Enhancement of the nematic ordering in cyanobiphenyl 5CB doped with salicylaldoxime due to supramolecular nanostructuring

P.V. Vashchenko [1], S.S. Minenko [1], K.O. Vus [2], M.Yu. Cherniakova [3], K.N. Belikov [3], L.N. Lisetski [1]

[1] Institute for Scintillation Materials, NAS of Ukraine, Kharkiv, Ukraine, lcsciencefox@gmail.com.
[2] V.N. Karazin Kharkiv National University, Department of Medical Physics and Biomedical Nanotechnologies, Kharkiv, Ukraine.
[3] Institute of Chemistry of Functional Materials, STC "Institute for Single Crystals", NAS of Ukraine, Kharkiv, Ukraine

ISMA Institute for Scintillation Materials

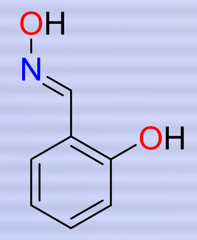
XXVIth Galyna Puchkovska International School Seminar "Spectroscopy of Molecules and Crystals" - 2024

Background & objectives

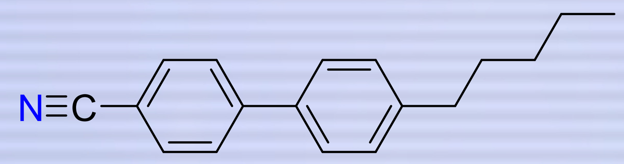
- Nanostructuring effects bring up perspectives of novel materials' development, especially those based on ordered media. Particularly, nanostructuring in liquid crystals (LC) media may result in enhancement of their physcochemical properties or emergence of qualitatively new unique features
- The present work is aimed to reveal supramolecular nanostructuring in a nematic LC medium under introduction of a non-mesogenic dopant

Materials & methods

- SA as a non-mesogenic dopant and 5CB as a LC matrix were used.
- The 5CB-SA phases were studied by differential scanning calorimetry (DSC), optical microscopy, UV-Vis spectroscopy (selective reflection spectra and the analysis of optical transmission at wavelengths outside the absorption bands (Fig. 5) as function of temperature close to the isotropic phase transition)
- FTIR and quantum chemical calculations were involved to elucidate guest-host intermolecular interactions
- To single out the molecular structure features responsible for the nematic ordering, studies under similar conditions were carried out with a mixture of cholesterol esters M5 as a LC matrix and *L*-menthol



Salicylaldoxime (SA), a well-known helating agent, a non-mesogenic dopant (guest)



4-Cyano-4'-pentylbiphenyl (5CB), a commonly used nematic liquid crystal (host)

Results & discussion

- It has been found that SA, added to nematic 5CB as a non-mesogenic dopant, increased the isotropic transition temperature T_{iso} (Fig. 3) up to SA concentrations of ~ 4 mass %, with the nematic LC phase persisting up to ~ 36 mass % of the dopant (Fig.2)
- FTIR and quantum chemical calculations showed possible creation of the different 5CB:SA complexes (Fig. 1), including π- stacking (Fig. 8) and H-bonds (Fig. 9) . Such interactions could hinder 5CB dimerization (Fig. 4), resulting in clusters of higher local anisotropy due to steric factors ensuring the optimum molecular packing

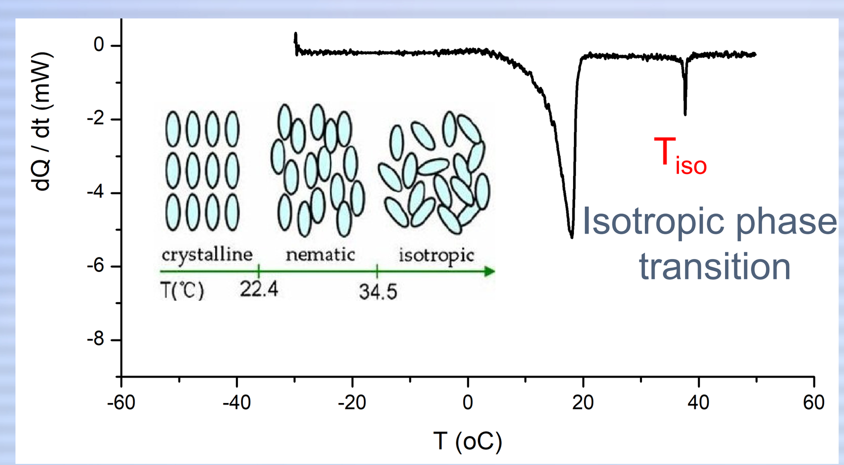


Fig. 3. *Phase transitions of 5CB matrix as evidenced by DSC technique*

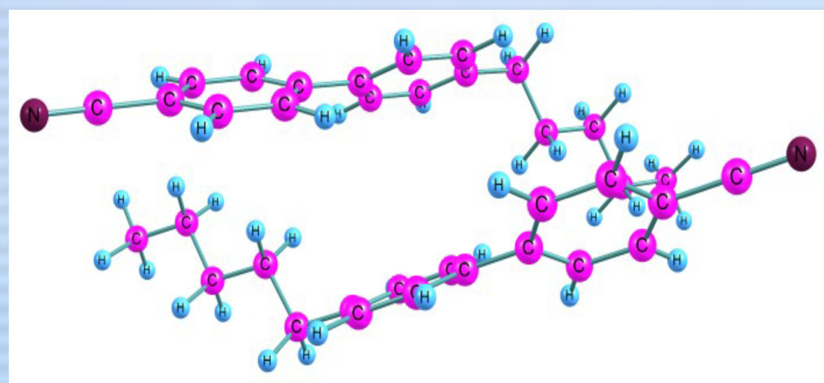


Fig. 4. *Antiparallel conformation of 5CB liquid crystal dimer [Chaudhary, 2020, DOI: 10.26713/jamcnp.v7i1.1391]*

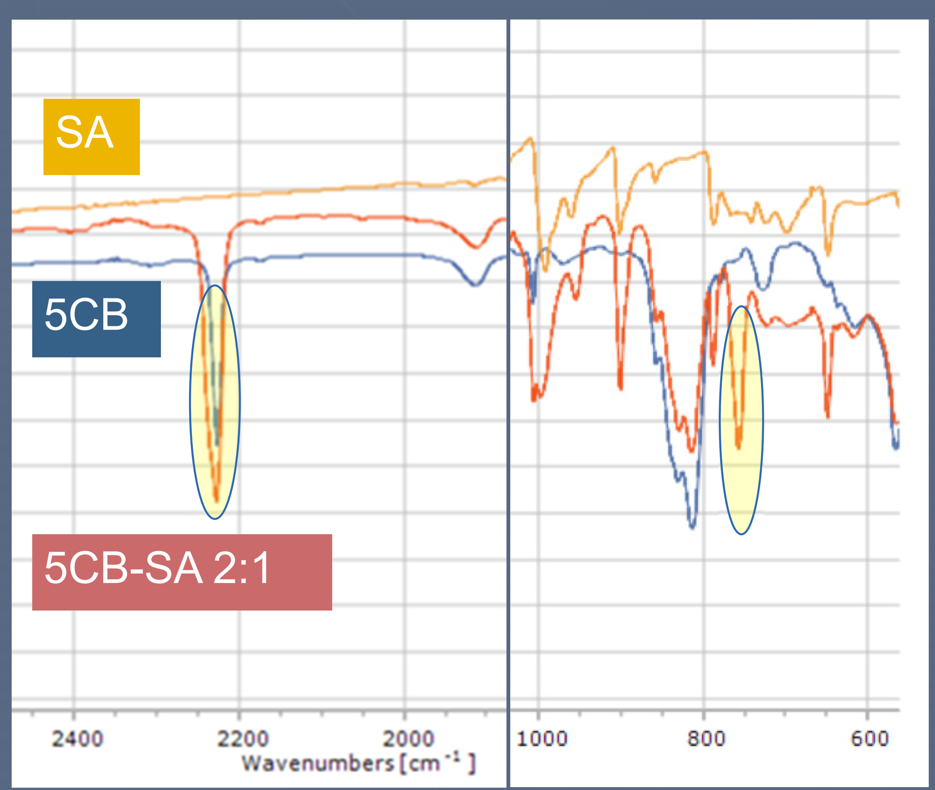


Fig. 1. *Fragments of FTIR spectra of SA, 5CB and 5CB-SA 2:1 binary mixture*

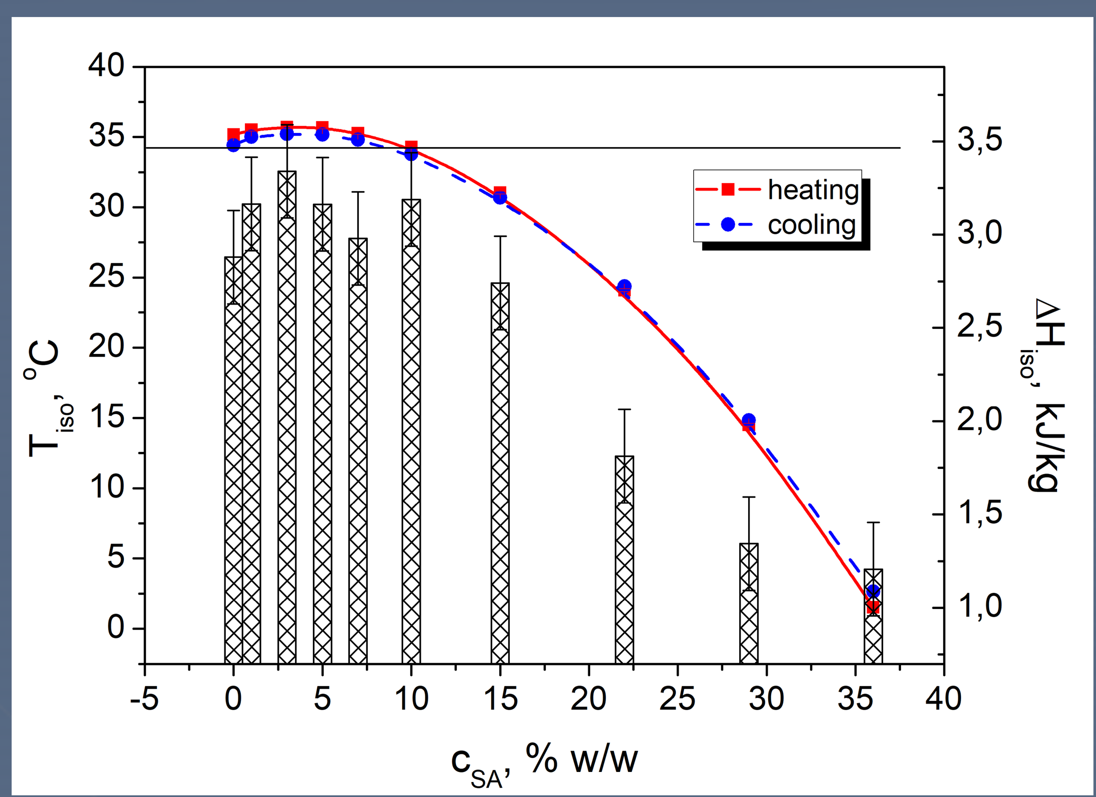


Fig. 2. *Nematic to isotropic transition temperature and enthalpy of 5CB doped with SA*

- The calorimetry and spectroscopy data obtained with the corresponding ternary systems (including changes in selective reflection of M5) were interpreted in terms of quasi-binary systems of interacting components in the allegedly indifferent solvent (Fig. 6,7)

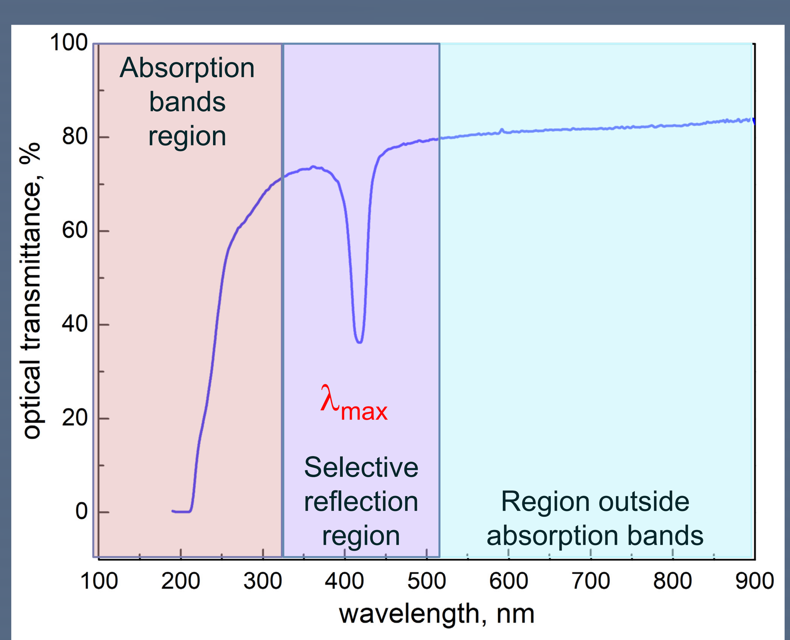


Fig. 5. *UV-Vis spectrum of a cholesteric LC matrix (a scheme).* λ_{max} *is the selective reflection maximum wavelength*

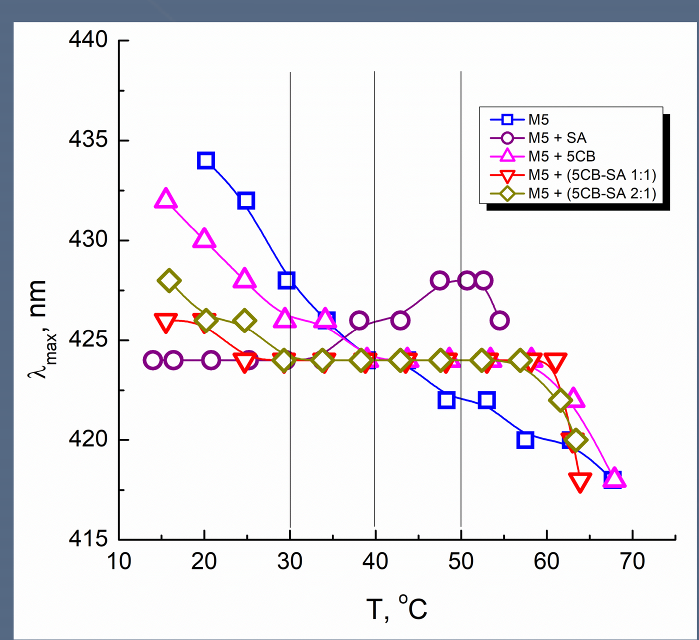


Fig. 6. *Temperature dependence of* λ_{max} *for M5 matrix containing 5CB and SA*

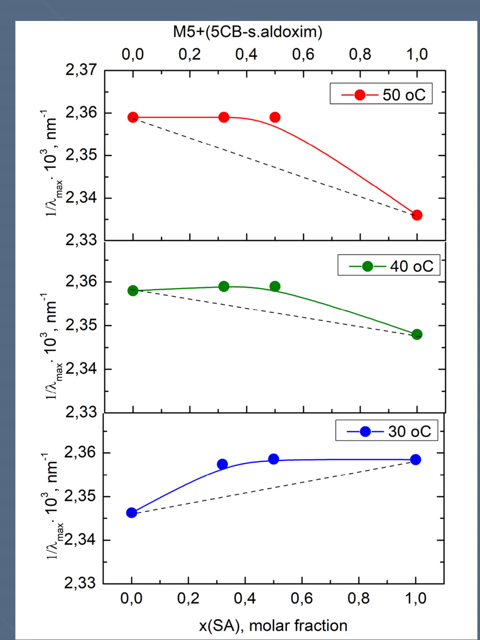


Fig. 7. *Quasi-binary diagrams of 5CB-SA mixtures in M5 cholesteric matrix by selective reflection parameter* $1/\lambda_{max}$

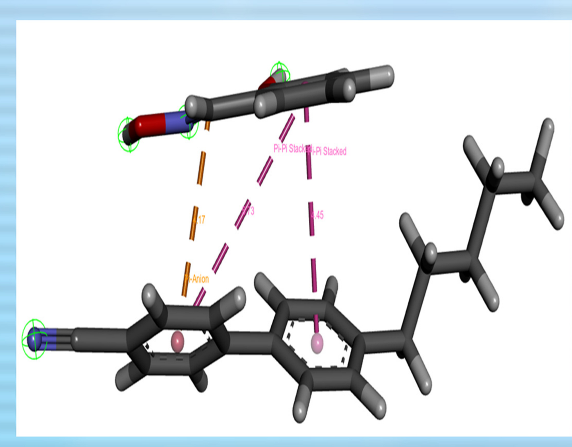


Fig. 8. *An example of 5CB-SA 1:1 complex (π– stacking)*

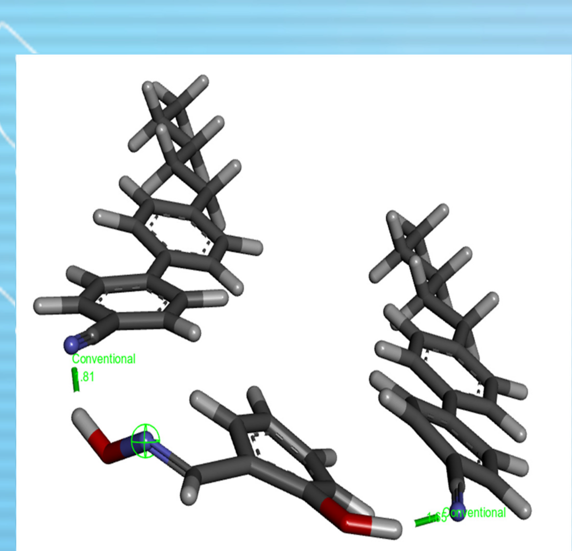


Fig. 9. *An example of 5CB-SA 2:1 complex (H-bonds)*

Conclusions

The results obtained show that doping a nematic system with purposely selected NMDs can substantially affect their mesomorphic and optical properties, making this approach an alternative to introduction of nanoparticles to LC systems