

B. K. Sadashiva (1946–2020)

Professor B. K. Sadashiva, a legendary scientist in liquid crystals research, at the Raman Research Institute, Bengaluru, passed away on 20 September 2020. Mentored by Professors S. Chandrasekhar at the Raman Research Institute and G. S. R. Subba Rao at the Indian Institute of Science, both stalwarts in their respective fields, Sadashiva (BKS) started his research career working on calamitic mesogens, a class of liquid crystals already established. But within a couple of years, the first synthesis of disc-like molecules that BKS prepared, created an altogether new and starkly different rich class of liquid crystals, namely the discotic liquid crystals. Published in 1997 in *Pramana* (1977, **9**, 471–480) by S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, this work pertained to (i) synthesis of hexaalkanoate of hexahydroxybenzene; (ii) structural aspects through X-ray diffraction patterns and (iii) unequivocal establishment of the proposed molecular arrangement, and already brought to light the mastery skills of BKS. This period of the late 70s, which culminated in his Ph.D. thesis submission in 1979, was also highlighted by another first in the field: A compound exhibiting the reentrant nematic phase at atmospheric pressure. The importance of this observation can be gauged by the fact that the appearance of the reentrant nematic phase completes the de Gennes' analogy between superconductors and liquid crystals. In fact, one of us (SKP) got initiated into liquid crystals working on the reentrant sequences of certain phenyl cinnamoyloxybenzoate derivatives that BKS prepared. The early period of his independent research career, during which he established a spectrum of metallomesogens – metal containing liquid crystals – based on β -diketones as valuable ligands, also led to the first paramagnetic liquid crystal. Through finesse in work, it was possible to show the importance of segmental change of aromatic and extended moieties for promoting mesomorphism. Chronologically, the next big issue in the field that his materials were investigated for, is the thermotropic biaxial nematic. Works on a diketonato–copper complex that BKS prepared ignited the quest for such a phase, which alas, continues even today.

Although he continued to work on metallomesogens, BKS had already embarked on the new topic of chiral liquid crystals. Employing acid derivatives, the skeletons of which were his early favourites, the team reported interesting structure–property correlations in ferroelectric and antiferroelectric structures. These studies brought out the importance of steric hindrance of the chiral moiety, the associated dipole moment and the proximity to the rigid core in the magnitude of the spontaneous polarization in these



fluid ferroelectric materials. In addition to small molecule rod-like mesogens, polymers, such as siloxane polymers, incorporated with naphthyl and chiral moieties, were studied for chiral mesophase emergence in these LC polymers. His interest in chiral systems also extended to using the simple cholesteryl-2-fluoro-4-*n*-alkoxybenzoates, to demonstrate the twist grain boundary (TGB) smectic A phase, the Abrikosov flux lattice analogue of liquid crystals.

Perhaps the most extensive contribution of Sadashiva during a couple of decades of his later research was in the area of bent-core or banana-shaped LCs. Intriguing to these mesogens, which have recently achieved prominence, is that mesomorphism emerges due to bent part of the core, which enhances the biaxiality of the molecule. The resulting mesophase organization into nematic, lamellar or columnar structures is unique, not seen readily with calamitic mesogens. The bent-core molecules exhibit chiral features, even if chemically achiral, leading to electro-optically switchable ferroelectric and antiferroelectric systems.

The structure-mesomorphism functional features have naturally become intensely studied aspects in the bent-core

systems. Design and synthesis became the most reliable source to expand the repertoire of these materials. Symmetric and unsymmetric substitutions about the core and bend angle considerations, positioning of the substituents, extent of rigid groups, the orientation of flexible linkers and lateral substituents, became the relevant parameters.

Molecules designed and synthesized by Sadashiva's team have significantly contributed to our present knowledge of these non-conventional architectures. Key to these contributions is the deployment of the naphthyl core having substitution at carbons 2 and 7. Sustained investigations have relied on this core for many years after BKS reported it first in 2001. The 2,7-disubstituted naphthyl core appeared to provide the optimal bend angle (around 160°), showing strong biaxiality as well as projecting tendency towards uniaxiality, leading to a direct transition between the phase identified as B2 antiferroelectric (or SmCPA) and the nematic phase. Conformationally flexible cinnamoyl linkers caught his attention, which he tuned using lateral wing groups, 5 or 7 ring-aromatic units and substituents at the arm, bay and apex sites, yielding several B phases.

Repartitioning of charges along the core was identified as yet another vital factor in bent-core mesogens. For this purpose, fluorine as a substituent was crafted carefully around the rigid aromatic rings. The ability of fluorine modification to reveal rich polymesomorphism with chiral character was put on a firmer ground. Aryl esters with differing substituents ranging from polar nitrile or fluoro-substituent to long alkyl chains were developed as the key molecular feature to induce mesomorphism yielding partially interdigitated structural arrangement in the mesophase. In addition to staple aryl ester linkage, imine connectivity was also utilized routinely in compounds prepared by BKS. Judicious placement of polar groups such as nitrile, nitro, hydroxy and halogen at the aromatic carbons, provided prime examples of realizing chiral aspects and electrical switchability from achiral bent-core molecules. His team showed the importance of the position of substitutions to substantially alter the charge distribution

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within the molecule. Attractive design aspects came out in terms of molecules having an assembly of multiple segments of terminal cinnamate moieties tethered with long alkyl chain, fluorophenyl ester, hydroquinol, lactic acid, and 2,7-dihydroxynaphthalene core, with ester bonds serving as segmental linkers. A notable observation that employed molecules of BKS is that of an orthogonal biaxial smectic phase due to the presence of a minor quantity of bent-core molecules in an otherwise calamitic system.

The masterly synthetic skills of BKS contributed immensely to the development of the field at large. Fine design principles, judicious execution of the

synthetic plan and in-depth structural characterization were hallmarks of his works, supplemented by meticulous documentation. His office being decorated with neatly labelled samples of thousands of liquid crystal compounds prepared and studied in his laboratory for decades is a rare feat, and indeed an eye-opener to any synthetic chemist.

Sadashiva had an equally good standing in sports, achieving great heights as an umpire at national and international levels of cricket. His trait to pay special attention to microscopic details in the lab also got reflected in capturing moments of the game in the fraction of a second crucial enough to make significant dif-

ferences to the game's outcome. With his demise, the field of liquid crystals and the game of cricket have lost a gentleman scientist juror who minced no words, always standing upright.

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