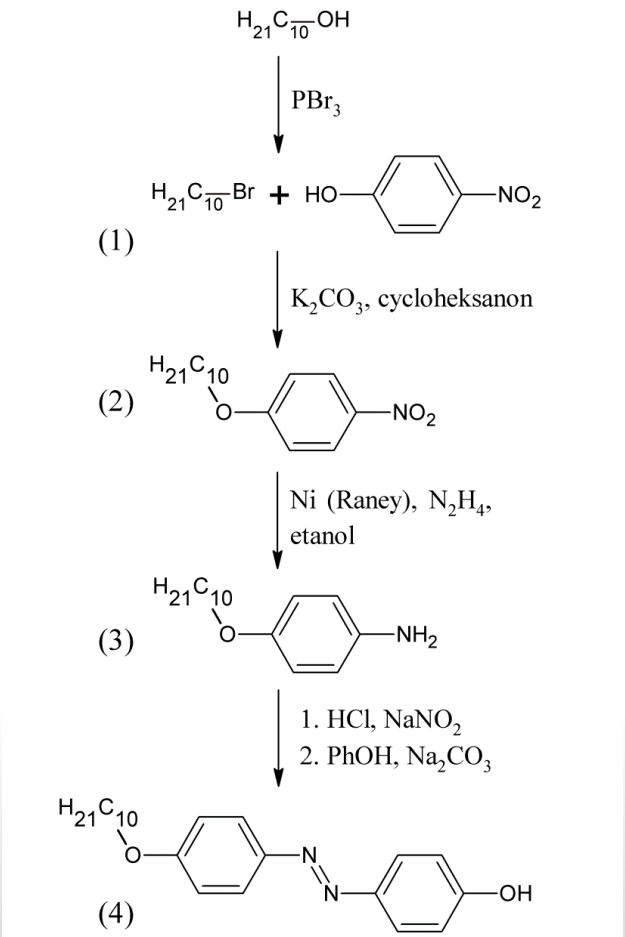
(for *n = 3, 5, 7, 8, 10*) (for *m = 1 - 19*)

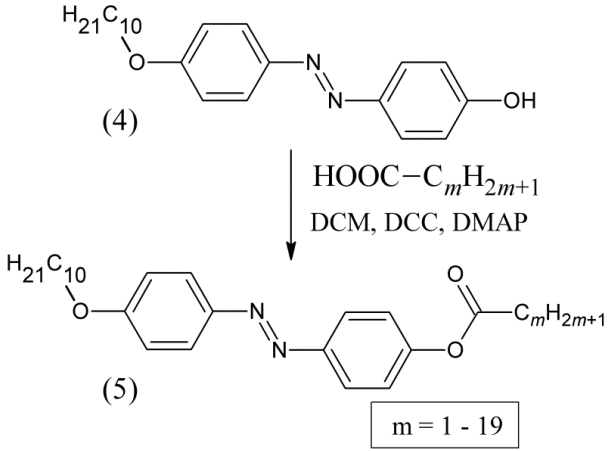
General structure of ***nOABOOCm*** *compounds.*

Total number of synthesized compounds: 94 (74 never described in literature!)

- Liquid-crystalline;
- Azo-dye compounds (yellow – red);
- Photosensitive (UV light).

Synthesis

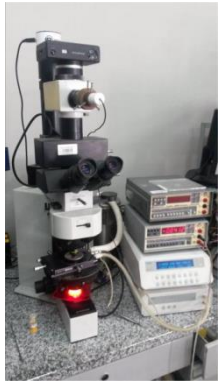




*Scheme of the synthesis of **nOABOOCm** compounds on the example of **10OABOOCm**.*

Basic Research

Polarized Optical Microscopy (POM)



Thermo-optical Analysis (TOA)

Differential Scanning Calorimetry (DSC)

IFJ PAN (NZ35):
POM, DSC, BDS, FTIR, XRD

University of Warsaw:
XRD

University of Wrocław:
TOA, UV-Vis

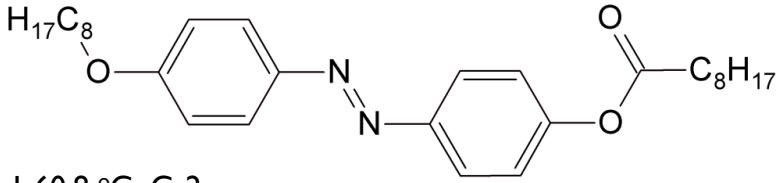
X-Ray Diffraction (XRD)

Broadband Dielectric Spectroscopy (BDS)

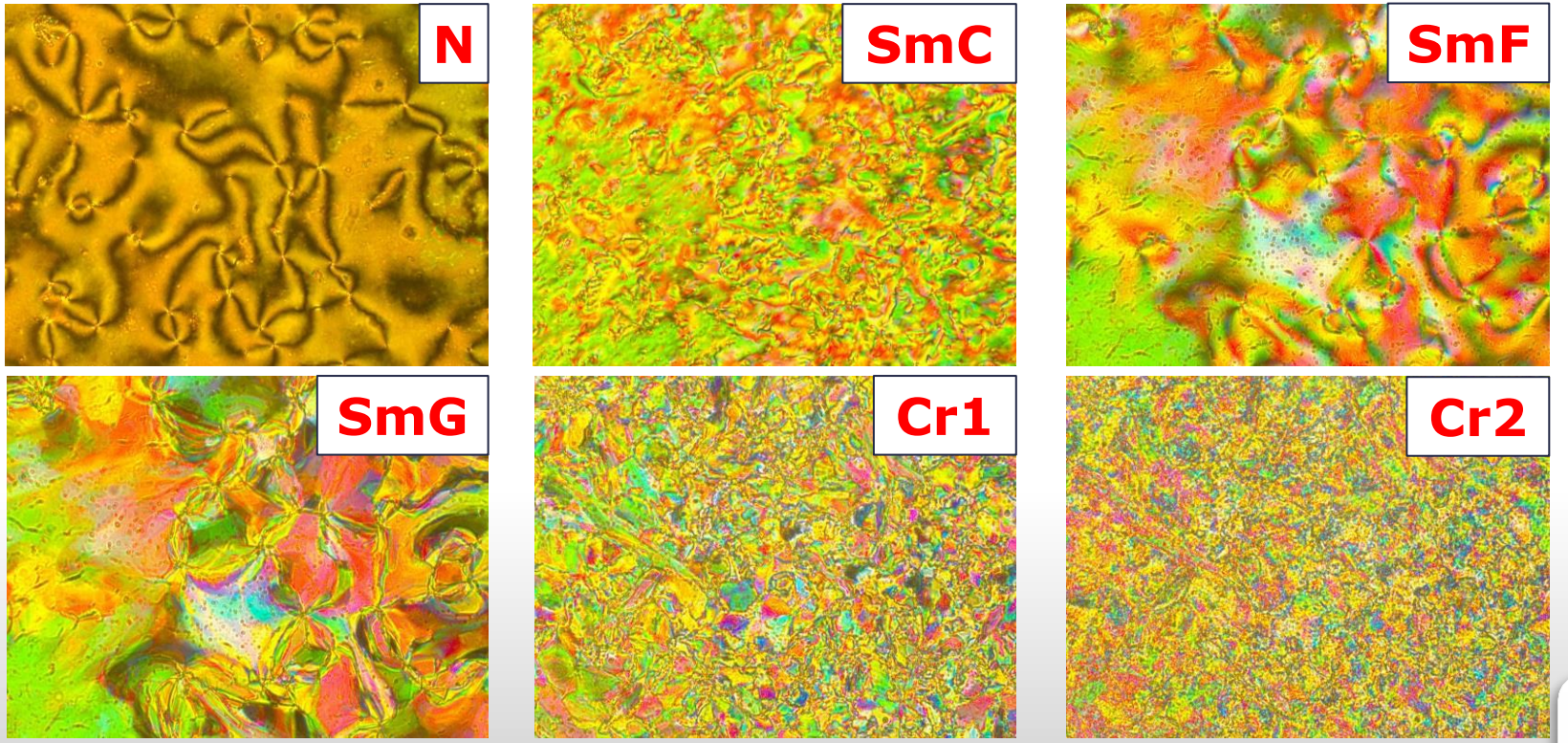
Fourier-Transform Infrared spectroscopy (FTIR)

Visible light and Ultraviolet spectroscopy (UV-Vis)

Textures

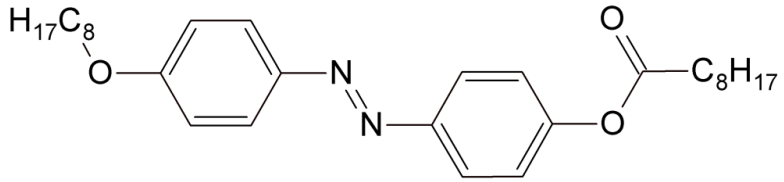


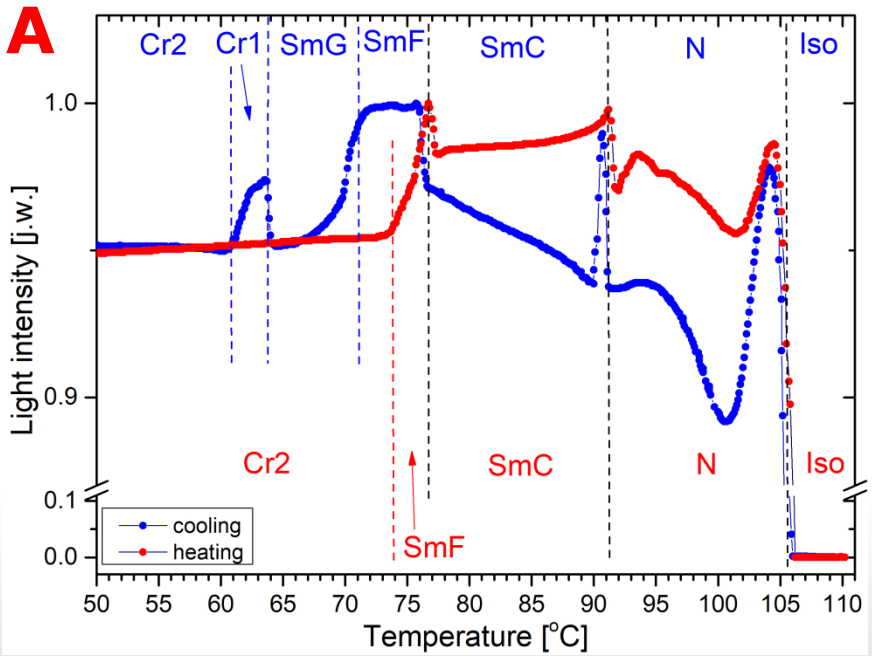
Iso 105.7 °C N 91.2 °C SmC 76.7 °C SmF 71.1 °C SmG 64.0 °C Cr1 60.8 °C Cr2

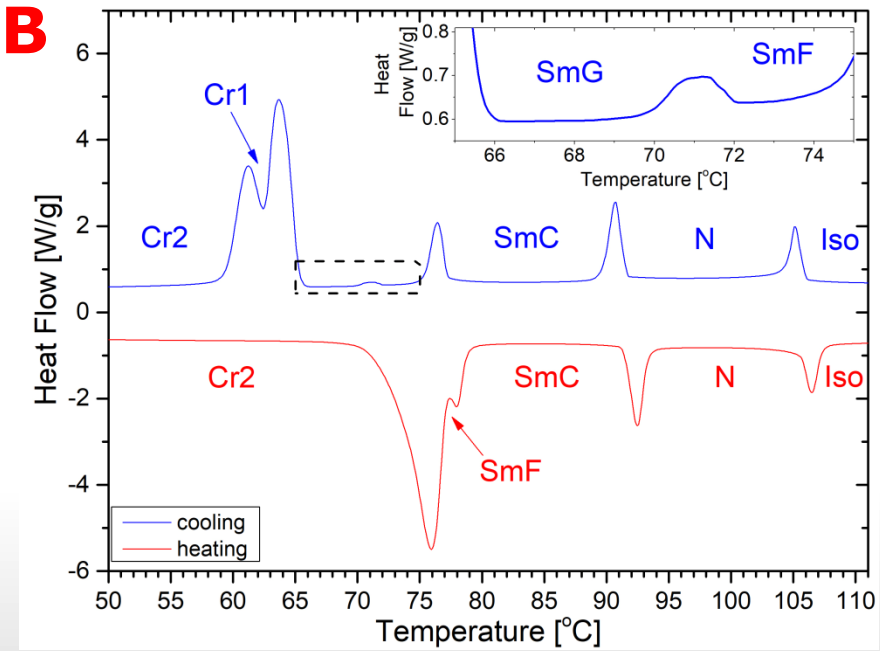


*Textures of **8OABOOC8** for cooling with rate of temperature change 10 °C/min.*

Phase Transitions

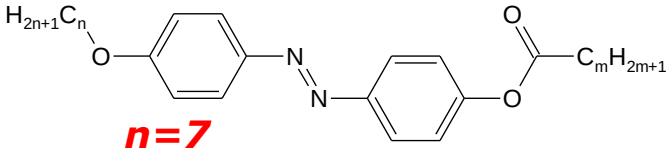




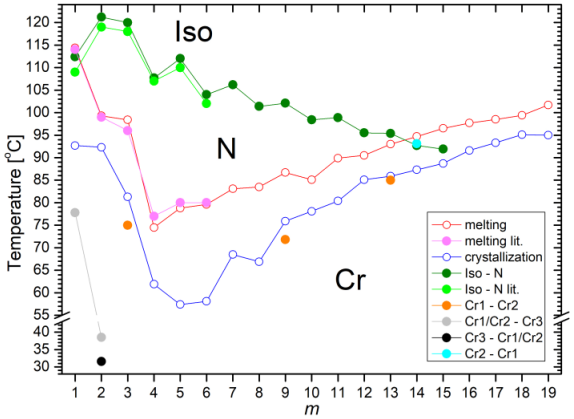


*TOA (**A**) and DSC (**B**) diagram during cooling (blue) and heating (red) (rate of temperature changes 10 °C/min) of **8OABOOC8**.*

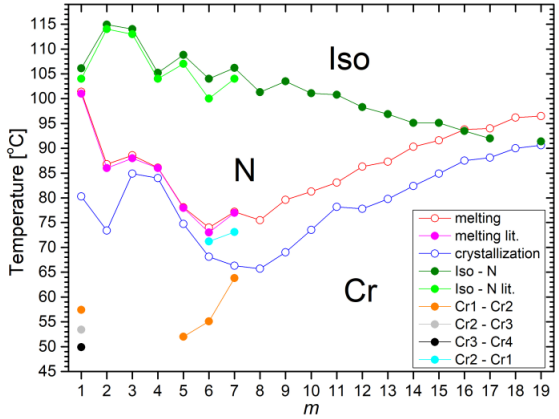
Phase Situation



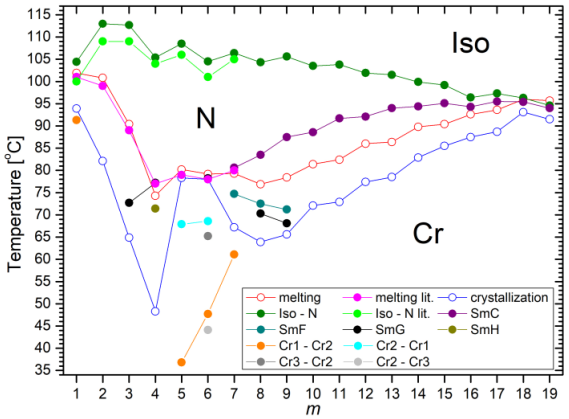
n=3



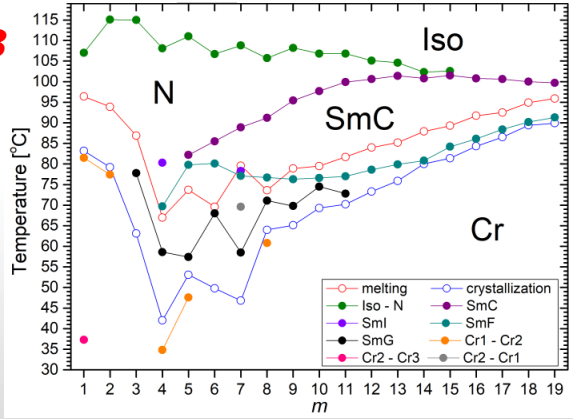
n=5



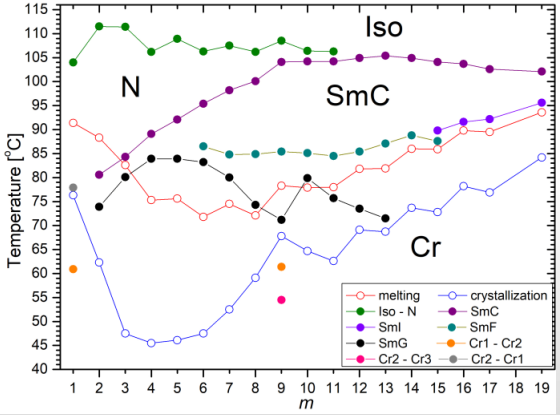
n=7



n=8

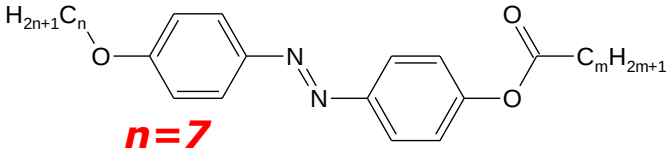


n=10

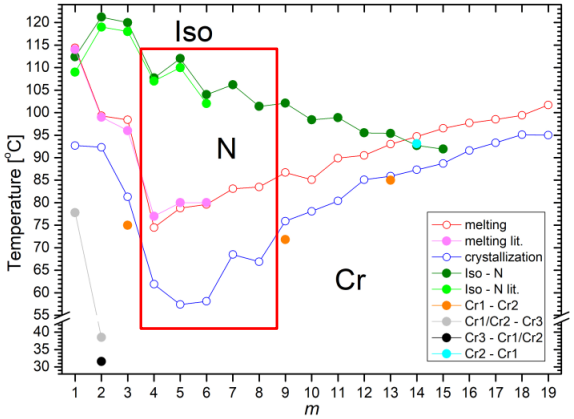


McCaffrey M.T., et al., Molecular Crystals Liquid Crystals, ***18****, 209 – 225 (1972).*

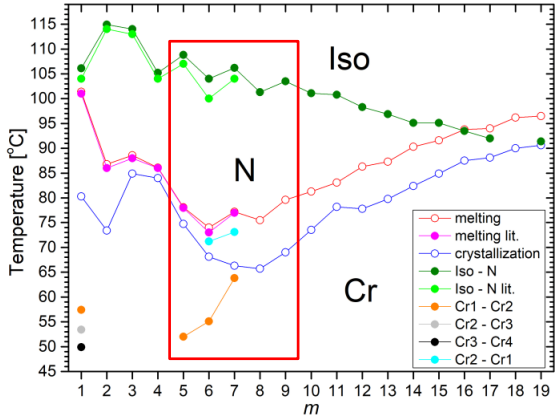
Phase Situation



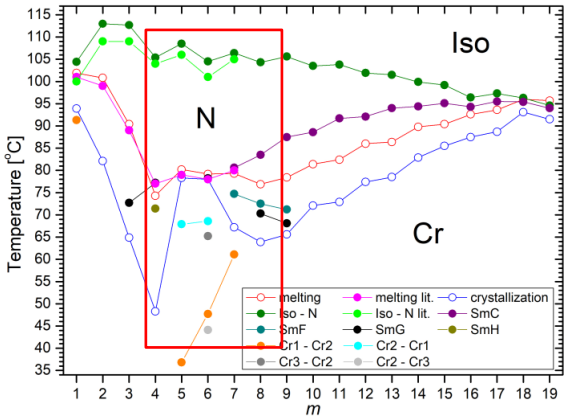
n=3



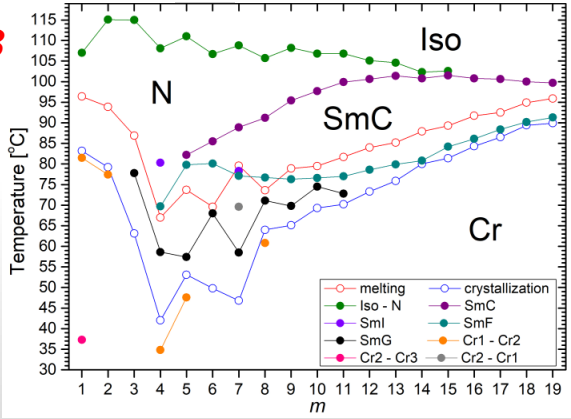
n=5

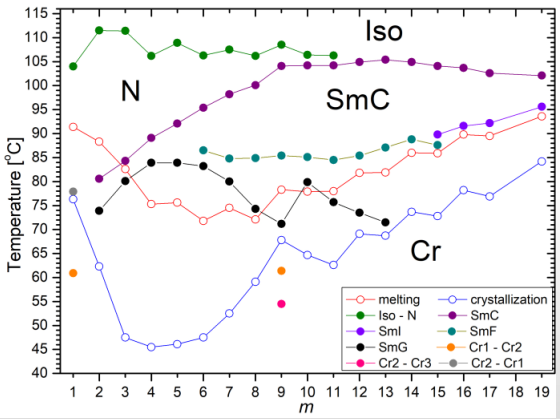


n=7



n=8





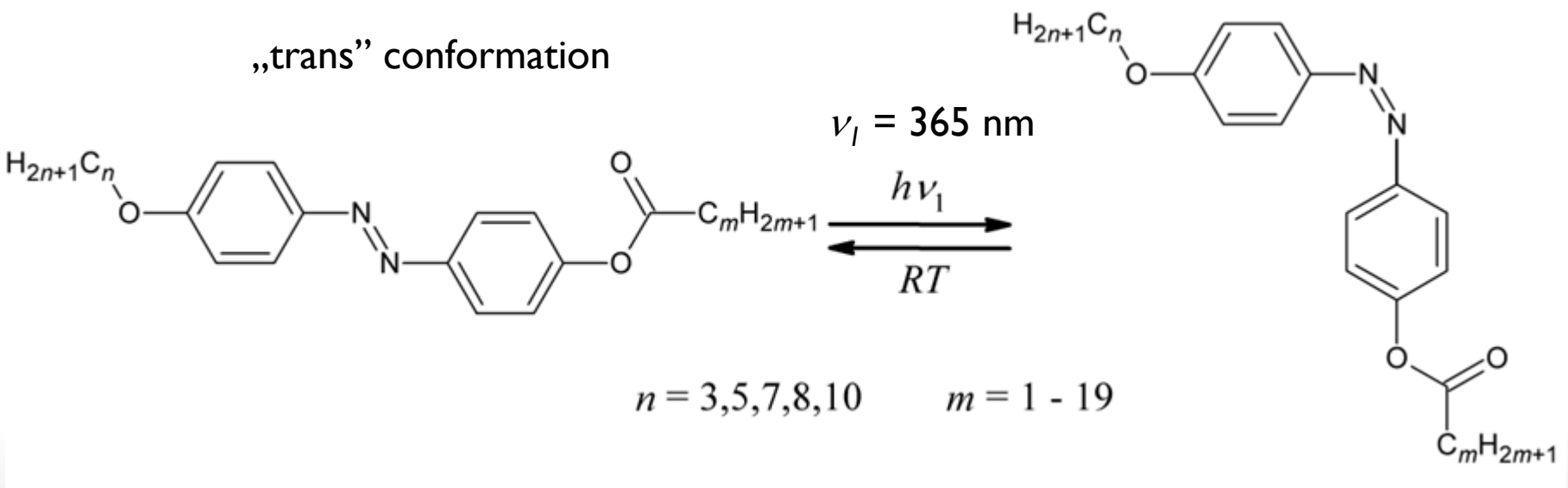
n=10

McCaffrey M.T., et al., Molecular Crystals Liquid Crystals, ***18****, 209 – 225 (1972).*

Influence of UV light

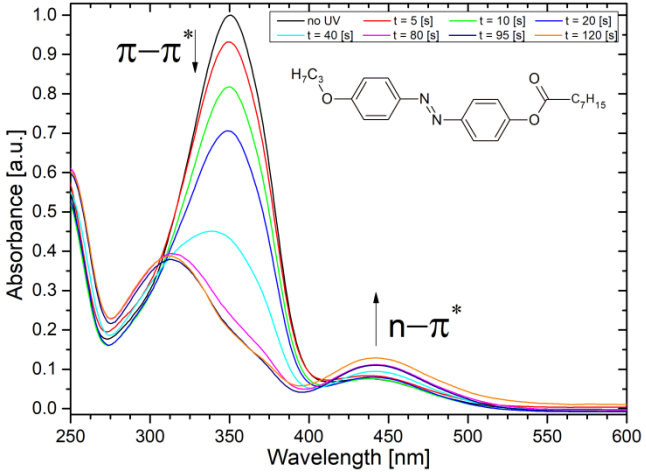
„trans" conformation

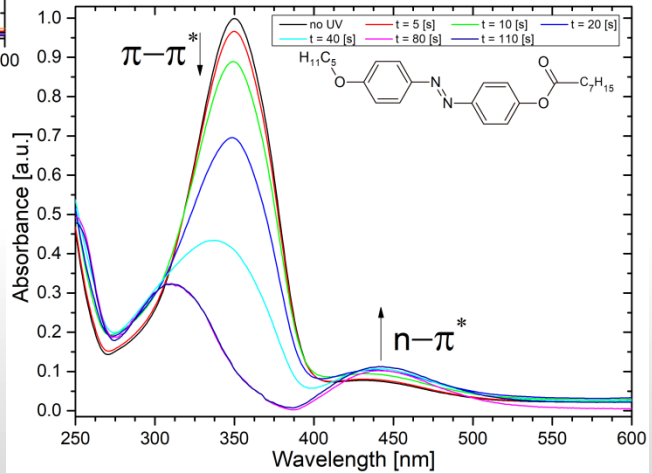
„cis" conformation

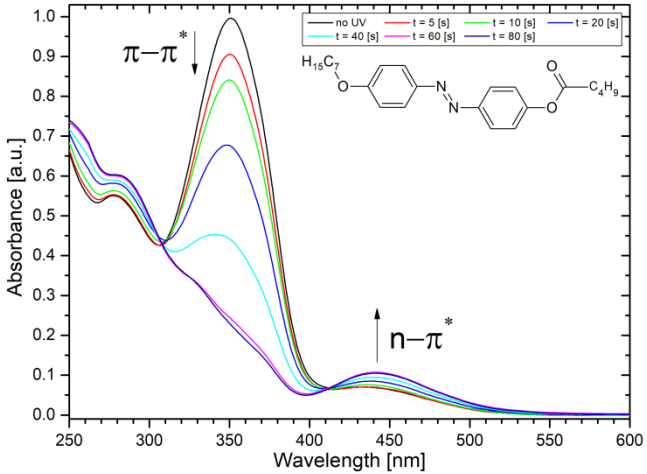


Process of trans-cis photoisomerization of ***nOABOOCm****.*

Influence of UV light

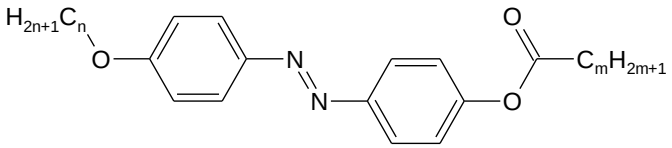


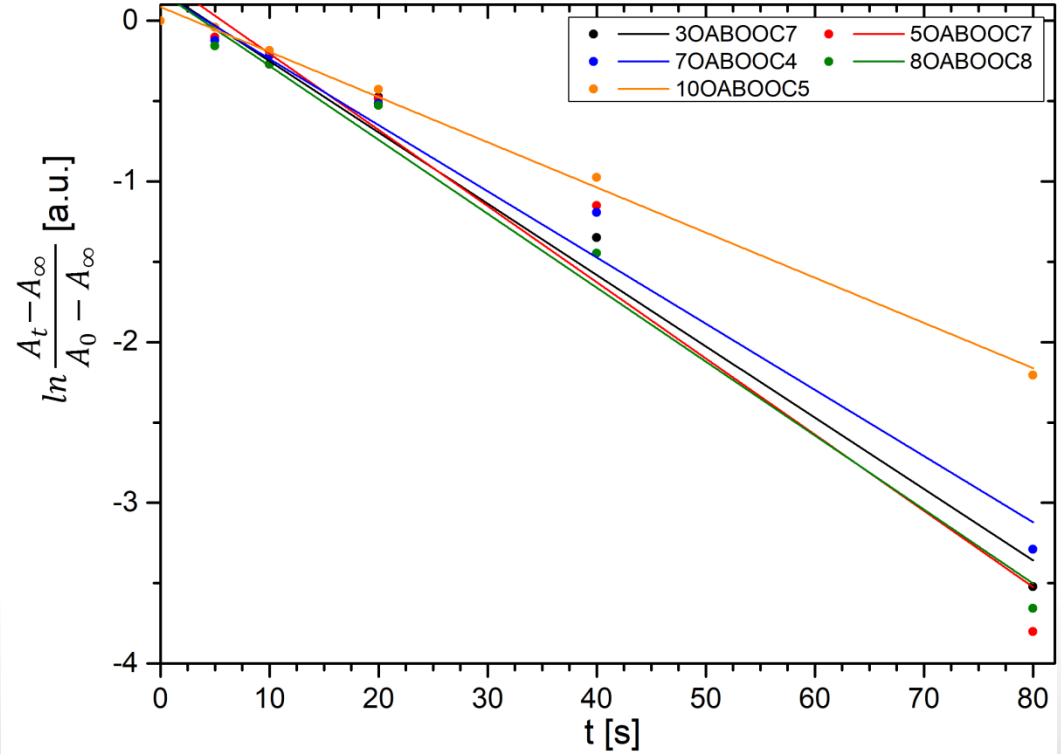




*UV-Vis absorption spectrum of selected **nOABOOCm** compounds: (A) **3OABOOC7**, (B) **5OABOOC7**, (C) **7OABOOC4**.*

Process Kinetics





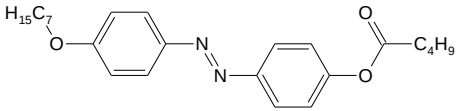
*Kinetics of trans – cis photoizomerization process of selected **nOABOOCm**.*

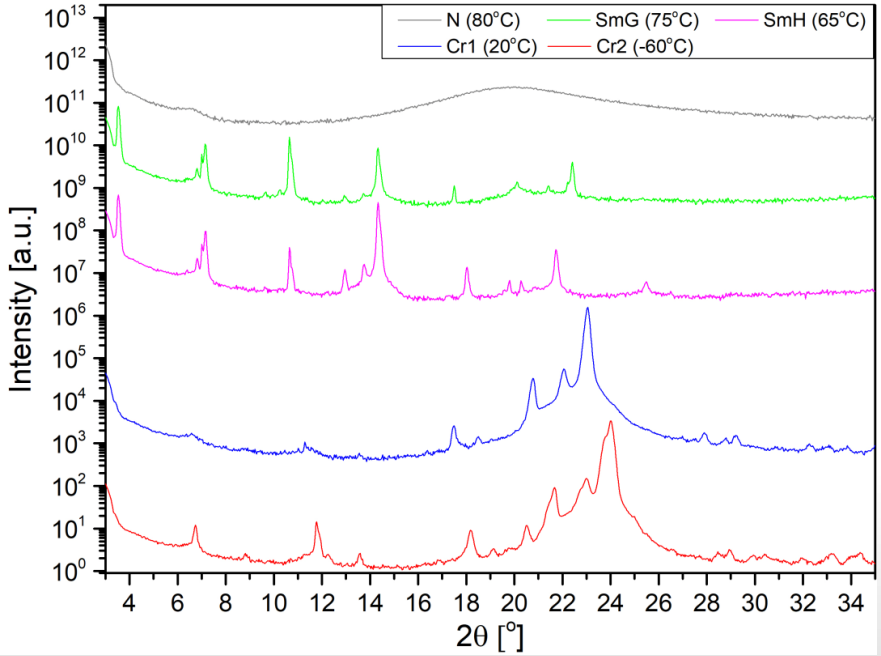
$$ln\frac{A_t-A_\infty}{A_0-A_\infty} = -kt$$

	λ [nm]	k [$10^{-2} * s^{-1}$]	k^{-1} [s]	ln2/k [s]
3OABOOC7	351	4.44	22.52	15.61
5OABOOC7		4.74	21.10	14.62
7OABOOC4		4.12	24.27	16.82
8OABOOC8		4.60	21.74	15.07
10OABOOC5		2.81	35.59	24.67

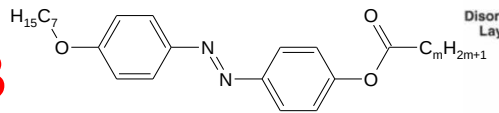
Structural Studies

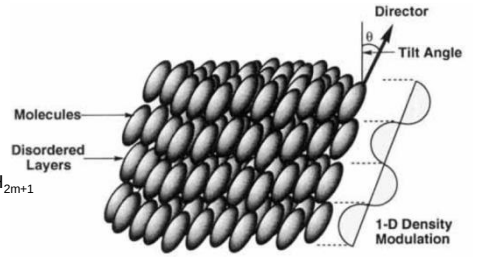
A

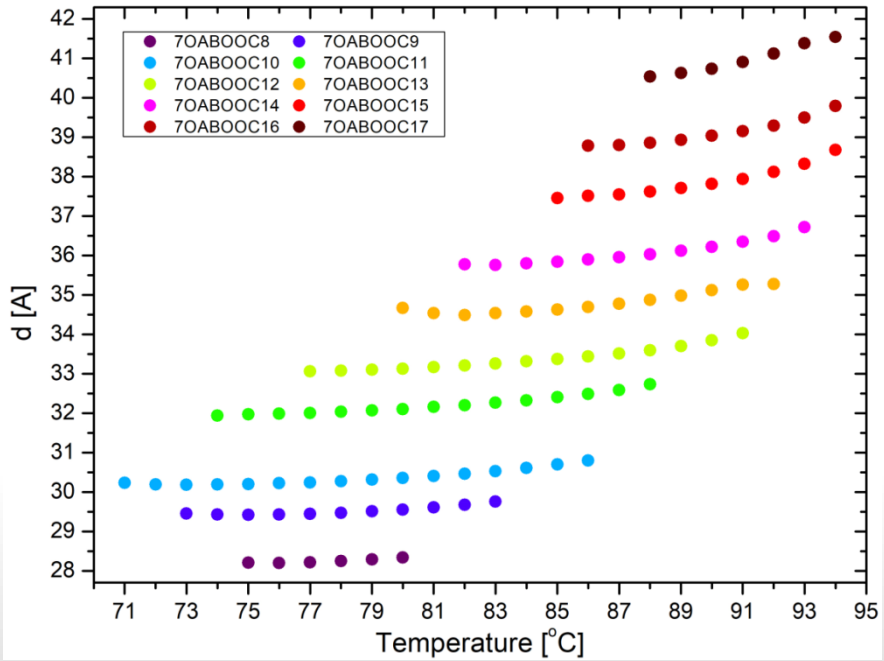




B

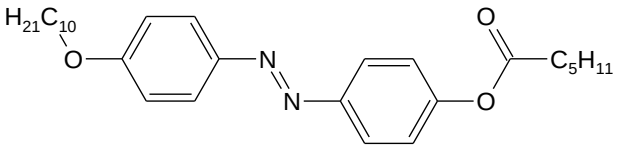


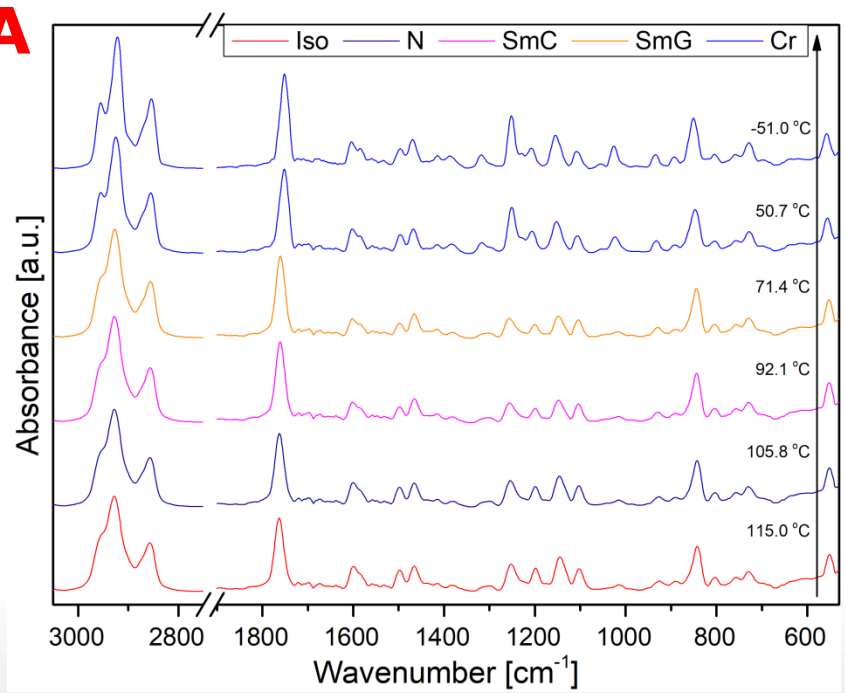


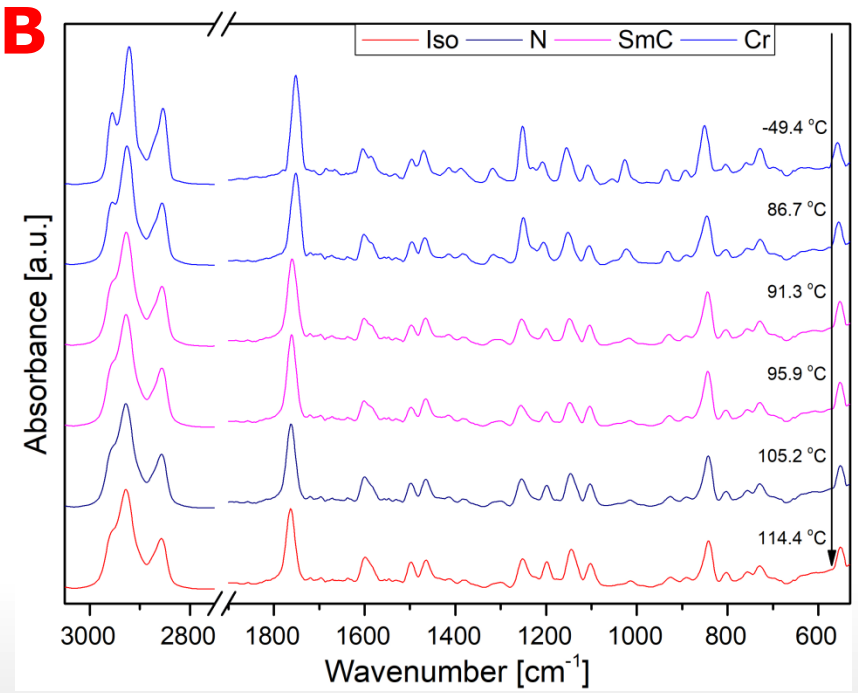


*XRD results: (**A**) patterns collected during cooling of **7OABOOC4** for selected temperatures; (**B**) temperature dependence of SmC layer thickness of **7OABOOCm**.*

Vibrational dynamics

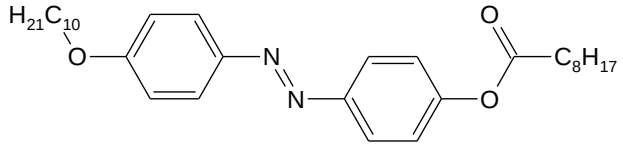




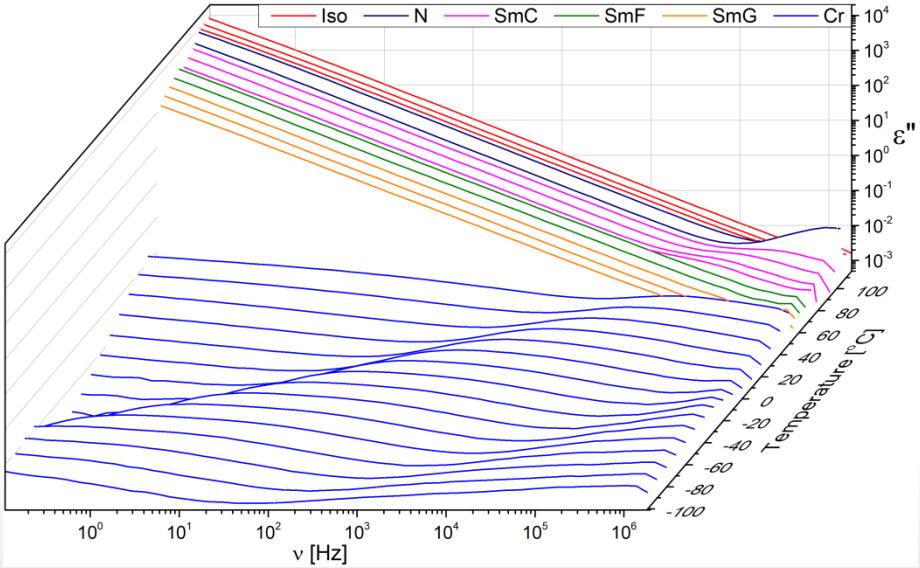


*FTIR spectra for selected temperature aquired during cooling (**A**) or heating (**B**) (rate of temperature changes 2°C/min) of **10OABOOC5**.*

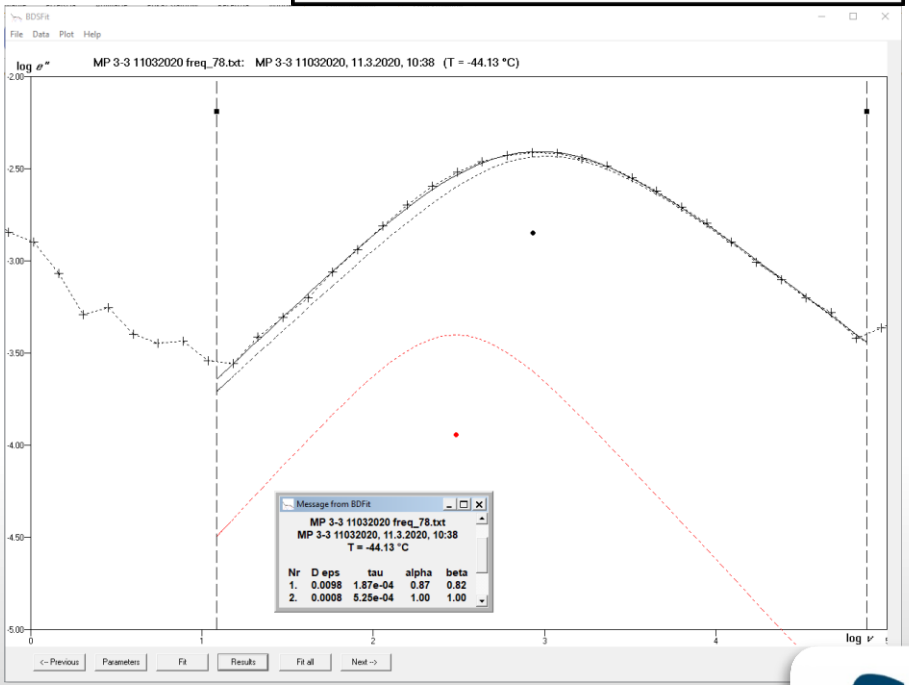
Dielectric Spectroscopy



$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + (i\omega\tau)^\alpha)^\beta}$$

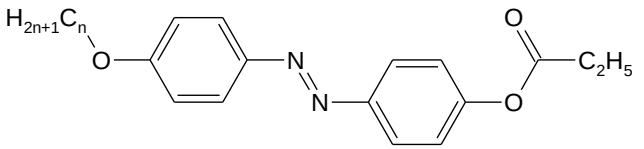


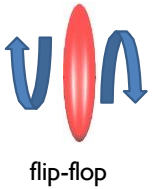
Temperature dependence of ε" value aquired during cooling of 10OABOOC8 derivative.

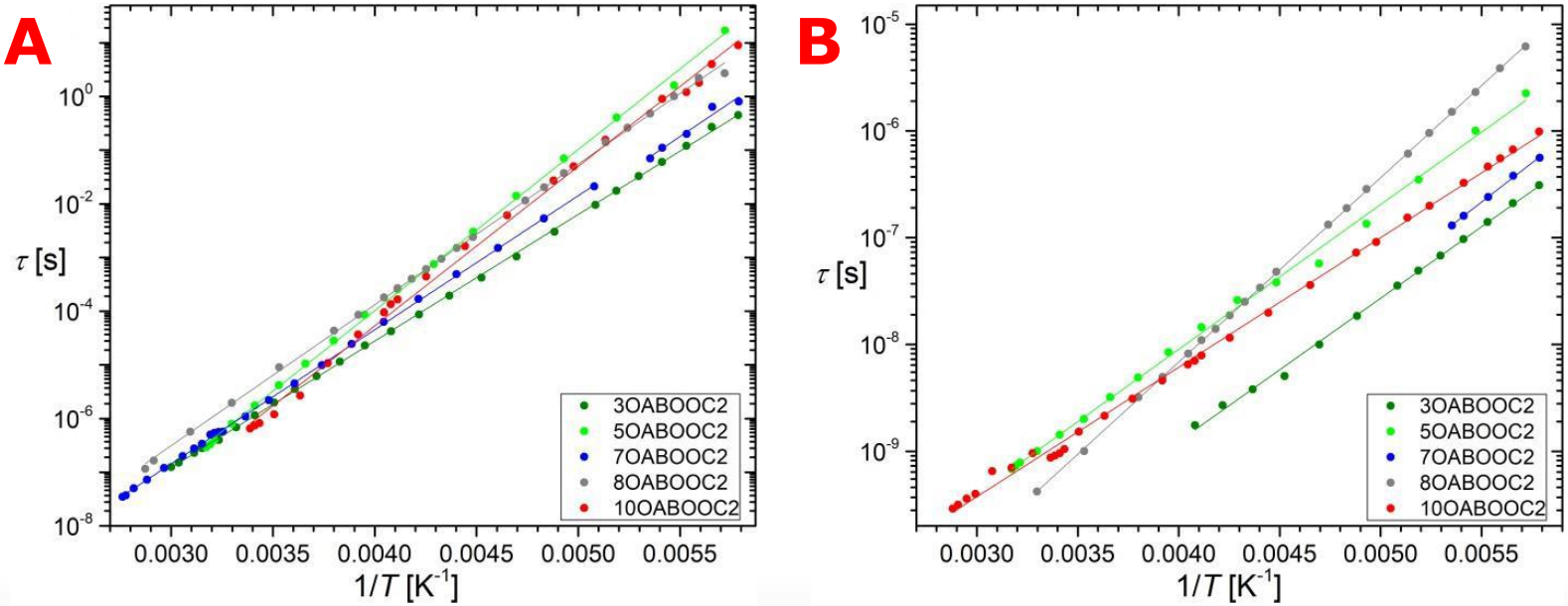


Example of fitting Havriliak-Negami model to experimental data of ε"(ν).

BDS







*Relaxation times of „flip – flop" (**A**) and „fast" (**B**) processes of **nOABOOC2**.*

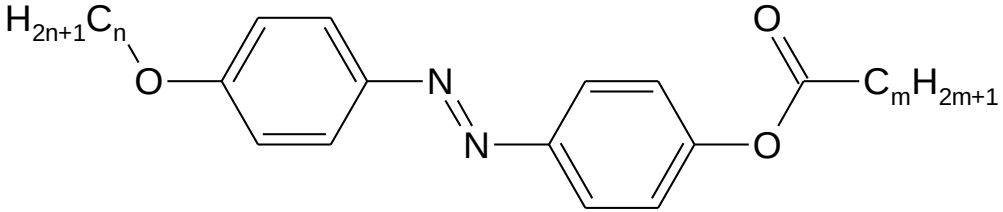
$$\tau = \tau_0 * e^{\Delta E/RT}$$

Activation Energy for:

„flip-flop" process 45 – 57 [kJ/mol]

„fast" process 25 – 34 [kJ/mol]

Summary



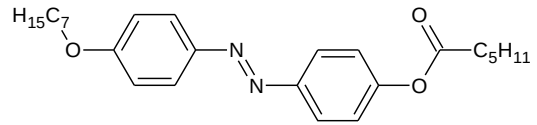
n*OABOOC*m compounds:

- 89 of 94 synthesized ***n*OABOOC*m*** compound exhibit the occurrence of at least one mesophase, including: N, SmC, SmI, SmF, SmG and SmH
- Some of the derivatives exhibit the presence of more than one crystal phases (up to four for **5OABOOC1**).
- UV-Vis spectroscopy showed the presence of trans-cis photoisomerization under the influence of irraddiation with UV radiation.
- Dielectric Spectroscopy studies showed the presence of two relaxation processes in the crystalline phase.

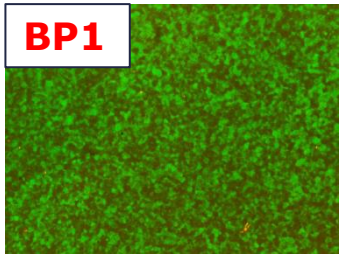
From derivatives with the widest temperature range of nematic phase, two were chosen to prepare mixtures: 7OABOOC5 and 7OABOOC8.

PART IV: MIXTURES

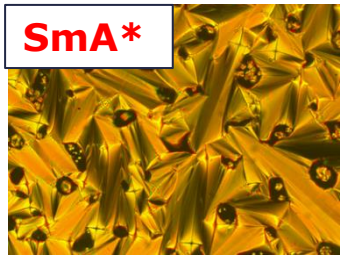
Mixtures



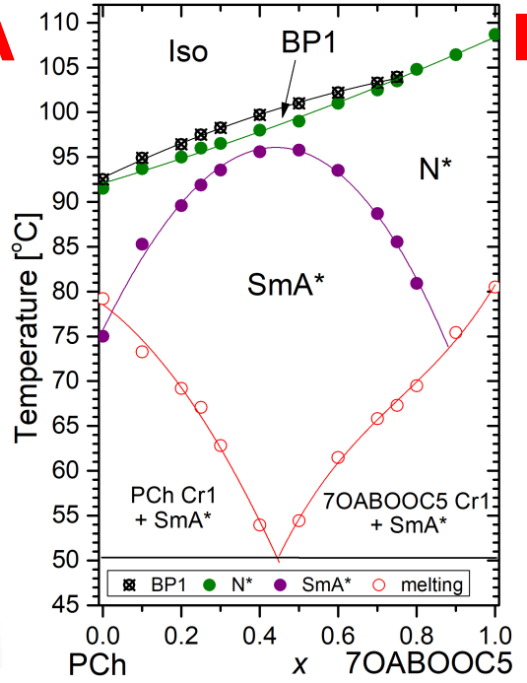
BP1



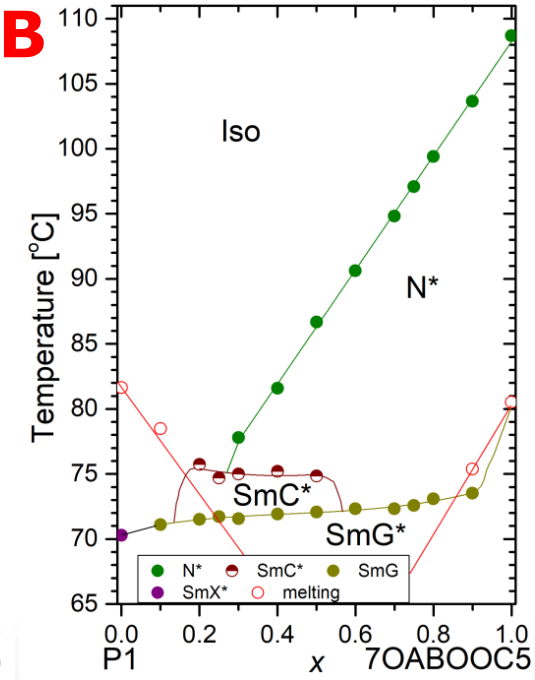
SmA*



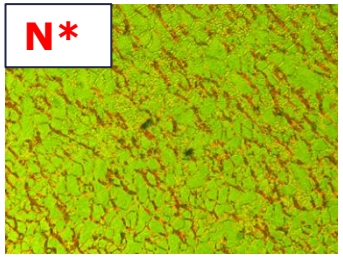
A



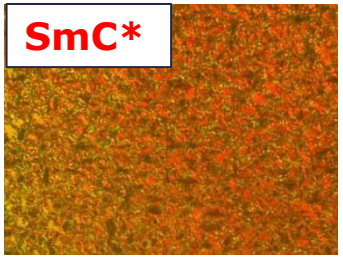
B

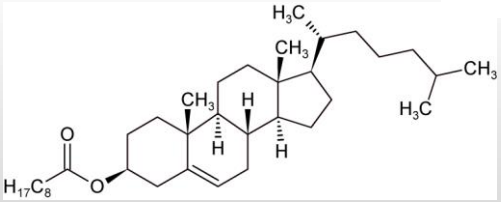


N*

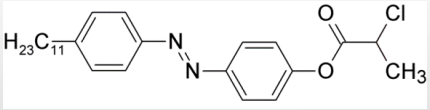


SmC*

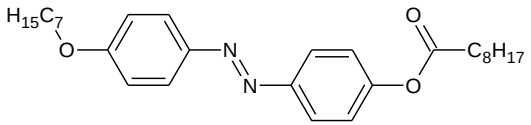


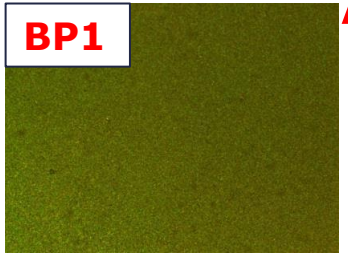


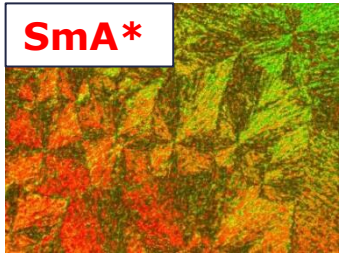
*Phase diagrams of **7OABOOC5** and cholesteryl pelargonate (**A**, PCh) or (E)-4-((4-undecylphenyl)diazenyl)phenyl 2-chloropropanoate (**B**, P1) mixtures. Temperature change rate 10 °C/min.*

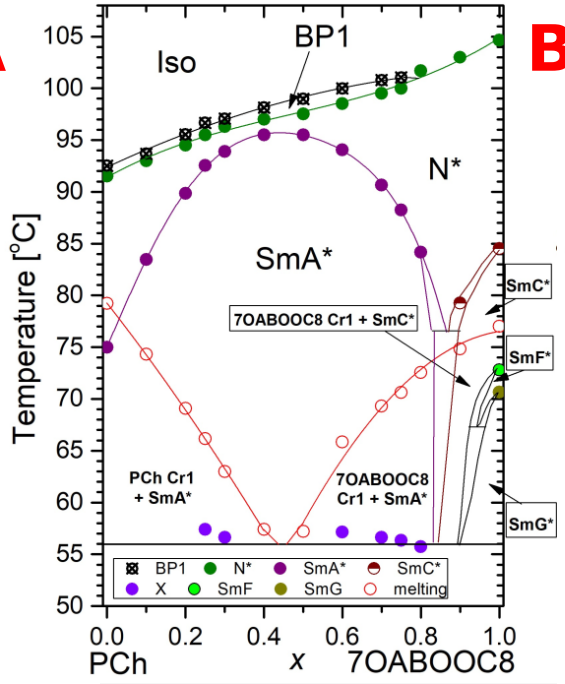


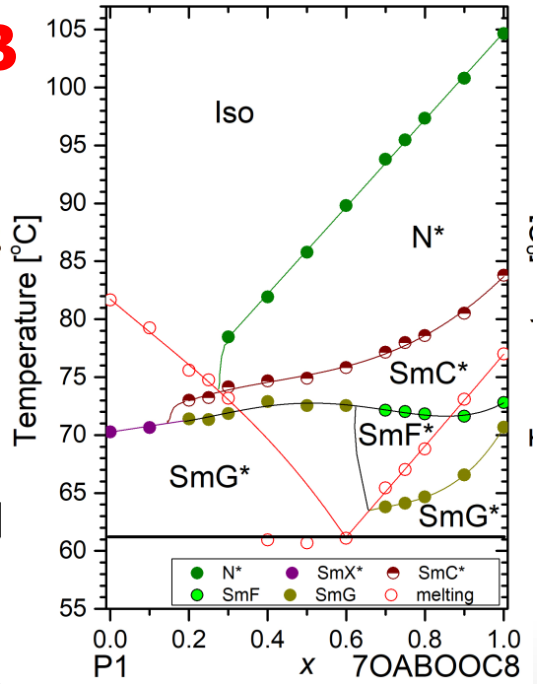
Mixtures

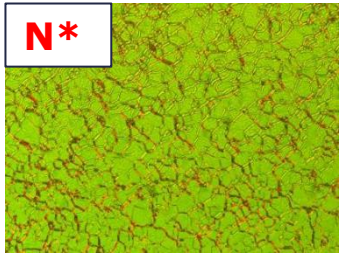


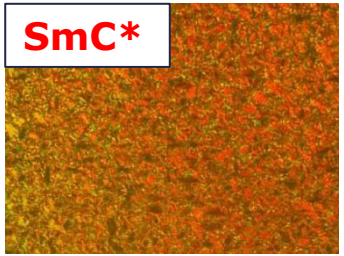


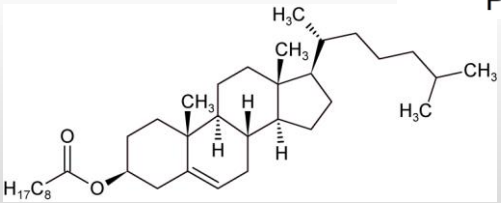




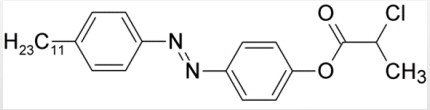








*Phase diagrams of **7OABOOC8** and cholesteryl pelargonate (**A**, PCh) or (E)-4-((4-undecylphenyl)diazenyl)phenyl 2-chloropropanoate (**B**, P1) mixtures. Temperature change rate 10 °C/min.*



Summary

Mixtures:

- 38 of 44 prepared mixtures exhibit presence of N* phase.
- Induction of the N* phase was observed for the mixtures containing P1 compound.
- There was a decrease in melting and crystallization temperatures in relation to pure compounds.

The widest temperature range (for heating) of the N* phase was observed for the mixture 7OABOOC5 - PCh (for x = 0.9) - from 75°C to 105°C.

Best candidate for further investigation!

Acknowledgement

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Thank You for your attention!