

2. Streszczenie w języku angielskim (abstract in English)

Liquid crystalline materials based on stable organic radicals constitute a unique class of connections, which combine features typical for liquid crystals and magnetic properties characteristic for open-shell systems of radicals. Selected issues regarding the fundamental properties of liquid crystals including the influence of the molecular structure on the type and organization degree of liquid crystalline phases are described in subsection 4.1. The introduction describes the basic properties of organic radicals, their use as structural elements of self-organizing systems, and the main techniques for studying magnetic properties and their analyses as well.

Among the wide range of stable radicals, the most commonly used in the design of liquid crystals are heterocyclic radicals. The first works on paramagnetic liquid crystals come from the mid-1970s, and are oriented to the use of π -localized aminoxyl radicals such as DOKSYL and TEMPO. In next decades, attention was also paid to other liquid crystal nitroxyl radicals, such as nitronyl-nitroxide and PROXYL derivatives, however, only in the latter ones it was possible to successfully locate the heterocyclic radical in the center of the rigid core of the molecule, with maintaining the liquid crystalline properties of the material. From the anisotropic properties (magnetic, dielectric, etc.) point of view, placement of the radical in the central core favors the self-assembly of paramagnetic fragments leading to effective spin-spin interactions in the LC phase.

This work briefly describes the achievements in the field of liquid crystal derivatives of nitroxyl radicals, which are summarized in subsection 4.4.1. Pioneer studies on a new class of paramagnetic liquid-crystalline 6-oxoverdazyl and 1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl radicals, carried out in recent years in the team of prof. Piotr Kaszyński, showed interesting photoconductive properties and strong and diverse magnetic interactions in the LC phase. The most important information on both connection classes is provided in subsections 4.4.2 and 4.4.3.

The main goal of this doctoral thesis, toward to a new class of paramagnetic liquid crystal materials based on π -delocalized radicals, was to design molecules to self-organizing their paramagnetic fragments into liquid crystalline phases, their synthesis and physicochemical studies, with particular emphasis on magnetic studies, and a thorough analysis of structure–liquid crystalline and magnetic properties relationships. The most attention was paid to the development

of the newly-known liquid crystal derivatives of the 1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl, focused on achieving strong magnetic interaction.

The assumption of the work was to provide valuable information how to obtain the intended magnetic and photoconductive properties by modification of the molecular structure of mesogens.

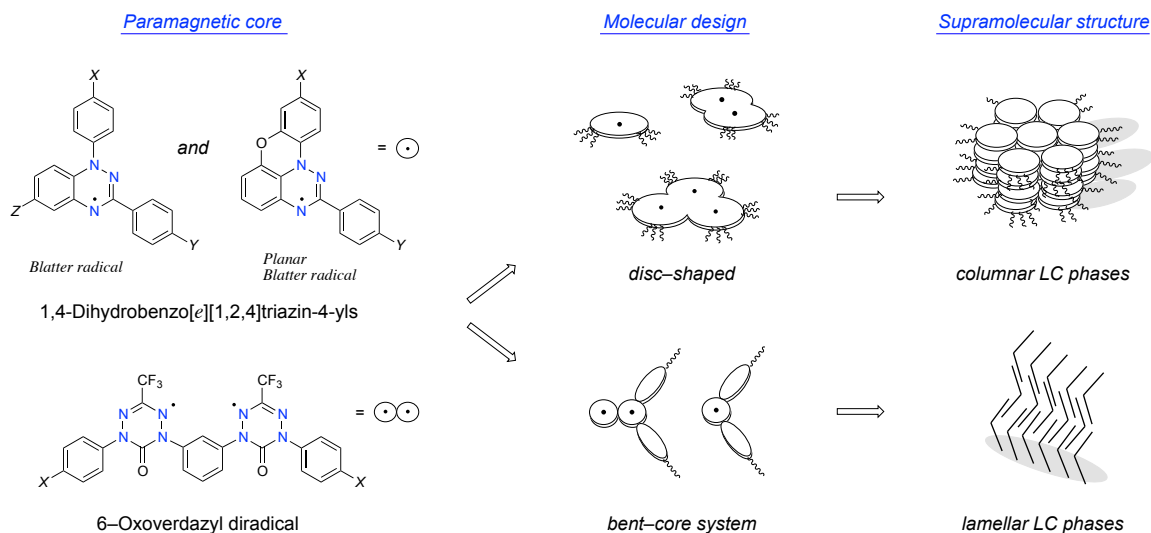


Figure 2.1. Purpose and scope of the work including the use of stable organic radicals for self-organizing magnetic liquid crystalline materials.

In subsection 6.1.1, the synthesis, as well as optical, thermal and magnetic properties of the first mesogens of bent-core derivatives of 1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl were described. In this area, mesogenic derivatives of the Blatter radical substituted in the C(3) and C(6) positions have been investigated, showing smectic phases A (SmA) and paramagnetic behavior. Furthermore the planar Blatter radical-based bent-core mesogens were prepared and studied showing photoconductive properties and strong spin-spin exchange interactions induced in chiral banana B2 phase.

The influence of the conformational effects in the core on stability of the columnar phase in half-discotic structural isomers was also investigated. Thermal analysis revealed that the steric factors of bulky substituents have a significant effect on the columnar phase stability. Increasing the complexity of the anisotropic structures of 1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl derivatives, disk-like molecules with bi- and tri-radical cores were prepared and studied showing columnar rectangular (Col_r and $\text{Col}_{r(o)}$) and columnar hexagonal (Col_h) phases, respectively. The magnetic properties of all mesogenic derivatives of this series were analyzed using VT-EPR spectroscopy.

The last section describes the synthesis and thermal and magnetic studies of the first verdazyl diradical with bent-core architecture. The analysis of magnetic measurements (EPR, SQUID) revealed a “open” singlet ground state for a simple derivative of the diradical, while the mesogenic properties of bent-core derivative were studied in two series of binary mixtures using selected liquid crystalline smectic matrices.