Simulations of spectra and some physical attributes of specific homologous series of nematic liquid crystals in the range of 0.4–7.6 THz

Karol Sielezin,* Rafał Kowerdziej, Urszula Chodorow, Marek Olifierczuk, Janusz Parka

Institute of Applied Physics, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland

Received November 20, 2025; accepted December 22, 2025; published December 31, 2025

Abstract—In this research, we provide the outcomes of spectral calculations and selected characteristics of the NLC homologous series of cyanobiphenyls (nCB) and phenylcyclohexanes (nPCH) within the frequency range of 0.4–7.6 THz. Geometry optimizations, assessments of harmonic frequencies, and calculations of intensity were performed utilizing Scigress – Molecular Modelling Software developed by Fujitsu. The numerical analyses were executed following the standard DFT procedure, employing the B88-LYP functional and DZVP basis sets. The results obtained for the absorption spectra, along with physical parameters such as dielectric permittivity, refractive index, and birefringence, are detailed herein. Notably, we demonstrate that the results align well with the referenced experimental findings.

Nematic Liquid Crystals (NLCs) exhibit a range of unique properties, including high birefringence, low losses in the terahertz (THz) frequency range, and the ability to dynamically modify anisotropy through the application of electric or magnetic fields. As a result, NLCs are outstanding materials for creating tunable optical devices, including phase shifters, phase gratings, phase modulators, lenses, filters, beam steering systems, and optical elements for metamaterials. NLCs have found use in numerous applications, and there is a considerable demand for tunable components based on NLCs that can efficiently manage IR and THz waves [1,2].

Density Functional Theory (DFT) represents a theoretical quantum methodology that is often utilized in molecular modeling to refine molecular geometry and functionality while identifying their energy minima. This approach has shown considerable promise in predicting spectral properties within the IR and THz ranges. Nonetheless, the presence of challenges in both measurement and calculation techniques results in certain inaccuracies, especially in the terahertz range [3-7]. The exploration of NLC compounds through theoretical frameworks, such as density functional theory (DFT), is crucial for predicting their spectral properties. Notably, computer simulations can significantly enhance the understanding of molecular properties that influence macroscopic characteristics [1, 2].

The fundamental structure and the optimized molecular design of the simulated NLCs compounds are presented in Fig. 1.

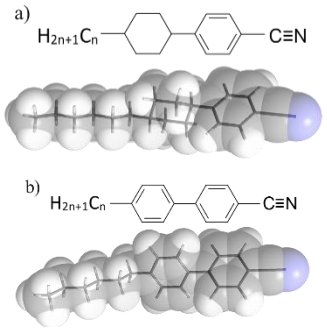

Fig. 1. The general structure (and example optimized molecular design) of: a) nPCH (i.e., 6PCH), b) nCB (i.e., 6CB).

For anisotropic materials, Vuks's equation (Eq. (1)) correlates with the refractive indices and the molecular polarizabilities:

$$\frac{n_{e,o}^2-1}{\langle n^2\rangle+2}\cdot\frac{M}{\rho}=\frac{4}{3}\pi\cdot N_A\cdot\alpha_{e,o}, \tag{1}$$

where $\langle n^2\rangle$ is defined according to the formula:

$$\langle n^2\rangle=\frac{n_e^2+2n_o^2}{3}. \tag{2}$$

Through the substitution of Eq. (2) into Eq. (1) and the separation of n_e and n_o, we can represent n_e and n_o as:

$$n_e=\sqrt{1+\frac{4\cdot\pi\cdot N\cdot\alpha_e}{1-\frac{4}{3}\cdot\pi\cdot N\cdot\langle\alpha\rangle}}, \tag{3}$$

$$n_o=\sqrt{1+\frac{4\cdot\pi\cdot N\cdot\alpha_o}{1-\frac{4}{3}\cdot\pi\cdot N\cdot\langle\alpha\rangle}}, \tag{4}$$

where N and $\langle\alpha\rangle$ are specified by equations [1,2]:

$$N=\frac{\rho\cdot N_A}{M}, \tag{5}$$

$$\langle\alpha\rangle=\frac{\alpha_e+2\alpha_o}{3}. \tag{6}$$

* E-mail: karol.sielezin@wat.edu.pl

In order to calculate polarizability, we utilized the sum-over-states method:

$$\langle\alpha\rangle = \frac{\alpha_{xx}+\alpha_{yy}+\alpha_{zz}}{3}, \tag{7}$$

$$\alpha_{ij}(-\omega,\omega) = \sum_{e\neq 0}\langle 0|\hat{\mu}_j|e\rangle\langle e|\hat{\mu}_j|0\rangle\left[\frac{1}{\Delta E_e-\hbar\omega}+\frac{1}{\Delta E_e+\hbar\omega}\right], \tag{8}$$

where ω represents the angular frequency of the incident light, ΔE_e denotes the transition energy, $|0\rangle$ signifies the total wave function of the ground state, $|e\rangle$ indicates the total wave function of the excited state, and *i* and *j* refer to the components of the Cartesian coordinates. The dipole moment operator of the *i*-component $\hat{\mu}_i$ is described by the equation:

$$\hat{\mu}_i = -e\sum_{S=1}^{Z} i_S, \tag{9}$$

where Z represents the number of electrons taken into account.

Geometry optimizations, harmonic frequencies, and intensity calculations were conducted utilizing Scigress – Molecular Modelling Software from Fujitsu [8]. The geometry optimization and frequency calculations for the evaluated NLC compounds were executed following the standard DFT procedure with the B88-LYP functional and DZVP basis sets. The resulting IR transition spectra were calculated at THz frequencies [1,2].

Figure 2 presents a comparison of the experimental results with those computed using the DFT method for the THz spectra of selected NLC compounds. It clearly shows that in all scenarios analyzed, the agreement between experimental results and theoretical predictions is satisfactory. Specifically, for both 5PCH and 5CB, the experimental spectra obtained (depicted in the red curves) exhibit only minor discrepancies when compared to the spectra theoretically calculated using DFT methods with various programs, including Scigress (illustrated in the green curves) and Gaussian (represented in the blue and orange curves). It is evident that the selection of the appropriate functional and computational basis sets has a significant impact on the results, which accounts for the differences noted in the spectra of the same compounds following Gaussian processing with different functionals and basis sets (shown in the blue and orange curves). It is clear that despite enhancements in simulation methods, achieving a perfect reproduction of the experimental results remains unattainable, particularly across such a broad spectral range.

The data presented in Table 1 highlights several significant relationships – for the majority of the NLCs examined, the polarizability of molecules tends to rise with an increase in the number of carbon atoms within the alkyl chain, whereas the refractive indices tend to decline; nonetheless, there are also exceptions to this generalization. [1,2] The calculated refractive indices and birefringence values align closely with both experimental results and those computed by Gaussian Software (DFT/B3LYP/difference basis sets level of theory) [4-6]. Table 2 contrasts the refractive indices (n_e and n_o) and birefringence (Δn) for 5CB assessed at a frequency of 0.5 THz, comparing both the experimentally obtained values and those calculated using the Scigress program with the B3LYP functional and various basis sets.

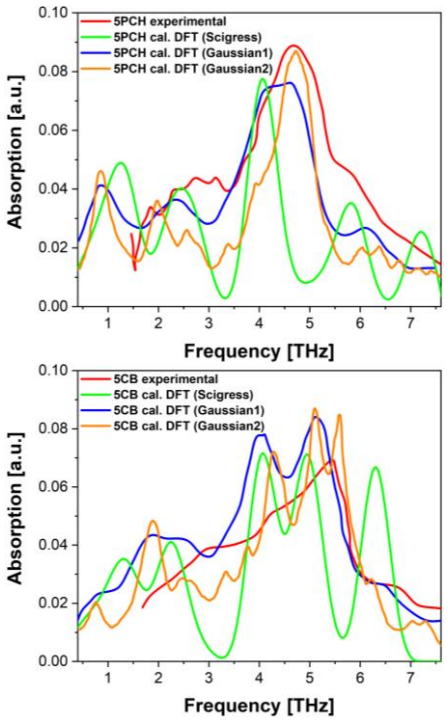

Fig. 2. Comparison of the 0.4–7.6 THz spectra for 5PCH and 5CB: the experimental data is represented by the red curves [6]; calculations performed using Gaussian (DFT/B3LYP/6-311G*) are shown as blue curves [4], calculations from Scigress (DFT/B88LYP/DZVP) are depicted in green curves [1,2], and calculations from Gaussian (3LYP-D3/6-311++G**) are illustrated with orange curves [7].

The calculated properties, including molecular polarizabilities, dielectric constants, refractive indices, and birefringence of the selected compounds from the tested homologous series, are presented in Table 1.

Table 1. Calculated properties of homologous series of nPCH, nCB (for n = 5, 6) at 0.5 THz including molecular polarizabilities (α_o, α_e) [$\times 10^{-24}$ cm^{-3}], dielectric permittivity (ε_o, ε_e), refractive indices (n_o, n_e) and birefringence (Δn).

NLC	α_o	α_e	ε_o	ε_e	n_o	n_e	Δn
5PCH	24.199	36.919	1.240	1.317	1.537	1.736	0.199
6PCH	25.635	38.561	1.237	1.314	1.530	1.727	0.198
5CB	30.174	39.671	1.241	1.328	1.541	1.764	0.223
6CB	35.156	39.695	1.266	1.305	1.602	1.702	0.100

Table 2. Comparison of the experimental and calculated refractive indices (n_o, n_e) and birefringence (Δn) of 5CB at 0.5 THz, utilizing the DFT/difference basis sets level of theory as implemented in Gaussian Software [5], alongside DFT with the B88-LYP functional and DZVP basis sets as employed by Scigress Software.

Method	n_o	n_e	Δn
Experimental	1.58	1.77	0.19
Gaussian DFT/B3LYP/6-31G*	1.4591	1.6634	0.2043
Gaussian DFT/B3LYP/6-31+G*	1.5384	1.7429	0.2045
Gaussian DFT/B3LYP/6-31+G**	1.5498	1.7506	0.2057
Gaussian DFT/B3LYP/6-311+G**	1.5384	1.7583	0.2085
Gaussian DFT/B3LYP/6-31++G**	1.5526	1.7607	0.2081
Scigress DFT/B88-LYP/DZVP	1.541	1.764	0.233

An examination of Table 2 reveals that all parameters derived from various programs and calculation bases closely align with experimental values. Nevertheless, it is evident that in every instance, the computed values of the refractive indices (both n_o and n_e) consistently fall short of the experimentally obtained values. Consequently, all calculated birefringence values exceed the experimental value in each scenario analyzed.

To summarize, we simulated the THz absorption spectra of four compounds from the homologous series of nCB and nPCH, employing the DFT method with the B88-LYP functional and the DZVP basis set to optimize the geometry of NLC compounds and to compute IR transition spectra. The resulting spectra are calculated at THz frequencies, and physical parameters such as dielectric permittivity, refractive indices, and birefringence are determined. The polarizability of the molecules under investigation increases with the length of the carbon chain in the alkyl group, whereas the refractive indices decrease. The results obtained are consistent with those reported by other researchers in this field [3-7].

Despite the existence of certain inconsistencies in the experimental validation of simulated parameters among various programs, theoretical approaches, such as DFT, are crucial for modeling NLCs and forecasting their spectral properties. Notably, computer simulations can significantly enhance our comprehension of the microscopic properties that affect macroscopic traits [1,2]. Notably, the achieved results can be utilized to enhance the molecular configuration of NLCs, thereby facilitating the production of materials that are physically optimized for specific applications, particularly in photonic applications [9-13].

This work was supported by the National Science Centre, Poland, Project nr 2023/05/Y/ST11/00238 – "INORIN – Optically addressed high-speed inorganic-organic interface for advanced optical and terahertz photonics", carried out within the M-ERA.NET 3.

References

[1] J. Parka, K. Sielezin, Mol. Cryst. Liq. Cryst. **657**, 66 (2017).
[2] K. Sielezin, R. Kowerdziej, J. Parka, Liquid Cryst. **1563918**, 1 (2018).
[3] Z. Chen, L. Jiang, H. Ma, Chem. Phys. Lett. **645**, 205 (2016).
[4] Z. Chen, Y. Jiang, L. Jiang, H. Ma, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **153**, 741 (2016).
[5] Z. Chen, Y. Jiang, L. Jiang, H. Ma, Liquid Cryst. **42**(7), 947 (2015).
[6] N. Vieweg, M. A. Celik, S. Zakel, V. Gupta, G. Frenking, M. Koch, J. Infrared Milli Terahertz Waves **35**, 478 (2014).
[7] P. Friebel, D. R. Galimberti, M. Savoini, L. Cattaneo, J. Phys. Chem. B **128**, 596 (2024).
[8] Molecular Modelling Software SCIGRESS, Fujitsu Limited, Tokyo, Japan 2016 http://www.fqs.pl/chemistry_materials_life_science/products/scigress
[9] R. Kowerdziej, L. Jaroszewicz, M. Olifierczuk, J. Parka, Appl. Phys. Lett. **106**(9), 092905 (2015).
[10] M. Olifierczuk, R. Kowerdziej, L. Jaroszewicz, M. Czerwinski, J. Parka, Liquid Cryst. **39**(6), 739 (2012).
[11] R. Kowerdziej, T. Stańczyk, J. Parka, Liquid Cryst. **42**(4), 430 (2015).
[12] J. Parka, S. Kłosowicz, Photon. Lett. Poland **7**(4), 90 (2015).
[13] U. Chodorow, J. Parka, O. Chojnowska, Photon. Lett. Poland **4**(3), 112 (2015).