The role of NMR in the study of partially ordered materials: Perspectives and challenges*

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Abstract: The development of NMR techniques applied in the last 10 years to partially oriented systems, and in particular to liquid crystals (LCs), is the object of this brief perspective. The evolution of NMR methods (i.e., new NMR pulse sequences) and the improvement of both theoretical models and mathematic tools for the analysis of NMR data (specifically, for partially ordered systems) allowed scientists to extend their research to increasingly complex materials, such as dendrimers, polymers, and membranes, and to investigate unique phenomena, such as field-induced alignment and confining effects. Furthermore, the fast development of nanoscience and biomedicine is offering a rich variety of new "physical chemical" problems related to partially ordered materials. Starting from a brief perspective of recent works on thermotropic and lyotropic LCs based on different NMR methods, new challenges in this field will be drawn. Moreover, recent selected research works will be discussed in detail with particular emphasis on: (i) the effect of high magnetic fields on the supramolecular structure of chiral liquid-crystalline phases, such as the SmC*, TGBA*, and "de Vries"-type SmA* phases, by means of solid-state ^{2}H NMR; (ii) the slow dynamics in the isotropic phase of bent-core LCs (BLCs) and of liquid single-crystal elastomers evidenced by ^{2}H NMR relaxation studies; and (iii) the influence of the LC environment on the conformational properties of rod-like mesogens studied by high-resolution solid-state ^{13}C NMR methods.

   This work aims to offer an occasion of reflection on this field of physical chemistry with a glance at future trends and challenges in view of the celebration of the International Year of Chemistry, 2011.

Keywords: carbon 13; conformers; deuterium; DNA; dynamics; elastomers; liquid crystals; lyotropic liquid crystals; magnetic properties; membranes; NMR; ordered systems; polymers; protons; soft matter; thermotropic liquid crystals; xenon.

PREFACE

When I was invited to write a contribution to this special issue of *Pure and Applied Chemistry*, I immediately felt highly honored and at the same time I sensed the responsibility of such an important and difficult task.

   During the writing of this perspective, I thought that a brief preface would help me and the readers. 2011 is the International Year of Chemistry, under the partnership of UNESCO and IUPAC [1], and it is a good occasion for reflecting on the new directions of this science and its impact on society.

Moreover, my scientific experiences of liquid crystals (LCs) suggest that another crucial issue to be considered in this circumstance is the complex relationship between chemistry and other sciences, such as physics and biology. As a curious coincidence, 2011 is also an anniversary to be celebrated by the "liquid crystal" community. About 100 years ago, the physicist and crystallographer Otto Lehmann described the fascinating structures of a new kind of material thanks to his home-made microscope*, giving a fundamental contribution to the discovery of *flüssigen kristallen* (German: liquid crystal) [2]. Besides that, 2011 is the 20th anniversary of the Nobel Prize awarded to Pier Gilles de Gennes [3], who explained the thermodynamics of liquid-crystalline phase transitions and physical chemistry of phenomena such as adhesion and wetting. As a visionary, he anticipated the existence of new molecular systems, which became reality after intense research by other scientists inspired by de Gennes's works.

INTRODUCTION

Liquid crystals (LCs) are very fascinating materials which nowadays touch many aspects of our daily lives [4]. As a part of the so-called "soft matter", LCs represent, better than other materials, the subclass of "partially ordered" systems, having a unique chemical and physical properties as well as a very rich variety of organized structures with different symmetries and complexity (Fig. 1). The presence of molecular chirality, for instance, introduces additional terms in the energetic balance, which lead to the formation of new mesophases with different supramolecular architectures [5]. Among thermotropic low-molecular-weight LCs, ferroelectric rod-like smectogens [6,7] and bent-core (or banana-shaped) liquid crystals (BLCs) [8,9] were the most studied LCs in the last 10 years, due to their high potentialities for new liquid-crystal display (LCD) technology. The fast switching of the ferroelectric and anti-ferroelectric smectic phases (SmC* and SmC*$_A$, respectively) under opposite voltages [4] and the possibility to play with two external stimuli in perpendicular directions in biaxial nematic BLCs [10] have focused many efforts in these fields. Recently, the evidence of temporary organized nanoscale-clusters in the nematic [11,12] and isotropic [13] phases of BLCs have inspired new interesting studies. Different applications, such as optically nonlinear devices including optical waveguides and electro-optic modulators or high-strength fibers, have driven the research in the field of polymer liquid crystals (PLCs) [14]. Polymer-dispersed liquid crystals (PDLCs), which are composite materials consisting of micron-sized droplets of LC dispersed in a polymer matrix [15], mainly studied for new LCDs, light valves, and modulators, are an example of LC-based composites. During the last decade, new research areas developed in a very dynamic way around liquid-crystal elastomers (LCEs) [16] and liquid-crystalline physical gels [17]. Their potential applications concern smart materials, such as artificial muscles, for converting electrical energy into mechanical energy and vice versa. An additional stimulus that can produce shape- or phase-switching in photosensitive LCs [18,19] is UV light. The tremendous increase of interest in nanoscience brought many scientists to use LCs as aligning solvents [20,21], inducing nanomaterials of different kinds and shapes (nanorods, nanoparticles, carbon nanotubes, etc.) to form organized aggregates [22]. Great efforts have been spent also in the preparation of more complex LCP- or LCE-nanoparticles composites [23,24]. Just in the last year, significant progress has been made in producing new systems based on nanoparticles dispersed in LCs [25] and liquid-crystalline colloids [26]. On the other hand, the spontaneous organization of micrometer- or nanometer-sized colloids or composites is of scientific importance for understanding the self-assembly processes and for bottom-up fabrication of functional devices. It is worth noticing the area of self-assembled functional LCs, such as 1D and 2D ion conductive systems composed of polymers, mesogens, and salts, which are very promising for ionic and electronic conduction [27].

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*As reported in ref. [2], in 1909 O. Lehmann gave a memorable one-day lecture at the Sorbonne (Paris) about his discoveries on liquid crystals. Around 1911 he published his contributions to the development of new crystallization microscopes and chemical microscopes for thermal analysis.
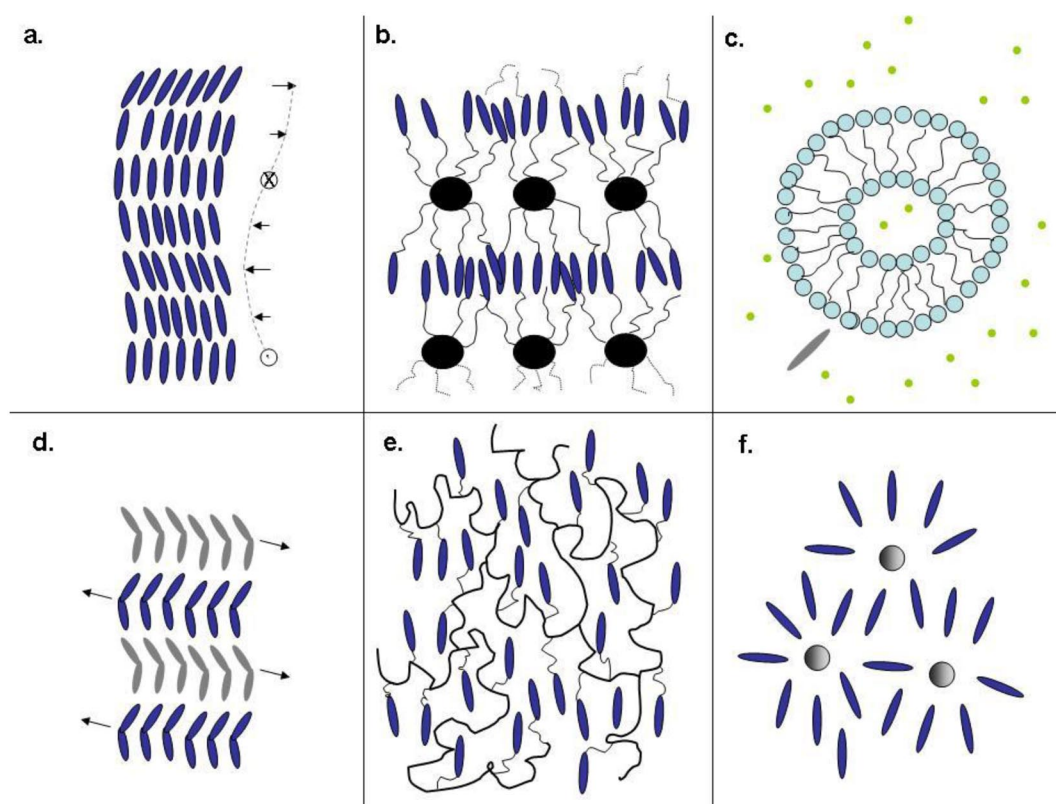
Fig. 1 Scheme of liquid-crystalline materials of technological interest: (a) the ferroelectric SmC* phase (the polarization vector is indicated by an arrow layer by layer); (b) liquid-crystalline dendrimers forming a SmA phase (the microsegregation between the dendrimer cores and the terminal mesogenic units is evidenced); (c) a liposome in water solution interacting with a small molecule (gray rod); (d) a switchable smectic polar phase formed by BLCs (the polarization vector is indicated by an arrow layer by layer); (e) a liquid-crystalline side-chain elastomer in the nematic phase; (f) a colloidal mixture of nanoparticles dispersed in a liquid-crystalline environment.

At the frontier between chemistry and biology, lyotropic LCs and biological LCs represent the second big area in fast development. The mechanisms at the basis of self-assembly, interface interactions, confinement, anchoring, and alignment of biopolymer solutions, such as DNA and RNA, polypeptides, collagen solutions, and membranes, were the object of recent intriguing research [28–30]. Future applications of these natural anisotropic soft materials are very promising and span from bio-mimetic technology [30] to drug delivery vehicles [31,32] and new DNA detection systems [33].

The main purpose of the present perspective is to show the variety of NMR studies applied to partially oriented systems, and in particular to LCs, and the implications of the various methods, developed in the recent years and used to investigate many different types of soft materials, in the "big" sciences, such as chemistry, biology, and physics. This work does not claim to explain the NMR methods, but to give to non-experts the perception of the fundamental role of NMR spectroscopy to the understanding of the molecular properties of partially ordered materials. For a comprehensive explanation of the NMR techniques applied to these materials, several books [34–36] and reviews [37–41] have been published. NMR is a very versatile spectroscopy that can solve many different "problems". In the case of partially ordered materials, the ability to study the local orientational order of molecular fragments, the distribution of molecules within a complex supramolecular architecture, and to get detailed information about the average conformer of a molecule dissolved in a liquid-crystalline environment represent some

of the advantages of NMR with respect to other experimental techniques. Moreover, dynamic processes involving groups of molecules, single molecules, or some of their moieties can be described by combining different NMR methods. These properties have a significant role in the technological and biological applications of these materials.

For the purpose of this perspective, and for brevity, emphasis will be given to the NMR studies of LC materials of major interest for technological applications or for their implications in the biological and medical sciences.

In particular, the development of NMR techniques and methods applied to partially oriented systems in the last 10 years will be the object of a first brief overview with a glance at future trends and challenges. The second part is a detailed report about three specific topics: (1) the effect of high magnetic fields on the supramolecular structure of chiral liquid-crystalline phases, such as the SmC*, TGBA*, and "de Vries"-type SmA* phases, investigated by means of ^{2}H NMR; (2) the slow dynamics in the isotropic phase of BLCs and of liquid single-crystal elastomers evidenced by ^{2}H NMR relaxation studies; (3) the influence of the LC environment on the conformational properties of rod-like mesogens studied by high-resolution solid-state ^{13}C NMR methods.

This perspective aims to offer occasions of reflection on the future challenges of this field in view of the International Year of Chemistry 2011.

NMR TO STUDY STRUCTURAL AND ORIENTATIONAL PROPERTIES OF LCs

The first successful application of NMR spectroscopy to LCs was reported in Alfred Saupe's milestone paper in 1963 [42]. It was about ^{1}H NMR spectra of benzene diluted in a nematic LC. Thereafter, new methods were explored, and just recently a series of papers was collected by Prof. G. Luckhurst [43] in a special issue of *Liquid Crystals* dedicated to Saupe. In the following, several recent studies, among the most significant ones, dealing with structural and orientational properties will be reviewed in the spirit of the present perspective.

From small molecular probes diluted in LCs…

Proton NMR spectra of molecules in a partially oriented solvent, such as LC nematics and smectics, are dominated by the direct dipolar coupling between protons, usually referred as D_{ij}. In the case of small molecules (methane, ethane,…) these quantities can be easily measured from the spectrum, and they can be related to both local orientational order parameters, S_{ab}, and to geometrical features, such as angles and bond lengths. The increase of molecular complexity returns into a nontrivial interpretation of ^{1}H NMR spectra which requires a combination of techniques [44]. Rotational/vibrational corrections to the observed dipolar couplings are indeed required [45], and several algorithms exist to solve complicated NMR spectra [46]. Nowadays, modern ^{1}H and ^{13}C NMR techniques in combination with theoretical models are employed in the study of solutes dissolved in LCs: the use of "magic mixtures" to separate orientational contributions, multiple quantum NMR techniques, model calculations based on the shape of the probes and computer simulations as well [47–49]. These methods avail to get detailed information about the average conformer of probe molecules [50] or to test new molecular models [51]. Further improvements concern the use of ^{2}H natural abundance [52], the high magnetic field orienting effect [53], and low-orientational-order liquid-crystalline solvents [54]. These approaches have also been successfully applied to study more complex molecules, such as biomacromolecules, partially ordered in anisotropic media [55]. For this purpose, and in particular, for applications in structural biology, genomics, and proteomics, the research on NMR of small molecules dissolved in LCs is crucial. It is, in fact, the analysis of the "residual" dipolar couplings (^{13}C-^{13}C, ^{13}C-^{1}H, ^{15}N-^{1}H, ^{15}N-^{13}C,…) of biomolecules partially oriented in an anisotropic environment which allows the structural information to be achieved [56].

Another field of NMR spectroscopy in rapid development is the one using noble gases as probes to study oriented materials. Thanks to the large polarizability of xenon, for instance, [129]Xe chemical shift is very sensitive to phase transitions and changes in the orientational order of LCs [57]. The sensitivity of this technique is such that [129]Xe chemical shift of xenon dissolved in isotropic liquids is used to calibrate temperature and to check the temperature stability [58].

Moreover, NMR is fundamental for investigating liquid-crystalline systems themselves. Commercial nematics and smectics, or relatively simple liquid-crystalline compounds are the object of intense research mainly with methodological purposes. In this sense, standard rod-like LCs are still very actual, and it is reasonable to think that they will be used in the future to test new NMR sequences and methods, or new molecular models. Recently, for instance, deuterium atoms at natural abundance (NAD NMR), 2D proton-detected ^{13}C local field (PDLF), and ^{13}C 1D NMR methods, usually applied to the solid state, were successful in the determination of conformational and orientational properties of LCs [59,60]. Among the most significant methodological improvements of the recent years, it is worth mentioning the technical improvements in the detection of ^{13}C NMR spectra in the presence of [13]C-^{19}F interactions [61] and the development of a 2D fluorine-detected local field (FDLF) NMR experiment, applied on a perfluorinate probe diluted in an LC [62]. ^{19}F and ^{2}H NMR spectroscopy applied to LC compounds represents another area developed during the last four decades. Now, these NMR approaches are carried out to study complex LC-based materials and to solve specific problems in the field of soft materials, as will be discussed in the following pages. Concerning the recent methodological advances tested on relatively simple LC compounds, the combined analysis of ^{19}F and ^{13}C NMR 1D and 2D methods [63]; ^{13}C, ^{1}H, ^{19}F, and ^{2}H NMR techniques; and advanced density functional theory (DFT) methods for the calculation of molecular conformations, chemical shift and quadrupolar tensors of nuclei in different molecular sites [64–68], represent the most promising ones.

… to complex liquid-crystalline materials

The increase of molecular complexity in liquid-crystalline materials introduces new tasks as a consequence of additional interactions between different moieties of the same molecule, between close molecules of the same species, and, in heterogeneous systems, between different components. As briefly described in the Introduction, the variety of new interesting LC materials developed in the recent decade stimulated NMR spectroscopists to perform new challenging experiments and to a deeper interaction with other scientific disciplines.

Starting from thermotropic LCs, ferroelectric smectogens [6,7] have been intensively studied in their SmC* phase for the switching behavior in the presence of electric fields. An important structural feature is the trend of tilt angle within the temperature range of the ferroelectric phase (Fig. 1a), commonly determined through X-ray and electro-optical measurements. However, the tilt angle measured with these two techniques is not the same quantity due to the different sensitivity and physical principles of these techniques. NMR provided an alternative and robust method, with the additional advantage to be able to "see" how different parts of the molecule are tilted with respect to the helical axis [69]. Recently, two reviews deeply addressed this topic [63,64].

The existence of the biaxial nematic phase represented a hot topic that is still driving the research on new BLC materials. In 2004, the phase biaxiality of a high-temperature bent-core nematogen was claimed based on ad hoc ^{2}H NMR experiments [10]: the simulation of the line shape of NMR spectra acquired under fast rotation in a direction perpendicular to the external magnetic field provided a non-zero value of phase biaxiality [70]. This attractive and fascinating mesophase was the object of investigation not only among BLCs [71,72] but also in LC polymers [73], and the role of ^{2}H NMR was often crucial in correctly determining both molecular- and phase-order parameters.

Disc-like liquid crystals (discotic LCs) are another type of calamitic LCs which form columnar phases very attractive for applications in nonlinear optics and charge/ions transport. The conformational

properties of discotic LCs were intensively investigated by Maliniak and his collaborators, combining several 1D and 2D ^{13}C NMR techniques with advanced molecular models [74,75].

Among thermotropic LCs, a new class of fascinating molecular systems is that of LC dendrimers (see Fig. 1b). Despite their spherical shape in solution or in the isotropic phase, LC dendrimers arrange in highly anisotropic structures when entering the LC mesophases. The microsegregation between the cores and the terminal units observed in smectic phases of carbosilane dendrimers, as well as the ordering properties of these LC dendrimers in the presence of external fields, were investigated by ^{2}H and ^{1}H NMR [76–78].

NMR works in the field of liquid-crystalline polymers and networks are numerous, and an overview of all of them would be unfeasible in this context. However, it can be safely said that the major contributions to the structural and ordering characterization of LC polymers and LC elastomers came from ^{2}H NMR spectroscopy. The possibility of selectively labeling a chemical position of the system under study and the relatively simple spectra arising, which are dominated by the ^{2}H quadrupolar interaction, are some of the reasons for the wide use of ^{2}H NMR. Alternatively, small deuterated probes can be dissolved in these materials to get "averaged" information. ^{2}H quadrupolar splitting is indeed very sensitive to the local orientational order and to the presence of heterogeneities and distributions of orientations, in addition to the previously mentioned phase biaxiality. The latter was indeed recently investigated in the SmA of side-chain LC elastomers [79]. ^{2}H NMR temperature and angular-dependent studies were fundamental in describing a particular type of LCEs, the so-called liquid single-crystal elastomers (LSCEs). These systems are usually in the form of monodomain films with all mesogenic units (rods in Fig. 1e) aligned on average along the main direction of the film. The thermodynamic nature of the paranematic–nematic transition in LSCEs was first described by means of microcalorimetry and ^{2}H NMR studies [80–82]. Its dependence on crosslinking density and the coupling between the nematic orientational order and thermomechanical behavior [83], revealed by means of ^{2}H NMR experiments, are important information for the understanding of the physical properties of these shape-memory materials. Other recent works based on ^{2}H NMR concern the heterogeneity and order–disorder transitions of LCE composites [84] and the polydomain (i.e., with an isotropic distribution of domains) LCEs [85].

Beside liquid-crystalline properties, NMR can help to study phenomena where LCs play a fundamental role. For instance, the mechanisms of surface-induced alignment of LCs are a crucial aspect in LCDs and other technological applications; this aspect was a great stimulus for NMR scientists who started to investigate confined LC systems, such as PDLCs [86,87]. LC nematogens and smectogens confined in anopores of different porosity, pore shapes, and dimensions and anchoring effects have been widely investigated through ^{2}H NMR methods [88,89]. ^{129}Xe NMR can detect induced phase-transition phenomena in confined LC systems, and it provided an alternative excellent way to determine the pore size when unknown [90]. A recent improvement in this field came from the ^{13}C NMR investigations of a small probe (CH_3I) in LCs confined in pores [91]. All these NMR investigations are very important for testing the phenomenological theories concerning the confinement of a few molecules into restricted volumes, such as micro- and nanodevices. Another application of LCs is related to chromatography for discriminating (and separate) different enantiomers. The proton-decoupled natural abundance ^{2}H NMR method has been used to study chiral molecules orientationally ordered in poly(g-benzyl-L-glutamate) [40]. It is worth mentioning other helpful NMR techniques for measuring the enantiomeric excess of chiral molecules dissolved in LCs, such as ^{19}F NMR and exchange ^{2}H NMR [92,93], as well as 2D correlation NMR experiments [94].

Lyotropic liquid crystals (LLCs) (the second big category of LCs) show various mesophases as a consequence of the addition of solvents [4]. Besides the chemical composition and the temperature, another fundamental parameter influencing the mesophase behavior is indeed the relative concentration of the LLC components. LLCs are highly heterogeneous systems (typically they have two or three components), and for this reason the study of LLCs is very challenging. One of the major problems of NMR studies on LLCs is the difficulty in getting oriented systems, especially in lamellar phases. Moreover,

the averaging of the NMR quantities (i.e., quadrupolar splitting, dipolar coupling, and chemical shielding) in this heterogeneous scenario during the NMR characteristic time has to be taken into due account. The use of small probes is, in fact, quite risky, since small molecules can diffuse quickly from bulk solvent to interface regions and inside the mesophase structures (i.e., micelles, lamellar layers, vesicles, and so on), thus averaging out the NMR signals. To get rise of that, several NMR experiments can be carried out, possibly combining the complementary properties of different nuclei, such as ^{13}C, ^{1}H, ^{15}N, ^{14}N, ^{31}P, ^{2}H, and ^{19}F [95–99]. Selective deuteration of single components of LLCs can be helpful in elucidating single-molecular properties, such as the orientation of molecules inside and/or at the interface of the typical LLC structures, the presence of specific interactions among different components and their average conformation. ^{2}H, ^{1}H, and ^{13}C NMR techniques can serve to study the alignment and conformational features of amino acids, polypeptides, and saccharide derivatives diluted in very low concentrations in lyotropic lamellar phases [100], as well as in lipid bilayers [101]. The significance of these studies is that these systems mimic those of biomolecules at the interface with cellular membranes, so they are connected to several biological issues.

Another fascinating area investigated in the last decade is that of heterogeneous clay suspensions [102] and colloidal systems [46]. Several experimental techniques have been applied in order to confirm the presence of weak orientational order and mesophase behavior. In many cases, NMR provided evidence of both degree of order and basic structural features in salt-clay suspensions [103] and heterogeneous colloidal phases [104].

Phase separations in microemulsion systems and the nature of coexisting mesophases in LLCs have attracted the interest of the scientific community for their applications in rheological and capacitor devices [105,106], membrane separation technology, and pharmaceutics [107,108]. Original studies based on solid-state ^{2}H NMR [109] and combined ^{1}H NMR and UV spectroscopy [110] were published several years ago. A recent renovated interest in these phenomena brought Lebar et al. [111] to study the separation in microemulsions of nanosized lyotropic inverse micelles crossing the isotropic–nematic transition by ^{2}H NMR microimaging in combination with microscopy and calorimetry. The analysis of ^{2}H NMR line shape at different concentrations and temperatures allowed the characterization of the thermodynamics and kinetics of microsegregation and phase separation phenomena in LLCs.

NMR TO STUDY MOLECULAR DYNAMICS OF PARTIALLY ORIENTED SYSTEMS

The anisotropy of partially ordered systems reflects on their dynamic behavior both at nano- and mesoscales; mobility of single molecules or groups of them is very important in determining the macroscopic physical properties of LCs [112]. Moreover, dynamics must be taken into account for the correct interpretation of all experimental data due to the motional averaging effect.

NMR spectroscopy has been widely used to study the molecular dynamics in liquid-crystalline materials, which can be rather complex due to the occurrence of several kinds of motions (Scheme 1) and to the partial overlapping between their characteristic times. The power of NMR in the study of molecular dynamics mainly relies on its versatility [35,37]. In fact, different types of NMR techniques [113–115] can provide information over a very wide range of frequencies, thus potentially allowing several molecular motions to be investigated. The behaviors of nuclei that are present, or can be quite easily inserted by selective labeling liquid-crystalline moieties, such as ^{1}H, ^{14}N, ^{13}C, and ^{2}H, allows one to explore different dynamic aspects. In the following two sections, a brief overview of the recent contributions to the study of dynamics by means of NMR spectroscopy is given, with the main purpose to put in evidence the novel technical developments and the applications of robust methods to new challenging LC materials.
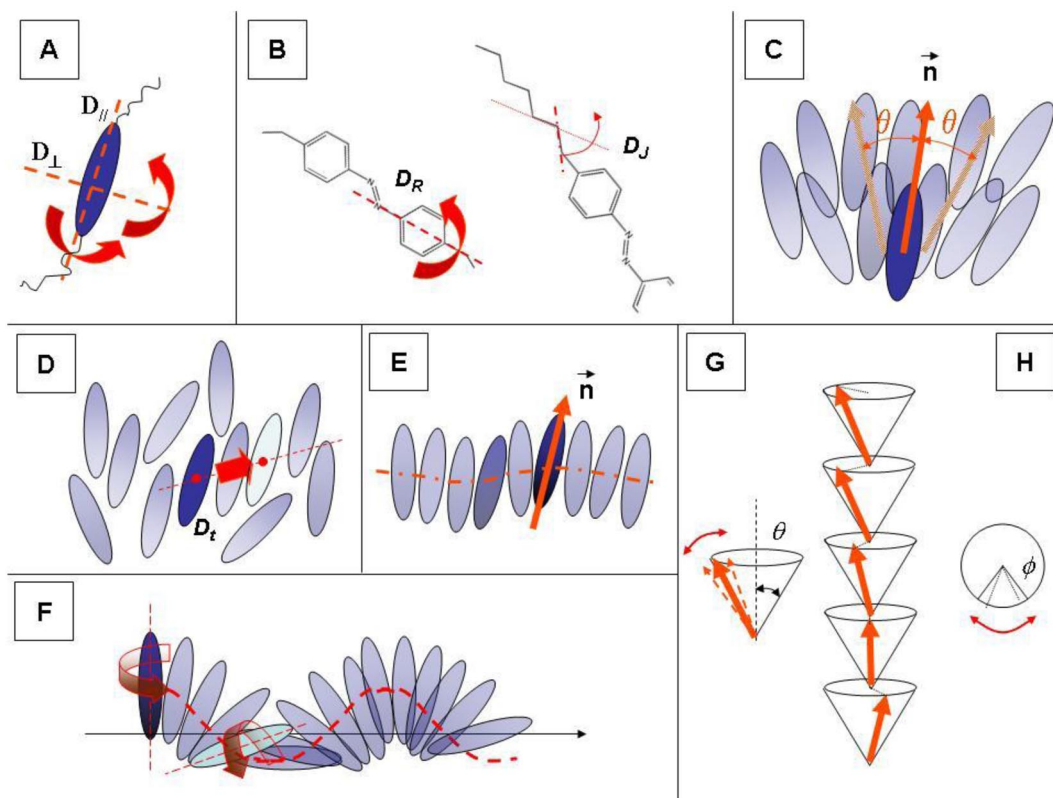
Scheme 1 Representation of the molecular motions affecting liquid-crystalline materials. (A) overall molecular reorientation motions (i.e., tumbling, $D_\perp$, and spinning motions, $D_{//}$); (B) internal motions: phenyl reorientation (D_R) and conformational change (D_J); (C) order director fluctuations; (D) translational self-diffusion (D_t); (E) layers undulations; (F) rotations mediated by translational displacements; (G) soft mode in SmC* phases; (H) Goldstone mode in SmC* phases.

Single-molecular motions

In low-molecular-weight LCs, overall molecular motions, such as the spinning (rotation parallel to the main molecular axis, "//") and tumbling (rotation perpendicular to the main axis, "⊥") rotational diffusions (see Scheme 1a), and internal motions, such as rotations around single or double bonds and *trans-gauche* isomerizations of alkyl chains (see Scheme 1b), are usually very fast, with typical correlation times, τ_c, in the range 10^{-7}–10^{-11} s. The possibility to get reliable information about the internal motions, thanks to the selective deuteration of different positions in the molecular system, makes ^{2}H NMR one of the most used techniques [37]. To this purpose, ^{2}H NMR longitudinal relaxation times, T_{1Z} and T_{1Q}, which are sensitive to motions in the fast regime, can be analyzed in the Redfield approximation [116], using specific theoretical models [117]. Within these theories, internal motions are commonly assumed to be independent from overall molecular motions [118], and they are treated as free diffusive reorientations [119] or strong collision diffusion [120]. Moreover, theoretical models, such as that developed by Nordio et al. [121], well describe the overall molecular motions of rod-like mesogens (approximated to ellipsoids) in uniaxial mesophases (i.e., nematic and Smectic A ones). ^{2}H NMR relaxation data collected in the nematic and smectic A phases of calamitic mesogens have been analyzed since the 1990s using a global target approach [119], which implies also an assumption of an Arrhenius behavior of diffusion coefficients vs. temperature. The development of a new mathematic tool [122] and

a critical analysis [123] over the previous published works revealed a large correlation among fitting parameters mainly due to the complexity of the models. For instance, this critical overview [123] put in evidence that the determination of the diffusion coefficient for the tumbling motion ($D_\perp$) is not safe in the case of a small dataset. This problem has been solved by using a larger dataset throughout different procedures such as: (1) angular-dependent ^{2}H NMR T_1 relaxation measurements [124]; (2) ^{2}H NMR T_1 relaxation measurements for different isotopomers labeled on different molecular sites [124,125]; (3) ^{2}H NMR T_1 relaxation measurements recorded at different Larmor frequencies (so-called "multi-frequency" approach) [126,127]. The comparison of ^{2}H NMR relaxation data with other techniques, such as dielectric relaxation and neutron scattering [128,129], confirmed the solidity of this approach in the self-consistent determination of rotational diffusion coefficients both for internal and overall molecular motions [123]. These robust methodologies have been successfully applied also to the ferroelectric SmC* phase [130], dendrimers [131], and polymers [132] in their mesophases, as well as to study the internal motions of a small probe diluted in two LLC phases [133]. This field is, however, still of great interest for methodological reasons, as seen from the recent work by Cifelli et al. [134]. ^{2}H and ^{14}N relaxation analysis were combined by Dong et al. [135] to describe the head-group motion of an amphiphilic molecule in a lamellar phase, while chain reorientations and segmental motions in LLCs and PLCs were also studied by solid-state ^{13}C and ^{2}H NMR [136–139], dipolar recoupling 2D magic-angle spinning (MAS) NMR [140], and ^{1}H double-quantum NMR techniques [141]. In a few cases, the analysis of ^{2}H NMR spin–spin relaxation times (T_2) was applied to the molecular reorientations of LCs or their moieties in the slow-motional limit [114,131,142,143], however, this technique has been most widely adopted to describe collective motions, as will be reported in the next subsection.

Among single-molecular motions, translational self-diffusion (see Scheme 1d) and jump diffusion, which are generally fast motions, represent another big category where the contribution of NMR is central. The anisotropy of the mesophases is such that LC molecules often diffuse with different velocities along different directions. Diffusion is a very important process for applications, for instance, in the case of columnar discotic LCs, and it is a crucial and actual issue in heterogeneous and complex systems. Field-gradient and pulsed field-gradient (PFG) NMR methods [144] dominate among the experiments used to detect the translational self-diffusion in the liquid-crystalline phases. These methods have been successfully applied to thermotropic LCs, as reported in this comprehensive review [145a], however, this technique is applied also to much more complex systems, such as ion-conductive polymers and columnar phases [145b]. Several NMR sequence improvements have been made in the last decade [144–146], and the increasing number of publications indicates that many efforts will still be devoted to this topic. Just in the recent year, a new method based on a combination between PFG NMR and MAS NMR [147] and a multiquantum stimulated echo-based pulsed-gradient spin-echo sequence (MQ-PGSTE) have been developed [148]. ^{1}H NMR and ^{129}Xe NMR techniques have also been applied to diffusion measurements in the SmA, ferroelectric, and antiferroelectric smectic LC phases [149], giving rise to basic information useful for both theoretical and applicative points of view. 2D exchange ^{2}H NMR and line-shape analysis is applied to determine jump diffusion of molecules in mesophases with spatial discontinuities (i.e., ferrielectric and TGB phases) [150], while ^{1}H NMR relaxometry [41,115] successfully described molecular rotations mediated by translational displacements (see Scheme 1f) in chiral LC [151] and TGB phases [152]. It is worth mentioning the basic role of NMR in studying single-molecular diffusion motions in lyotropic systems, membranes, and vesicles [153–155]. New methodologies were recently published which also use NMR imaging techniques to "see" the anisotropy of molecular diffusion in lyotropic systems [156]. The study of diffusive processes in partially ordered and anisotropic systems is indeed a crucial issue, for many aspects still under controversial scientific debate, and a comparison among different NMR techniques is undoubtedly the best approach.

Collective motions

One of the peculiarities of anisotropic systems is the occurrence of collective motions: groups of molecules fluctuate or diffuse in anisotropic ways, maintaining a symmetry which reflects that of the mesophase. Contrary to single-molecular motions, collective dynamics is typically in the intermediate-slow regime (characteristic times in the range 10^{-1}–10^{-7} s). One of the most studied collective motion is the so-called order director fluctuation (ODF) (see Scheme 1c) in uniaxial phases, such as the nematic one: groups of molecules fluctuate with respect to the average direction of alignment (i.e., the local phase director, **n**). The best NMR approaches to investigate ODFs are ^{2}H NMR spin–spin relaxation times (T_2) analysis [117] and ^{1}H NMR relaxometry [41] at low frequencies (below 0.1 MHz). The extraction of dynamic information from T_2 relaxation times, employing the Carr–Purcell–Meiboom–Gill sequence, for instance, requires solution of the stochastic Liouville equation valid in the slow-motional regime, and only recently Frezzato et al. [157] developed a consistent theory for the characterization of ODFs from T_2. This novel theoretical approach has been applied to study the fluctuation modes in standard nematics, LC polymers, membranes, and vesicles as well [158]. Softening and fluctuation modes of membranes and lipid bilayers, similarly to ODFs in thermotropic LCs, are also studied by ^{2}H NMR relaxation [159]. However, the complexity of the theoretical model needed to analyze T_2 is a disadvantage with respect to ^{1}H NMR relaxometry.

In smectic phases, an additional collective motion is the "layer undulation" (LU) (Scheme 1e) which can be partially overlapped to ODFs. Several theories [160] have been developed in the 1980s in order to extract the LU and ODF contributions from longitudinal relaxation times, and ^{1}H NMR relaxometry recently has been revealed as a very good technique to well estimate and quantify their role also in unconventional LCs and in chiral mesophases [151,152,161]. The increase of the complexity of the LC phases gives rise to additional motional processes, such as the Goldstone (Scheme 1g) and soft (Scheme 1h) fluctuations typical of the ferroelectric SmC* phase [162]. Two angles define the position of a molecule within the helical supramolecular structure: the tilt angle, θ, and the azimuthal angle, ϕ. It is the modulation of these two angles along the helical axis which characterizes the Goldstone and soft modes. Despite a few works based on ^{13}C NMR relaxation [163], a quantitative description of these motions and their contributions to NMR relaxation in the ferroelectric phase was never completely done. Recently, ^{2}H NMR T_1 and T_2 relaxation times recorded in the SmC*, SmC*$_A$, and re-entrant SmC* phases [142] revealed the presence of several slow motions, but further investigations and theoretical improvements are needed. So far, the best technique to investigate fluctuation and collective modes is indeed dielectric spectroscopy [164].

A very important issue is related to the mechanisms of reorientation and realignment of the phase director **n** after the application of external fields. The knowledge of these phenomena is basic for optimizing technological devices where, for instance, the on-off switching is determined by applying variable voltages. To this aim, the studies of director realignment and director dynamics performed by Luckhurst, Sugimura, and co-workers [165] by means of ^{2}H NMR spectral shape simulations in the presence of the electric field have to be considered really pioneering and fundamental works. The understanding of the dynamics and changes in the distribution of the phase director when electric or magnetic fields are applied [166], or in the presence of surface and confining effects, is another important result of these investigations [167].

RECENT STUDIES BASED ON NMR

This section is devoted to a selection of recent studies based on different NMR techniques applied to several liquid-crystalline materials, from low-molecular-weight rod-like and BLCs to high-molecular-weight LC elastomers. These topics are reported and discussed in detail.

How the magnetic field influences the order and the supramolecular structure

^{2}H NMR spectroscopy has been widely used to investigate the structural features of the chiral ferro-electric SmC* phase (see Fig. 1a), and recent reviews [64,65] demonstrate how this technique is solid in determining both orientational order and molecular tilt in this mesophase. Chiral LC phases are characterized by helical supramolecular structures which can be destroyed or deformed under the effect of high magnetic fields, as those typical of NMR instruments. Several NMR studies were carried out to investigate these phenomena in the SmC* phase [168–170]. Moreover, few papers [171,172] appeared about the effect of external magnetic fields on the supramolecular structure of frustrated twist grain boundary (TGB) phases. The simulation of ^{2}H NMR spectral line shape and the comparison between the measurements performed at different magnetic fields allowed the determination of several structural features of the TGB* phases, such as the value of the tilt angle in two TGBC* phases [152]. An analogous methodology has been newly adopted to study the SmA-SmC* phase transition in a "de Vries" mesogen, giving interesting clues in the understanding of this new type of LC [173].

Ferroelectric SmC phase*

It is well known that the helical supramolecular structure typical of the ferroelectric SmC* (Fig. 1a) phase can be unwound by applying external electric fields [174], and this aspect has been investigated in order to design appropriate technological devices, such as ferroelectric LC displays. On the contrary, the effect of external magnetic fields has been less studied [175–177], even though it is supposed to show similar interesting features. For this purpose, NMR spectroscopy has the advantage of working in the presence of magnetic fields of high intensity with the possibility to explore different geometrical orientations between the helical axes of the SmC* phase and the magnetic field, H.

The first angular study proposed by B. Zalar et al. [169] and applied to a ferroelectric smectogen (i.e., the DOBAMBC) evidenced the dependence of the critical field, H_c, able to unwind the helical structure, by the angle $\beta \neq 0$, between the helices and the field.

However, later ^{2}H NMR investigations on a different smectogen [169,178] revealed that also in the case of $\beta = 0$, namely, with the magnetic field parallel to the helical axes, it is possible to observe the transition between the SmC* and the unwound SmC* (uSmC*). This study was a stimulus in developing a theoretical model [179], based on the Landau–de Gennes theory [179], to describe the dependence of the temperature transitions SmA-SmC*, SmA-uSmC*, and uSmC*-SmC* by the magnetic field as well as in synthesizing new smectogens having the critical magnetic field, H_c, in the range of 2–20 T (typical of NMR instruments). So far, several experimental cases [169,170,179–181] in which the supramolecular helical structure of the smectic C* phase is unwound by a magnetic field parallel to the helical axes were found, and this theoretical model could be partially verified. As suggested in refs. [170,179], the value of H_c is different from one smectogen to another, and this can be explained by the dependence of H_c on several phenomenological parameters which are specific for each investigated compound.

"Frustrated" TGB phases*

Despite several studies that have been performed in order to characterize the structures of TGBA* and TGBC* phases by means of different techniques [182–185], few NMR studies have been performed so far [126,152,186,187]. Moreover, the electrical response [188,189] of these complex phases has been investigated, showing that the structure of the TGB phases can be unwound or strongly distorted by the electric field. The effect of the external magnetic field was the subject of recent investigations on a chiral LC containing a (*S*)-2-methylbutyl-(*S*)-lactate unit, namely, the HZL 7/* compound (see Fig. 2A), which shows a rich variety of TGB mesophases stable in a wide range of temperatures [190].

^{2}H NMR measurements performed at two Larmor frequencies (i.e., two different values of the magnetic field) show different spectral features depending on the supramolecular structure of the phase under investigation. The effect of the magnetic field in unwinding or deforming the supramolecular structure of both the TGBA* and TGBC* phases was investigated in detail [171,172]. The unwinding
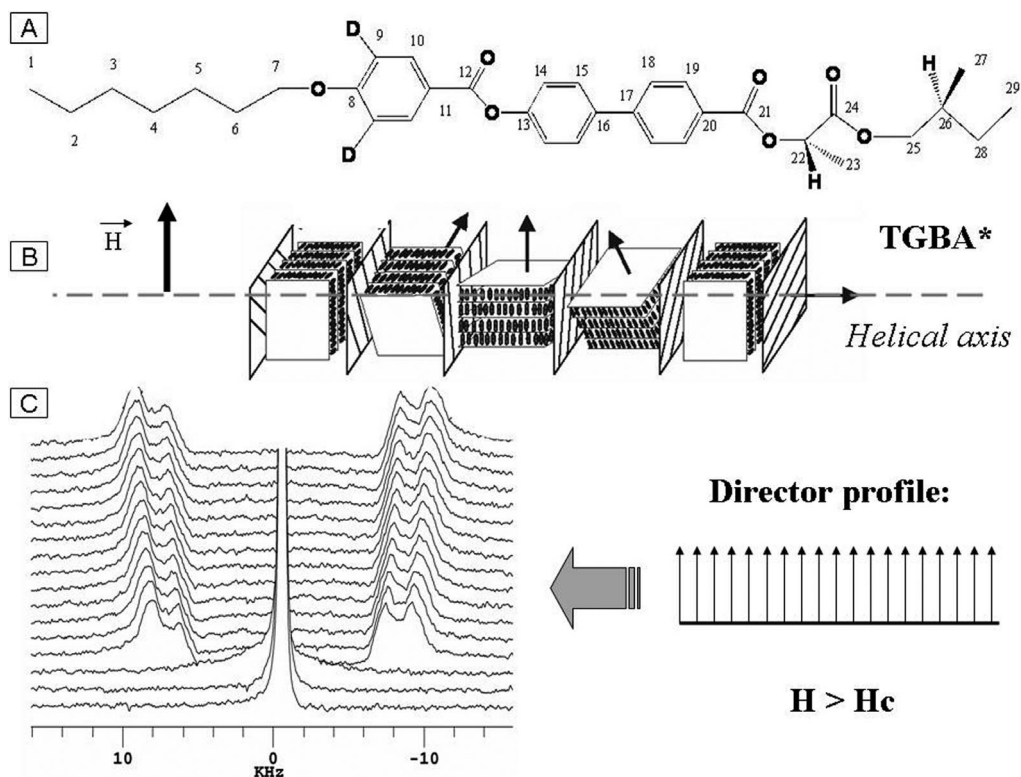
Fig. 2 (A) Molecular structure of the rod-like mesogen HZL 7/* (deuterium labeled on the phenyl ring) forming several TGB phases stable in a wide temperature range. (B) Scheme of the TGBA* supramolecular structure in the presence of an external magnetic field, H (the orientation of the local phase director in several TGB blocks and of the helical axis is indicated, the helical pitch is around 1 μm). (C) Series of ^2H NMR spectra recorded by cooling the HZL 7/* from the isotropic to the TGBA* phase in the presence of an external field H larger than the critical field, H_c; the uniform alignment of the director as derived from the spectra is indicated on the right.

of the TGB helical structure is complete and particularly evident at higher magnetic fields, while intermediate behaviors are observed at lower magnetic fields. This indicates that the supramolecular structure is very sensitive to magnetic fields of the order of a few tesla [173].

As an example, let us consider the helical structure of the TGBA* phase (see Fig. 2B): in each TGB block, molecules are ordered similarly to the SmA phase, packed in layers, and aligned on average along the normal to the layers. When moving from one TGBA* block to the next one along the TGBA* helical axis the local director **n** rotates on a fixed angle γ describing a complete helical pitch after a certain number of TGB blocks (usually between 25 and 30). In the presence of an external magnetic field, the TGBA* helical axes distribute perpendicularly to the field, H. However, if the field is strong enough ($H > H_c$), the TGBA* helical structure is unwound and the TGBA* blocks are all aligned with the local phase director **n** parallel to the field, H (see Fig. 2C). The resulting ^2H NMR spectra in these two cases ($H < H_c$ and $H > H_c$) are completely different. In the first case, the spectra have "Pake-like" features, given by a distribution of different orientations and the line-shape is usually influenced by many factors, structural and dynamic, which can be rationalized by simulating the total spectral shape. This procedure, however, is far from trivial. In the second case ($H < H_c$), the uniform alignment of the phase directors simplifies the spectrum and, as in the HZL 7/* sample, if there is a single type of deuterium on an aromatic ring (as in Fig. 2A), the ^2H NMR spectra are characterized by a quadrupolar

doublet further split by the dipolar ^{2}H-^{1}H splitting (see Fig. 2C). From the analysis of the temperature dependence of both quadrupolar and dipolar splittings, phase features, such as the local-order parameters, and molecular structural quantities can be determined.

Similarly to the TGBA* phase, the tilted TGBC* phases are also affected by the magnetic field, even though in a more complicated way, and for each phase it is possible to determine the critical value of unwinding the TGB structure. In the case of the HZL 7/* compound, the simulation [173] of the ^{2}H NMR spectral line-shapes recorded at different magnetic fields (lower than H_c) in terms of a simple structural model for all the TGB phases gave interesting results: (i) confirming the structural hypothesis for the two TGBC* phases; (ii) evaluating the level of distortion of the helical TGB and in-block SmC* structures at different magnetic fields; (iii) confirming several structural features, such as the tilt angle, previously determined by independent measurements (i.e., X-ray and optical methods) for the tilted TGBC* phases.

In principle, NMR can be used to build phase diagrams where the phase stability and orientation is plotted as a function of both temperatures and external magnetic fields. The only limitation of this approach is related to the need of different NMR instruments for each value of the magnetic field, but, on the other hand, this is a good method to obtain structural properties and phase behaviors at the same time.

"de Vries" liquid-crystalline phase (or phase transitions)

Differently from usual ferroelectrics, "de Vries"-type liquid-crystalline smectogens do not show any layer shrinkage at the SmA-SmC* transition [191]. A. de Vries proposed that in these systems the molecules are tilted, with respect to the layer normal, also in the SmA phase; however, the azimuthal angle is randomly distributed within the smectic layer. The SmA-SmC* phase transition is thus seen as a disorder–order transition in the azimuthal directions of the molecular tilt [192]. This model, known as "diffuse cone", is generally accepted and was validated by several experimental studies [191]. However, only recently NMR spectroscopy [173] has been employed to study a "de Vries" compound, namely, 9HL (see Fig. 3) [193], giving an important contribution to the understanding of the molecular origin of such interesting behavior. A sample selectively labeled on a phenyl ring (9HL-d$_2$) was studied at two different magnetic fields, 7.05 T (300 MHz of ^{1}H Larmor frequency) and 16.45 T (700 MHz). The analysis of the ^{2}H NMR spectra in the SmA and SmC* phases allowed one to obtain the local-order parameter, S_{zz}, defined in the local frame of the deuterated phenyl ring, at the two fields, as reported in Fig. 3. A very strong effect of the magnetic field can be noticed in both mesophases: the higher magnetic field (hf) is able to completely unwind the helical axis of the SmC* phase, as already observed in other ferroelectric LCs, and the molecules are aligned parallel to the field; on the contrary, the lower magnetic field (lf) is smaller than the critical field and the SmC* phase is wound with molecules tilted with respect to the magnetic field. In the SmA phase, there is also a significant effect of the magnetic field. In fact, differently from "standard" SmA phases [38,39], in the present case the values of the S_{zz} are very different at the two magnetic fields. A possible explanation is the presence of a tilt angle of the *para* axis of the labeled phenyl ring with respect to the magnetic field not only in the SmC* phase, but also in the SmA one, as predicted for "de Vries" compounds. Using the following relationship:

$$S_{zz}^{\text{lf}}(T) = S_{zz}^{\text{hf}}(T) \cdot \left(\frac{3}{2}\cos^2\theta - \frac{1}{2} \right) \tag{1}$$

the values of the tilt angle θ could be determined at each temperature. In the SmA phase, θ increases by decreasing the temperature from 6 to 11 degrees. These values confirm the peculiarity of the SmA phase formed by "de Vries" materials, envisaging also an alternative way of evaluating the tilt angle by recurring to a comparison of NMR measurements acquired at different magnetic field intensities. Interestingly, additional measurements on the 9HL-d$_2$ sample at different values of the magnetic field (even higher than 16.45 T) substantially confirmed these results [194]. Another important consequence
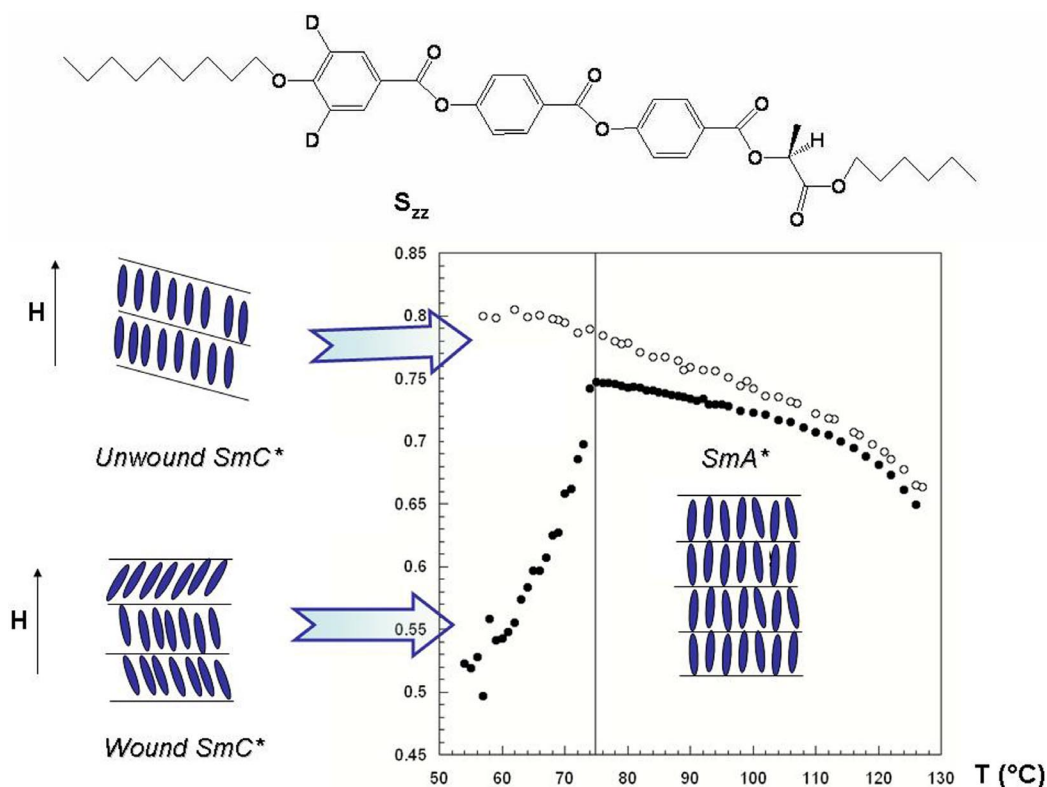
Fig. 3 From top to bottom: Molecular structure of the "de Vries" smectogen 9HL (deuterium labeled on a phenyl ring). Trend of the order parameter S_{zz} of the 9HL in its SmA and SmC* phases as a function of temperature, obtained by analyzing the ^{2}H NMR quadrupolar and dipolar splittings, at 7.05 T (solid circles) and 16.45 T (empty circles). The helical pitch of the wound SmC* phase is in the nanoscale range. The orientation and the supramolecular structure of the SmC* phase unwound by the higher magnetic field and those not unwound by the lower magnetic field are reported on the left. A scheme of the "de Vries" SmA phase is also provided.

of these measurements concerns the model for the "de Vries" SmA phase. Indeed, the large magnetic effect observed in the SmA phase is not compatible with a complete random "diffuse cone" model, suggesting the presence of a spatial modulation of the azimuthal angle within the SmA layers, and probably the presence of local clusters of molecules with the same tilt and azimuthal angles, as recently observed for other "de Vries" systems by different experimental techniques [195]. As mentioned in the Introduction, "de Vries" materials represent a hot topic in LCs due to the possible applications for a new generation of LCDs. NMR could be crucial in understanding the molecular properties and peculiar packing in the presence of external fields, and this will certainly be an object of future works.

Slow dynamics in the isotropic phase of LCs

Isotropic phase of banana-shaped LCs

The macroscopic behavior of BLCs in the isotropic phase, unusual with respect to common calamitic LCs, have attracted the interest of the scientific community. The long time needed to stabilize the isotropic phase of BLCs and to fill glass cells (several hours instead of a few minutes) and their high viscosity brought scientists to investigate the isotropic phase of BLCs. Several five-ring bent-core mesogens [196] were studied almost concurrently by independent research groups using different experimental methods, such as dynamic light scattering and electroconvection [197], ^{2}H and ^{13}C NMR spec-

troscopy [198,199]. ^{2}H NMR methods were also applied to the study of selectively ^{2}H-labeled BLCs and their subunits [200,201] in the presence of external magnetic fields and in different anisotropic environments. These works show the crucial role of the molecular packing and magnetic susceptibility anisotropy [202] in the alignment and ordering properties of bent-core molecules. Among the main results of the ^{2}H NMR studies, the identification of slow dynamic motions of BLCs in the isotropic, nematic, and smectic B$_2$ phases certainly represents the most significant one [143,178,203,204]. In particular, the trends of ^{2}H NMR line widths and spin–spin relaxation times, T_2, of two mesogens, namely, ClPbis11BB and Pbis11BB [143], in the isotropic phase (see Fig. 4) revealed the presence of unusual slow dynamics. In fact, the ^{2}H NMR spectra of these BLCs, deuterium-labeled on the central ring (see, e.g., Fig. 4B), recorded in the isotropic phase, present an unusual line-broadening, not ascribable to pretransitional effects. In order to clarify its origin, the measurement of T_2 (Fig. 4C) by means of the quadrupolar echo (QE) sequence [205] was of help both at qualitative and quantitative levels. In fact, the matching between the measured homogeneous contribution to the line width, through the relationship $\Delta\nu^{homo} = 1/(\pi * T_2)$ (empty circles in Fig. 4D), and the experimental line-broadening $\Delta\nu^{exp}$ (black circles in Fig. 4D) gave a clear indication of the dynamic nature of the observed line-broadening [143]. To identify the type of motion responsible of this broadening, a simple model was adopted consisting in the assumption of a single-molecular motion, characterized by a correlation time τ_c. Within this simple approach, the relaxation times T_2 and the generic spectral densities $J(\omega)$ can be expressed, in the Redfield approximation [116], as [143,206]

$$\frac{1}{T_2} = K_Q \left[\frac{3}{2} J_0(0) + \frac{3}{2} J_1(\omega_0) + J_2(2\omega_0) \right] \tag{2}$$

$$J(\omega) = \frac{2\tau_c}{\left(1 + \omega^2 \tau_c^2\right)} \tag{3}$$

with K_Q a constant equal to $(3\pi^2/2)(e^2qQ/h)^2$. An Arrhenius trend for the values of the correlation time as a function of temperature was assumed, with the time at infinite temperature, τ^∞, and the activation energy, E_a, as free parameters. The measured T_2 were fitted in the whole isotropic phase of the two BLC mesogens by using eqs. 2 and 3 (see, e.g., Fig. 4C). The main results of this analysis indicate the presence of a hindered molecular process in the isotropic phase of both ClPbis11BB and Pbis11BB samples, with activation energy of ~71 and ~60 kJ/mol, respectively (about double than in 5CB [207]) and correlation times at $T = 10$ K + T_{I-N} two orders of magnitude larger than in common rod-like LCs. This slow motion could be identified with a restricted reorientational motion of BLC molecules, as later confirmed by ^{1}H NMR relaxometry [208]. As recently shown by X-ray studies [12,209], BLC molecules tend to form temporary organized aggregates, or clusters (dimension of few nanometers), in the isotropic phase even at temperatures much higher than the clearing point. This partial and short-range order could be the reason for the restricted motions revealed by NMR and the very high viscosity of these systems [210]. In addition to scientific speculations, this variety of different unusual properties is very much attractive for potential technological applications [9,211] in the field of ferroelectric and pyroelectric devices, memory and information storage, optical sensors, and LC displays.
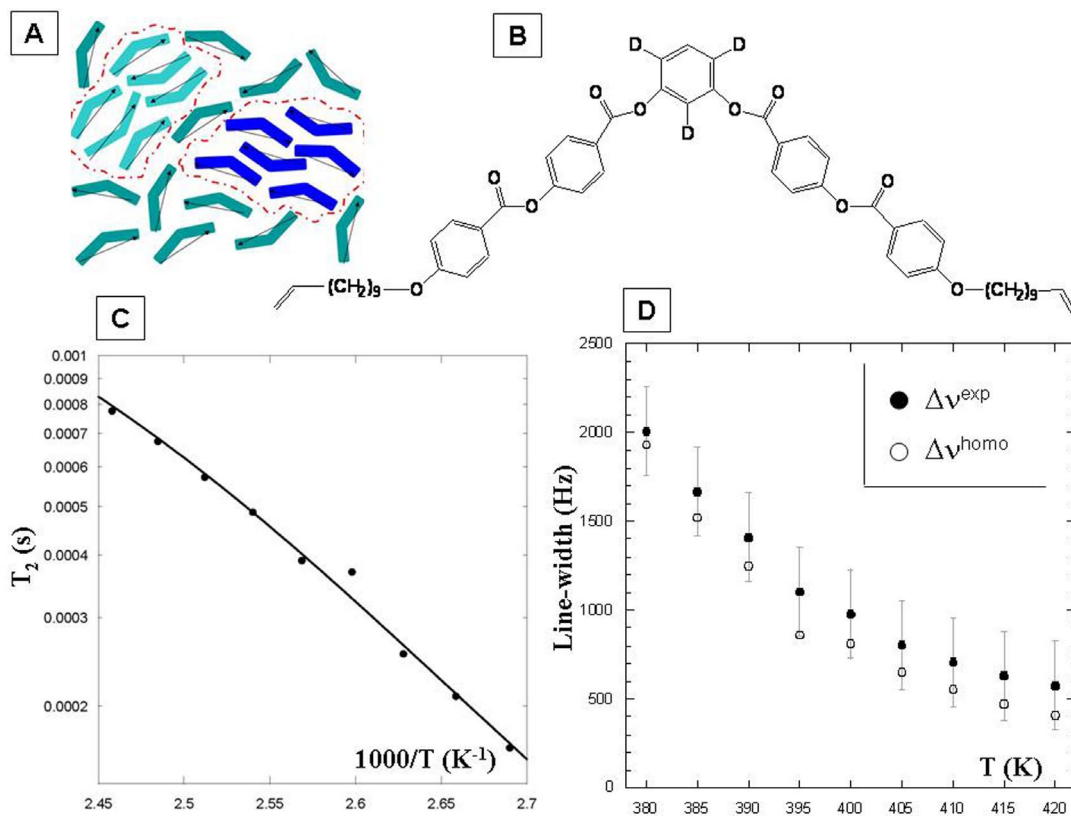
Fig. 4 (A) Scheme of the isotropic phase formed by BLCs. Small temporary clusters are put in evidence. (B) Molecular structure of the banana-shaped mesogen Pbis11BB (deuterium labeled on the central phenyl ring). (C) Trend of the measured spin–spin relaxation times T_2 (symbols) in the isotropic phase of the Pbis11BB as a function of temperature. Solid curve represents the best fitting curve. (D) Trend of the experimental spectral line width (Δv^{exp}) and the homogeneous contribution calculated from the measured T_2 [$\Delta v^{homo} = 1/(\pi T_2)$] in the isotropic phase of the Pbis11BB as a function of temperature.

Residual order and restricted motions in the "isotropic" phase of LSCEs

Among liquid-crystal elastomers, the so-called LSCEs [212] are the most challenging materials due to their high thermo-mechanic responses and shape-memory properties [16]. Several studies based on ^{2}H NMR have been done on monodomain side-chain [80,81,83] (Fig. 1e) and main-chain [82] LSCE films doped with deuterated probes, namely, 8CB-(α)d$_2$. These investigations successfully showed the fundamental role of crosslinker density in determining the thermodynamic features of the paranematic–nematic phase transition (PN–N) [80,81]. Recent ^{2}H NMR studies of side-chain LSCE monodomain films selectively deuterated on the crosslinker were published [213,214], confirming the criticality of the PN–N phase transition as an intrinsic property of LSCE monodomain systems. Since the particular two-step crosslinking reaction [213] is considered the "key-point" of the shape-memory properties of LSCEs, a detailed study was performed on several LSCE films ^{2}H-labeled on the crosslinker, as reported in Fig. 5.

In the paranematic phase, far above the PN–N transition temperature ($T \gg T_{PN–N}$), the ^{2}H NMR spectra of a standard LSCE monodomain film are characterized by an "isotropic-like" single peak. Lowering the temperature, in the vicinity of $T_{PN–N}$, the line width of the peak increases and its shape cannot be fitted by a single Lorentzian, but a second, much broader, Lorentzian function is needed to
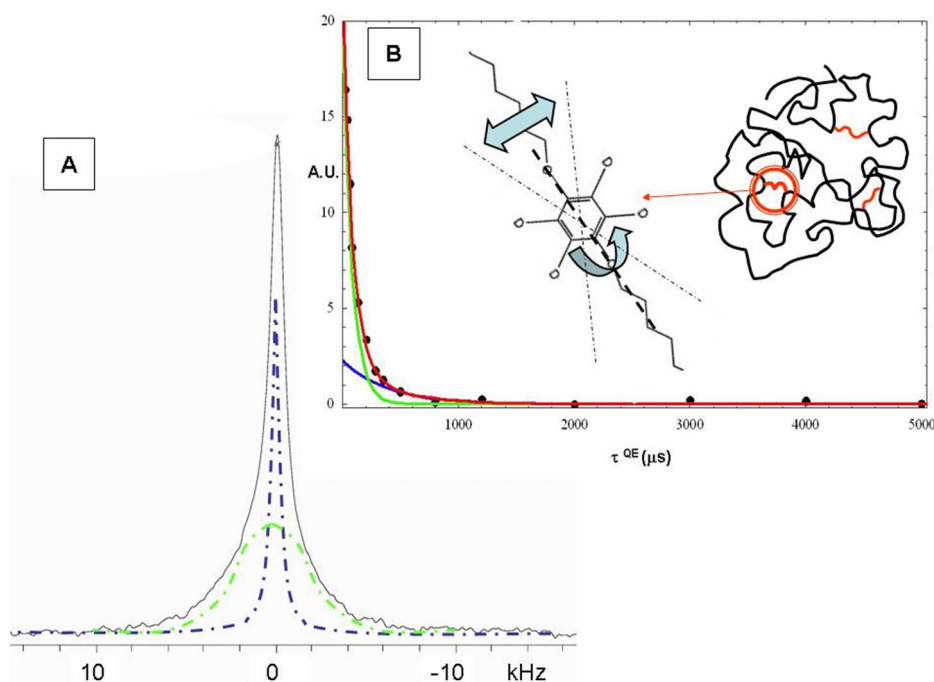
Fig. 5 (A) ^{2}H NMR spectrum of a standard liquid single-crystal elastomer deuterium labeled on the crosslinker (see inset) recorded at $T = 368$ K in the isotropic phase (or paranematic phase). Two Lorentzian components of the line shape are shown in blue (the sharp one) and green (the broad one). (B) Biexponential decay of the magnetization M vs. the delay τ^{QE} as measured by the QE sequence on the same sample as point A at the same temperature. Blue and green curves represent the two exponential contributions which correspond to the sharp and broad components of the spectrum. Hypothetical motional processes affecting the crosslinker of the LSCE are drawn (i.e., reorientation around the *para* axis and small fluctuation of the local phase director).

reproduce the ^{2}H NMR spectrum. An example can be seen in Fig. 5A, where a sharp Lorentzian peak (in blue) and a broad Lorentzian peak (in green) are obtained from the deconvolution of the recorded spectrum. It should be noted that this feature has been observed in other LSCE systems selectively labeled on different types of crosslinker units all prepared according with the Finkelmann procedure [213], so this can be safely considered a typical property of these systems [215]. To clarify the origin of the two components, the sharp and the broad ones, ^{2}H spin–spin relaxation times, T_2, were measured through the QE pulse sequence [205], and the trends of the magnetization, proportional to the experimental integral of the signal, $I(\tau^{QE})$, as a function of τ^{QE}, were analyzed. In the paranematic phase (see Fig. 5B) the trend $I(\tau^{QE})$ vs. τ^{QE} is clearly not monoexponential, but it can be well reproduced by using a biexponential function [215,216]

$$I\left(\tau^{QE}\right) = A \cdot e^{-\tau^{QE}/T_2^a} + B \cdot e^{-\tau^{QE}/T_2^b} \qquad (4)$$

with two characteristic spin–spin relaxation times, T_2^a and T_2^b, which can be determined from the fitting of the experimental $I(\tau^{QE})$ decay. In Fig. 5B, the total fitting curve is reported in red, while the two exponential components are in blue and green colors; the experimental $I(\tau^{QE})$ measured in the paranemtatic phase in the vicinity of the phase transition are in black points. The two relaxation times, T_2^a and T_2^b, can be put in relationship with the line width of the two peaks, the sharp and broad ones,

obtained from the deconvolution of the ^{2}H NMR spectrum [215,216]. In fact, the ^{2}H NMR spectral line width of a peak, Δv_{exp}, is related to the relaxation time T_2^* through the relationship

$$T_2^* = \frac{1}{\left(\pi \cdot \Delta v_{exp}\right)}$$ (5)

If the measured T_2 is equal to T_2^* this means that the line width is homogeneous, thus due to molecular motions. In the paranematic phase, two values of T_2^* could be calculated from the line width of the two Lorenztian peaks used to fit the spectrum (see Fig. 5A). Interestingly, these values match those of T_2^a and T_2^b obtained from the fitting of the QE decays. This finding indicates that the line-broadening of the ^{2}H NMR signals is fully homogeneous, and consequently the origin of the observed line-broadening is a dynamic one. As seen in Fig. 5, the decay of the magnetization, as well as the values of T_2 ($T_2^a \sim 500$ μs and $T_2^b \sim 70$ μs), indicate the presence of slow motions. A rough way to estimate the characteristic time of these dynamics is the one proposed in the previous section, through eqs. 2 and 3. The two trends of T_2^a and T_2^b as a function of temperature were fitted by assuming two independent motional processes characterized by a correlation time with an Arrehnius behavior in the Redfield approximation. As main results, two characteristic correlation times, τ_c, of the order of 2.1 × 10^{-8} s and 1.2×10^{-7} s at $T = 10$ K + T_{PN-N} were found, corresponding to the sharp and broad line width components [215,216]. These values, if compared with those of conventional LCs, are very large and clearly indicate the presence of slow motions, whose identification and complete description would require more complex theoretical models, specific for the slow regime of motions and for network systems. The two motions revealed with our approach could be related to local ODFs, similar to conventional nematic LCs, and to restricted molecular reorientations of the crosslinker itself (see inset of Fig. 5B). The reason for these slow motions, affecting in particular the deuterated crosslinkers in the LSCE matrix, can be explained with the residual order evaluated from ^{2}H NMR data above the PN–N transition temperature [215,216]. The presence of local organized domains in the paranematic phase of the monodomain LSCE films, as suggested by the residual order (S larger than 0.025 for $T > 20$ K + T_{PN-N}), could be at the origin of the shape-memory properties of LSCEs and will certainly be an object of investigations in the near future.

Conformational changes at mesophase transitions in rod-like LCs

Accordingly to several theoretical works [216–218], the transition from the SmA to the SmC* phases in rod-like LCs is related to a conformational change. ^{13}C NMR measurements in the ferroelectric phase of a smectogen [219] were interpreted based on a transition from an elongated conformer to a bent conformer, most stable in the ferroelectric phase due to the different molecular packing between the two phases. Also, Fourier transform infrared (FT-IR) spectroscopy [220] succeeded in showing a significant conformational change at the mesophase transitions of ferroelectric LCs. ^{13}C NMR spectroscopy is known to be an excellent method to reveal conformational changes also in flexible mesogens, as suggested by the many works in discotic LCs [74,221]. Recently, a detailed comparative study between ^{13}C NMR and DFT molecular computations on a ferroelectric mesogen [222] gave rise to additional details of the "average" conformers in the different mesophases. ^{13}C NMR spectra of aligned liquid-crystalline materials, acquired by using the proton-carbon cross polarization (CP) technique [223] and proton decoupling throughout the SPINAL-64 sequence [224], are characterized by signals (one for each nonequivalent carbon nucleus) with a certain value of the chemical shift and a line-broadening which depends on many factors, such as the viscosity and molecular mobility of the mesogen. The observed chemical shift of a carbon (δ^{obs}) can be related to the orientational order parameters S_{ij} and the chemical-shift tensor elements (δ_{ab}, with $ab = xx,yy,zz,xy,xz,yz$) by the following equation [225]:

$$\delta^{\,obs} = \delta^{\,iso} + \delta^{\,aniso} =$$

$$\delta^{\,iso} + \frac{2}{3}\left[\Delta\delta \cdot S_{zz} + \frac{1}{2}\left(\delta_{xx} - \delta_{yy}\right)\cdot\left(S_{xx} - S_{yy}\right) + 2\delta_{xy}S_{xy} + 2\delta_{xz}S_{xz} + 2\delta_{zy}S_{zy}\right] \tag{6}$$

where

$$\Delta\delta = \delta_{zz} - \frac{1}{2}\left(\delta_{xx} - \delta_{yy}\right) \tag{7}$$

is the anisotropy of the chemical shift tensor, δ, with respect to the molecular z-axis. In these equations, the Saupe ordering matrix S and the tensor δ are written in the molecular (MOL) frame (x,y,z). The observed chemical shift, $\delta^{\,obs}$, has two main components, $\delta^{\,aniso}$ and $\delta^{\,iso}$, which is defined as one-third of the trace of the chemical shift tensor δ. In rod-like mesogens forming uniaxial phases, eq. 6 can be further simplified to

$$\delta^{\,obs} = \delta^{\,iso} + \frac{2}{3}\left[\Delta\delta \cdot S_{zz} + \frac{1}{2}\left(\delta_{xx} - \delta_{yy}\right)\cdot\Delta_{biax}\right] \tag{8}$$

where the $\Delta_{biax} = S_{xx} - S_{yy}$ is the molecular biaxiality. The quantities $\delta^{\,obs}$, $\delta^{\,iso}$, and $\delta^{\,aniso}$ are, in principle, temperature-dependent. If no conformational changes exist, the trend of the observed chemical shift as a function of temperature mainly reflects the trend of the order parameters, and, in particular of the main order parameter, S_{zz}, since the molecular biaxiality is usually much smaller. As seen in Fig. 6 for the mesogen HZL 7/*, showing the TGBA*, TGBC$_1$*, and TGBC$_2$* phases [170,171], the aromatic region (from 120 to 240 ppm) is characterized by an increase of the chemical shift by decreasing the temperature within the TGBA* phase, due to the increase of the order, S_{zz} (i.e., $\Delta\delta > 0$), while in the two TGBC* phases, $\delta^{\,obs}$ decreases due to the increase of tilt angle. In the aliphatic region (from 0 to 40 ppm) the trend is the opposite (i.e., $\Delta\delta < 0$), however, due to the motional averaging, the local order in the chains is very low and $\delta^{\,obs}$ is almost constant. Different, and unexpected, is the trend of the chemical shift in the region 40–80 ppm, typical of the aliphatic alpha methyloxy and methylenoxy carbons (carbons 22, 25, and 7 in Fig. 6). A possible reason is the presence of conformational changes affecting mostly the two linking groups between the aliphatic chains and the aromatic core. A similar behavior was observed for the ferroelectric LC, namely, M10/** [181,222], where a detailed analysis allowed the shedding of light on the peculiar trends of the ^{13}C NMR chemical shift observed in this spectral region. DFT calculations of the potential energy surfaces of different conformers of M10/** by varying the dihedral angles defining the conformation of the chains with respect to the aromatic core and the DFT computation of the ^{13}C chemical shift tensors have been performed by using the appropriate level of theory [226,227]. The aim was the understanding of the relationship between the conformational properties of the ferroelectric molecule in the different mesophases and the observed changes in the chemical shift trends at the phase transitions. In particular, DFT calculations of the δ tensors of the aliphatic alpha methyloxy and methylenoxy carbons as a function of different conformations of the M10/** smectogen were performed. By comparing the observed chemical shift and the computed δ_{iso} (in the hypothesis of substantial neglecting of the anisotropic contribution $\delta_{aniso} \approx 0$), it was possible to identify the most populated conformers of M10/** in the different mesophases. In the particular case of M10/**, the occurrence of significant conformational changes at the blue–cholesteric and cholesteric–SmC* phase transitions has been demonstrated through a detailed analysis of the flexible parts of the mesogen, which resulted in playing a significant role in its mesomorphic behavior. At the two phase transitions of M10/**, the conformational changes concern the lateral aliphatic moieties: (i) the achiral chain undergoes a reduction of degrees of freedom by decreasing the temperature, while (ii) the chiral chain assumes different stable conformational states (molecular shapes) in the three different mesophases. In particular, in the SmC* phase, the stable molecular conformation, which has an overall bent shape, gives rise to a molecular biaxiality rather largely in agreement with recent studies on sev-
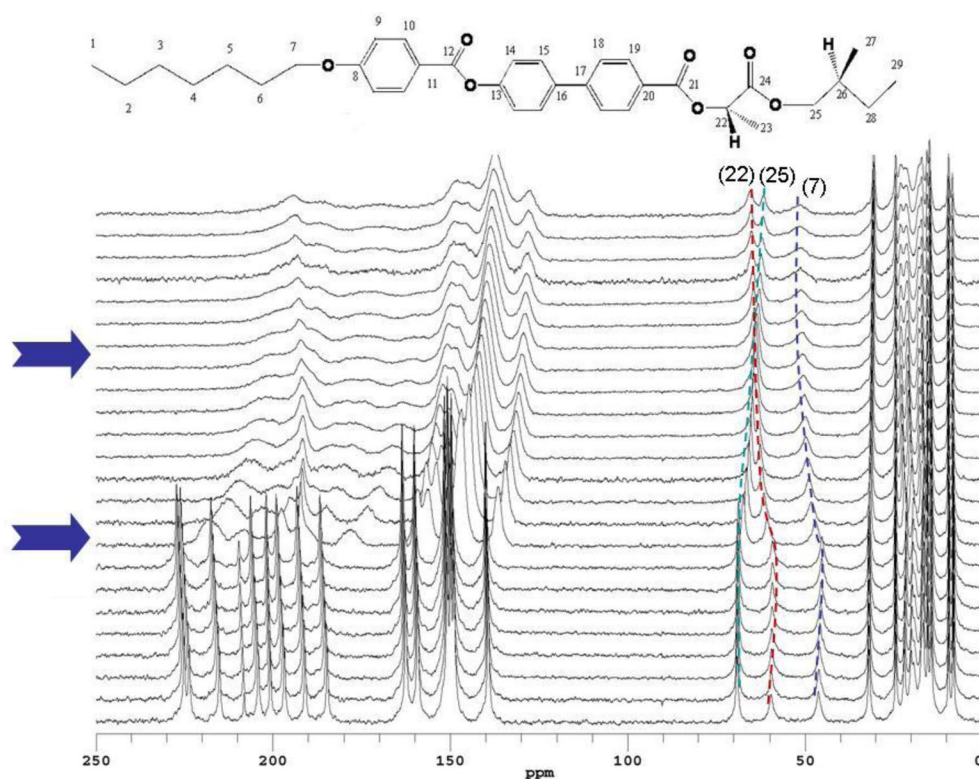
Fig. 6 From top to bottom: Molecular structure of the rod-like mesogen HZL 7/*. Carbons are labeled with progressive numbers. Series of ^{13}C NMR spectra recorded by cooling the sample from the isotropic phase into the TGBA*, TGBC$_1$*, and TGBC$_2$* phases. Blue arrows indicate the TGBA*-TGBC$_1$*, and TGBC$_1$*-TGBC$_2$* phase transitions. The region between 45 and 80 ppm is typical of the alkoxyl (C–O) carbons (namely, carbons 22, 25, and 7) and a change of the observed chemical shift is observed at the phase transitions.

eral ferroelectric LCs [64,65]. As a main result, this study supports the idea of a significant conformational change of the mesogens at the origin of the ferroelectric SmC* phase. Similar results apply to the case of HZL 7/* (reported in Fig. 6), showing that this procedure can be used where the chemical shift of a carbon has a different temperature dependence than the other molecular carbons. This example shows the high sensitivity of NMR to probe local molecular properties, which can then be interpreted with the help of molecular models or computational methods, as demonstrated by other recent research [66,215,228–230].

FINAL REMARKS

In this brief and, evidently partial, perspective, the role of NMR spectroscopy in the study of partially ordered systems and, in particular, LCs, has been traced through an overview of original and challenging works mainly performed in the last decade. The evolution of NMR techniques (i.e., new NMR pulse sequences) and the improvement of mathematical tools for the analysis of NMR data specifically for partially ordered systems allowed the research to be extended to increasingly complex materials and unique phenomena, such as field-induced alignment and confining effects. This trend is a clear indication of the liveliness of this scientific area. Furthermore, the fast development of nanoscience and biomedicine is offering a rich variety of new "physical chemical" problems related to partially ordered materials. It is in these directions that the field of "NMR of LCs" is moving. New challenges are related,

for instance, to the understanding of the mechanisms of alignment of nanomaterials in liquid-crystalline environments, the enhancement of physical properties in LC-based composites, the mobility and orientation of polypeptides inside and outside vesicles, as well as the mechanisms of penetration through bilayered membranes in concert with conformational changes. The effect of the external fields, electric and magnetic ones, on the supramolecular structure of biological LCs is another big challenge with medical implications.

In realizing these challenges, scientists will have to step forward and expend new efforts in favor of a proactive collaboration among different scientific disciplines. The complexity of the problems to be addressed requires a free and unreserved exchange of both ideas and acquired knowledge as well as the possibility to work in a stimulating and interdisciplinary environment. NMR spectroscopy is, owing to its history and its main uses, an area at the frontier of physics, chemistry, and medicine. On the other hand, LCs, discovered by a botanist (F. Reitzner) and a physician (O. Lehmann), have always been the focus of chemists, physicists, and engineers. In this regard, the community of scientists studying NMR of partially ordered systems is well representative of this interdisciplinary attitude.

ACKNOWLEDGMENTS

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