Coherent Reduction of Dipolar Interactions in Molecules Dissolved in Anisotropic Media Using a New Multiple-pulse Sequence in a COSY Experiment

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A new multipulse sequence, named Flip-Flop 16, which acts coherently on the spin Hamiltonian, is described. To avoid some of the technical difficulties encountered in multipulse experiments synchronized to the sampling of the magnetization, the sequence is applied during the $\tau_1$ period of a COSY experiment. A scaled spectrum thus appears in the $\tau_2$ dimension. An experimental study is presented using a simple $A_2$ spin system dissolved in a nematic liquid crystal. It is then demonstrated that the technique can be used to turn an AB deceptively simple or A|B second-order spectrum into an AX or A|X first-order spectrum, respectively. © 1994 Academic Press, Inc.

Multiple-Pulse COSY NMR Spectroscopy of Oriented Molecules in Thermotropic Cholesterics

P. LESOT, F. NIELSEN, J.M. OUVRARD, J. COURTIEU*


The coherent reduction of anisotropic NMR interactions in molecules oriented in a thermotropic cholesteric phase, using a multiple-pulse COSY experiment, is described. The technique, which directly modifies the spin part of the nuclear spin Hamiltonian, allows the transformation of second-order spectra into first-order spectra. An experimental study of the evolution of the chemical shift and dipolar reduction factors is presented. The effects of the finite pulse duration in the multiple-pulse sequence are discussed, and explicit equations for the anisotropic interactions which take into account the pulse widths are obtained. The technique in cholesteric solvents is illustrated by using two specific examples for AB and ABC type of spectra: 2,6-dichloro-3-nitropyridine and 2-cyanoferan.

Visualization of Enantiomers in a Polypeptide Liquid Crystal Solvent through Carbon-13 NMR Spectroscopy

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High-resolution, proton-coupled and decoupled, carbon-13 NMR in natural abundance is used to observe the spectra of enantiomers in chiral molecules dissolved in the poly(γ-benzyl-L-glutamate) (PBLG) CDCl3 liquid-crystalline system. Discrimination between enantiomers can be obtained either through differences in their dipolar interactions or in their chemical shift anisotropies. This technique provides a new tool for the visualization of enantiomers and the measurement of the enantiomeric ratio. Several specific examples are presented and discussed.

Measurement and Analysis of the Molecular Ordering Tensors of Two Enantiomers Oriented in a Polypeptide Liquid Crystalline System

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High-resolution proton and natural abundance carbon-13 NMR spectra of a rigid chiral molecule, (±)-β-(trichloromethyl)-β-propioloactone, dissolved in the liquid-crystalline phase of poly(γ-benzyl-L-glutamate) (PBLG), in methylene chloride, were analyzed. From the NMR data and the X-ray structure, the full order matrix was determined and analyzed in detail for each optical isomer of the molecule. It is shown that the spectral discrimination of the enantiomers in this lyotropic medium arises mainly from the difference in their average molecular orientation and the principal axis systems of orientation are compared.

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Discrimination and analysis of the NMR spectra of enantiomers dissolved in chiral liquid crystal solvents through 2D correlation experiments

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The discrimination and analysis of the NMR spectra of optically active molecules dissolved in chiral liquid crystal solvents through 2D correlation experiments is studied. The technique allows the identification of the line positions of each enantiomer, thus providing a notable simplification of the spectral analysis. The 2D HMQC and multiple-quantum experiments are investigated and discussed. The potential of the method is illustrated using a sample of (±)-3,3-trimethoxypropylpropanediol dissolved in a thermotropic cholesteric solvent. The case of chiral molecules bearing a fluorine or deuterium nucleus has also been studied. In addition, it is shown that 2D heteronuclear correlation experiments are powerful methods for correlating carbon and proton spectral data of two enantiomers. A specific example is given through (±)-3-hydroxypropylpropene acid dissolved in a lyotropic polypeptide liquid crystal. Spectral parameters of each enantiomer are calculated for the different examples.

Proton-Decoupled Carbon-13 NMR Spectroscopy in a Lyotropic Chiral Nematic Solvent as an Analytical Tool for the Measurement of the Enantiomeric Excess

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Proton-Decoupled Carbon-13 NMR Spectroscopy in a Lyotropic Chiral Nematic Solvent as an Analytical Tool for the Measurement of the Enantiomeric Excess

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Abstract: Organic solutions of poly-γ-(benzyl-L-glutamate) (PBLG) generate a sufficient differential ordering effect (DGE) to discriminate enantiomers using proton decoupled carbon-13 NMR in natural abundance. Discrimination between enantiomers is observed through the carbon-13 chemical shift anisotropy (CSA) differences. This method is successfully applied to a large number of chiral molecules including a case of axial chirality and offers the advantage that no labeling or chemical modification of molecules is needed. In most cases, the chemical shift differences are large enough to measure the enantiomeric excess with accuracy. We show that this new tool is an attractive and powerful alternative to the existing enantiomeric analytical techniques.

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Calculation of the Molecular Ordering Tensors of (±)-3-Butyn-2-ol in an Organic Solution of Poly(γ-benzyl-L-glutamate)

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The proton and natural abundance carbon-13 NMR spectra of (±)-3-butyn-2-ol enriched in the S enantiomer (ee = 72%) and oriented in the chiral nematic liquid crystalline phase of poly(γ-benzyl-L-glutamate)/demerozidronium] have been obtained and analysed. The residual [H-15]H and [13C] dipole couplings were corrected for the effects of molecular harmonic vibrational motions and used to determine the $r_h$ structure and the five independent order parameters, $S_{ijh}$, for each enantiomer. It is shown that the data is consistent with the two enantiomers having an identical $r_h$ structure, but the order matrices differ in both the magnitudes of their elements and the orientation of their principal axes.

Steric Hindrance Influence of a Diazo Link upon Mesogenic Properties of some Ligands and Related Copper Complexes

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Steric hindrance influence of a diazo link upon mesogenic properties of some ligands and related copper complexes

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ABSTRACT

Some new polymethylated compounds containing three rings and four rings have been synthesized. The crystalline structures of 2,3-dimethyl-4-ethoxy benzyloxy-4’-(4-methoxyacridylaldimine)-azo benzene (DIM) and 2,3,6-trimethyl-4-methylbenzoyloxy-4’-butylazobenzene (TRIM) are described. Due to larger steric interactions, the diazo linkage makes a larger dihedral angle in TRIM than in DIM. The effect of steric hindrance of the diazo linkage upon the mesophase stability is discussed by the use of isotopic Carbon-13 chemical shifts, molecular modelling and transition temperatures, $T_{NI}$. For the three rings core, the thermal stability of the mesophase decreases with substitution pattern dissymetry. The effect of the conjugation loss is evidenced by the decrease of $T_{NI}$ versus the carbon number within the chain. For the four rings core, the effect on the transition temperatures of polymethylated ligands is nearly independent of the length of the mesogenic core and depends only on the lateral substituent positions within the core. For the related copper complexes, the $T_{NI}$ transition temperatures exhibit a small dependence upon the methyl substitution.

key words: liquid crystal, X-ray, lateral substitution, copper complex.
Structural-Dynamical Relationship in Silica / PEG Hybrid Gels
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Structural–dynamical relationship in silica PEG hybrid gels

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Hybrid organic-inorganic materials have been prepared from mixtures of tetraethoxysilane and poly(ethylene glycol) (PEG) of low molecular mass. These materials are biphasic systems in which silica aggregates, controlling the mechanical properties, are wrapped around by the polymer phase. Strong correlations between the synthesis scheme, the structure and the properties of these materials are evidenced. Solid-state 29Si NMR points out the change of the silica morphology with the nature of the catalyst (acidic, [HCl] or nuclophilic, [NH4F]). In addition, these changes induce strong variations of the thermal properties of the PEG phase. The structural and dynamical inhomogeneities of the PEG are analyzed using 13C NMR and EPR spectroscopies. Near the SiO2 surfaces, hydrogen bonding hinders the motion of the PEG chains, while the bulk of the polymeric phase possesses the same properties as the polymer melt. Thermal analyses (DSC) disclose the difference between materials prepared with the various catalysts which are related to the degree of interpenetration between the two phases.

Quantitative Description of the Facial Discrimination of Molecules Containing a Prochiral Group Oriented in a Chiral Liquid Crystalline Solution
D. MERLET, A. LOEWENSTEIN, W. SMADJA, J. COURTIEU, P. LESOT*

Quantitative Description of the Facial Discrimination of Molecules Containing a Prochiral Group by NMR in a Chiral Liquid Crystal

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Abstract: The quantitative description of the facial discrimination in molecules containing a prochiral group oriented in a polypeptide liquid crystalline system is reported. From the analysis of proton, carbon-13, and deuterium NMR spectra of ethanol dissolved in an organic solution of poly-$\gamma$-(benzyl-L-glutamate) (PBLG), the full molecular order matrix and the principal axis system were determined. It is shown that five nonzero independent order parameters are necessary to describe correctly the molecular ordering of ethanol in this medium, which clearly demonstrates that in this chiral liquid crystal, the symmetry of the ordering in a prochiral molecule is broken. Due to the nonequivalence in terms of the dipolar couplings of the two enantiomeric protons of ethanol, it is possible to determine the sign and the magnitude of geminal scalar couplings between them. This new approach to obtain the geminal $J_{HH}$ constants is tested on a series of linear alcohols and compared to values derived from $J_{HH}$ of the same molecules by the isotopic substitution method.

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Unusual Ordering of a Dioxyethylene Chain in Dialkoxy Laterally Substituted Nematogen as Evidenced by $^{13}$C NMR

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ABSTRACT

We report the synthesis of a liquid crystalline compound containing four rings in the main core, two lateral hexyloxy chains and a terminal dioxyethylene methyl ether chain. This compound presents a wide nematic range starting from room temperature. The ordering of the chains has been studied by $^{13}$C NMR in the liquid crystalline phase. The $^{13}$C chemical shifts proved folding back of the lateral chains along the main core, and extended conformation of the dioxyethylene chain. The values of order parameters were derived from the transient oscillations of $^{13}$C magnetization observed during variable contact-time cross-polarization experiments. For the dioxyethylene chain, the order parameters decrease monotonically along the chain without exhibiting odd-even oscillation and are noticeably smaller than those found in terminal alkoxy chains. These effects are interpreted by the change in geometrical and conformational characteristics of the dioxyethylene chain.

Key words: NMR, nematic, lateral substitution, dipolar oscillation, oxyethylene unit.

Simplification of $^{19}$F NMR Spectra of Liquid Crystalline Samples by Multiple-pulse COSY experiments

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A general method is presented of converting second-order fluorine-19 spectra of liquid crystalline samples into first-order spectra. This is achieved by recording a $^{19}$F COSY spectrum with a multiple pulse dipolar reducing sequence (MPS) operating in the $t_2$ period, leading to a $F_2$ projection which is first order. The method is illustrated by recording spectra on a sample of 1,3-dichloro-4-fluorobenzene dissolved in the nematic solvent ZLI 1167. Experiments have been done in which the MPS is either the MREV-8 or Flip-Flop-16 sequence. The first-order $F_2$ projections are analyzed to give reduced total $^{1H-19}$F couplings, $K_{max}$ and the reduction factors, $K_{red}$, are obtained by comparison with the $T_{1H}$ available from an analysis of the ordinary 1D spectrum. The reduction factors are compared with values predicted by average Hamiltonian theory (AHT). The reasons for the differences found between observed and predicted values of $K_{max}$ have been investigated by performing numerical simulations of the 2D MPS COSY experiments. © 1998 Academic Press

Key Words: liquid crystalline samples; NMR; average Hamiltonian theory; heteronuclear total spin-spin coupling; multiple pulse sequence; and reduction factor.
The Magnetohydrodynamics of a Chiral Nematic Liquid Crystal: The Existence of two Critical Speeds Revealed by Deuterium NMR

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Preliminary communication

The magnetohydrodynamics of a chiral nematic liquid crystal: the existence of two critical speeds revealed by deuterium NMR

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The magnetohydrodynamics of a chiral nematic liquid crystal made from a mixture of PBLG and deuterated chloroform was investigated by deuterium NMR. The first critical speed for the sample was determined using a dynamical approach, and the existence of a second critical speed, which is not predicted by theories which take into account only the viscous and magnetic torques, is revealed.

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Enantiomeric Visualisation using Proton-Decoupled Natural Abundance Deuterium NMR in Poly(γ-benzyl-L-glutamate) Liquid Crystalline Solutions

P. LESOT*, D. MERLET, A. LOEWENSTEIN, J. COURTIEU


Enantiomeric visualization using proton-decoupled natural abundance deuterium NMR in poly(γ-benzyl-L-glutamate) liquid crystalline solutions

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Abstract

We report the first visualization of chiral molecules oriented in a polypeptide liquid crystalline system (PBLG) using proton-decoupled natural abundance deuterium NMR. The chiral discrimination is observed through measurements of the quadrupolar splitting differences and we demonstrate that the sensitivity of natural abundance deuterium NMR is sufficient to measure the differential ordering effects (DOEs) without the need for isotopic enrichment. The feasibility and the potential of this novel method were investigated using a 5.87 T spectrometer (proton frequency 250 MHz). Several examples of chiral discrimination are presented and particular emphasis is given to demonstrate the potential of this approach. © 1998 Elsevier Science Ltd. All rights reserved.

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Analysis of the Natural Abundance Deuterium NMR Spectra of Enantiomers in Chiral Liquid Crystals through 2D Auto-correlation Experiments

D. Merlet, B. Ancian, W. Smadja, J. Courtieu, P. Lesot*


Analysis of natural abundance deuterium NMR spectra of enantiomers in chiral liquid crystals via 2D auto-correlation experiments

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Natural abundance deuterium auto-correlation 2D NMR experiments of enantiomers orientated in a chiral polypeptide liquid crystalline solvent (PBLG) are used as a novel analytical tool for the study of chiral solutes.

Two-dimensional Deuterium NMR Spectroscopy of Chiral Molecules Oriented in a Polypeptide Liquid Crystal: Application for the Enantiomeric Analysis through Natural Abundance Deuterium NMR

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Two-Dimensional Deuterium NMR Spectroscopy of Chiral Molecules Oriented in a Polypeptide Liquid Crystal: Applications for the Enantiomeric Analysis through Natural Abundance Deuterium NMR

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Abstract: We describe several two-dimensional NMR experiments to facilitate the analysis of overcrowded proton-decoupled deuterium spectra of chiral molecules oriented in poly-γ-benzyl-L-glutamate liquid crystalline solutions. These 2D NMR experiments allow the correlation between the components of each quadrupolar doublet in the deuterium spectra and then their assignment on the basis of chemical shift. The 2D pulse sequences proposed in this work were developed using the Cartesian spin-operator formalism for spin I = 1 nuclei with a small quadrupolar moment, such as deuterons in high magnetic field. The features and analytical potentialities of each pulse sequence are discussed and compared. Illustrative applications of these sequences in natural abundance deuterium NMR spectroscopy using a 9.4 T magnetic field and standard NMR equipment are reported and examined. With this technique, it is demonstrated that quantitative measurements are possible within a precision of 10%.

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First Evidence of a Photoinduced Spin Change in an Fe(III) Complex Using Visible Light at Room Temperature

Angélique Sour, Marie-Laure Boillot, Eric Rivière and Philippe Lesot

Keywords: Spin crossover / Light-induced spin change / cis-trans isomerization / Visible light irradiation / Iron(III)

An iron(III) complex [Fe(salen)(Mepepy)]BPh₄ containing only one photosomerizable ligand (Mepepy) has been synthesized, it exhibits a thermally-induced spin crossover in the solid state and in solution (H-salen = 4-azahexyl-1,4-bis(2-pyridyl)benzene; Mepepy = 1-pyridyl-2-pyridin-4-yl-2-(N-methylpyrrol-2-yl)ethene). The photosomerizations of both the free and coordinated Mepepy ligand have been observed at room temperature with visible-light irradiation and monitored by UV/Vis and ¹H NMR spectrometries. trans-to-cis isomerization of only one photosensitive ligand in the iron(III) complex is sufficient to detect a partial spin change of the iron(III) ion. This photoinduced spin change is seen for the first time from a high-spin state to a low-spin state.

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Double Diastereoselection in Asymmetric [2+3] Cycloadditions Reactions of Chiral Oxazoline N-Oxides and Application to the Kinetic Resolution of a Racemic α,β-Unsaturated δ-Lactone

O. DIRAT, C. KOUKLOVSKY, Y. LANGLOIS, P. LESOT, J. COURTIEU

Abstract

The asymmetric [2+3] cycloaddition reaction between chiral oxazoline N-oxide 1 and α,β-unsaturated lactone 2 was studied. A double diastereoselection was observed, (1R)-1 and (R)-2 gave a mismatched pair with almost no cycloadduct obtained. A transition state model is proposed, accounting for the destabilization of transition state in the cycloaddition reaction. This result has led to kinetic resolution studies, in which both enantiomers of 1 were reacted with racemic lactone 2. The enantiomeric excess of the recovered lactone 2 was determined to be up to 70% ee, by ¹H-¹H NMR analysis in a chiral liquid crystalline solvent. The experimental results are in agreement with predicted enantiomeric excesses and consistent with the transition state models. © 1999 Elsevier Science Ltd. All rights reserved.

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The relationship between molecular symmetry and second-rank orientational order parameters for molecules in chiral liquid crystalline solvents

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From group theoretical arguments, we demonstrate that the effective molecular symmetry is reduced in a chiral liquid crystalline phase. This reduction changes the location of the principal axes of the orientational order matrices for four molecular point groups, namely $C_{1}$, $C_{2v}$, $S_{4}$, and $D_{2d}$. These symmetries correspond to compounds which have prochiral faces, groups, or directions. The change in effective molecular symmetry can be detected by NMR spectroscopy, and this is illustrated by the example ofacenaphthene dissolved in a chiral nematic solvent. © 1999 American Institute of Physics. [S0021-9606(99)31937-5]

Highly enantioselective propargylic monofluorination established by carbon-13 and fluorine-19 NMR in chiral liquid crystals

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Carbon-13 and fluorine-19 NMR experiments in a chiral polypeptide liquid crystalline solvent (PBLG) are used to establish enantioselective propargylic monofluorination.
Description of Natural Abundance Deuterium 2D NMR Experiments in Weakly Ordered Liquid Crystalline Solvents using a Tailored Cartesian Spin-Operator Formalism

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DOI: 10.1039/b000834f

Description of natural abundance deuterium 2D-NMR experiments in weakly ordered liquid-crystalline solvents using a tailored cartesian spin-operator formalism

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We report an appropriate cartesian spin-operator formalism which retains all physical insights and provides a pictorial representation for I = 1 spin nuclei subjected to both a chemical shift and a small quadrupolar moment such as deuterons in liquid crystals with low order-parameters. Using a tree-like pictorial representation, this approach allows a straightforward description of natural abundance deuterium autocorrelation 2D-NMR experiments in weakly ordered solvents. As illustrative examples we study the 2D Q-COSY and Q-resolved NMR sequences which have been recently developed to facilitate the analysis of overcrowded proton-decoupled deuterium spectra in natural abundance of enantiomers oriented in liquid-crystalline solutions of poly-γ-benzyl-γ-glutamate (PBLG). These 2D-NMR experiments allow the correlation between the two components of each quadrupolar doublet in the deuterium spectra to be obtained, and their assignment on the basis of chemical shifts. Several improvements of the basic sequences are proposed and discussed. Applications of these sequences in natural abundance deuterium NMR spectroscopy using a 9.4 T magnetic field and standard NMR equipment are examined.

Deuterium NMR Stereochemical Analysis of Threo-Erythro Isomers Bearing Remote Chiral Centres in Racemic and Non-Racemic Liquid Crystalline Solvents

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DOI: 10.1016/S0957-4166(00)00125-7

Deuterium NMR stereochemical analysis of threo-erythro isomers bearing remote stereoegenic centres in racemic and non-racemic liquid crystalline solvents

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Abstract

We report the proton-decoupled deuterium NMR study of labelled diastereomers with remote stereogenic carbons dissolved in various mixtures of poly-γ-benzyl-γ-glutamate (PBLG) and poly-γ-benzyl-β-glutamate (PBDG) liquid crystalline solutions. The evolution of quadrupolar splitting as well as the diastereometric and the enantiomeric discrimination versus the proportion of PBLG and PBDG in the liquid crystalline phase is studied. It is shown that racemic liquid crystalline solutions of PBLG and PBDG may be used to measure diastereomeric excess (δe). Thereafter the spectrum in PBLG solution allows for measuring the enantiomeric excess (ee) of each diastereomer. These first results suggest substantial prospects in the field of the analysis of diastereomers with remote stereogenic carbons. © 2000 Elsevier Science Ltd. All rights reserved.

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First Successful Enantiomeric Discriminations of Chiral Alkanes using NMR Spectroscopy

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DOI: 10.1039/b002806l

First successful enantiomeric discrimination of chiral alkanes using NMR spectroscopy

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Natural abundance deuterium NMR spectroscopy in a chiral polypeptide liquid crystal solvent (PBLG) is used to successfully discriminate between chiral alkanes.

Theoretical and Experimental Aspects of Enantiomeric Differentiation using Natural Abundance Multinuclear NMR Spectroscopy in Polypeptide Liquid Crystals

M. SARFATI, P. LESOT*, D. MERLET, J. COURTIEU*
ISSN: 1359-7345

Theoretical and experimental aspects of enantiomeric differentiation using natural abundance multinuclear nmr spectroscopy in chiral polypeptide liquid crystals

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Liquid crystalline organic solutions of poly-p-benzyl-L-glutamate generate a sufficient differential ordering effect to visualize enantiomeric using multinuclear high-resolution NMR spectroscopy at natural isotopic abundance levels. Chiral discrimination can be observed through a difference in the order-sensitive NMR observables, namely; proton-proton, carbon-proton and carbon-carbon residual internuclear dipolar couplings, carbon chemical shift anisotropies, and deuterium quadrupolar splittings. In most cases, the enantiomeric discrimination is large enough to allow determination of the enantiomeric excesses satisfactorily. All theoretical considerations and significant experimental parameters that affect the efficiency of this methodology are presented and discussed. The various possible anisotropic NMR techniques provide a very reliable and powerful alternative to the current analytical techniques which operate in the isotropic phase.
Determining Enantiomeric Purity by NMR: Deuterium 2D NMR at Natural Abundance in Weakly Oriented Chiral Liquid Crystals

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Determining Enantiomeric Purity by NMR:

Deuterium 2D NMR at Natural Abundance in Weakly Oriented Chiral Liquid Crystals

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The differentiation of enantiomers and their stereochemical characterization is the ultimate challenge in asymmetric synthesis, and requires methodologies which can be successfully applied to a wide range of chemical types. In this respect, NAD-NMR spectroscopy of chiral compounds in liquid-crystalline PBLG solutions provides an efficient and convenient analytical tool for resolving and characterizing a large number of the possible chiral isomers. Of major interest is the fact that the polypeptide helices in the liquid-crystalline phase are able to interact enantioselectively with both polar and apolar chiral compounds to give sufficiently large differences in the order parameters and the NMR-detectable quadrupolar splittings for R and S forms. This direct analytical method is an attractive alternative to classical chiroptical and chromatographic techniques or other NMR methods for investigating small to medium-size chiral molecules. Undoubtedly, ultra-high magnetic field strengths and cryoprobe technology will further enhance the potential of this technique in the near future.

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Enantiomeric Recognition of Chiral Invertomers through NMR in Chiral Oriented Solvents: A Study of the cis-Decalin

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Enantiomeric recognition of chiral invertomers through NMR in chiral oriented phases: a study of cis-decalin

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Abstract—We describe a deuterium 1D and 2D NMR study of cis-decalin in various chiral and achiral polypeptide oriented solvent systems and the effect of the acquisition temperature. Organic solutions of poly-L-phenylalanine (PBLG) or poly-L-carboxyphenylalanine (PCBLL) in dichloromethane or chloroform allow the chiral invertomers of cis-decalin to be differentiated at low temperature. At high temperature, it is possible to distinguish between deuterium nuclei of the molecule which become enantiotropic under rapid kinetic averaging. The results obtained illustrate the capability of such polypeptide liquid-crystalline solvents to enantioselectively interact with unfuctionalized chiral cycloalkanes and highlight the analytical potential of NMR analysis in chiral liquid crystal based solvents in the investigation of interconverting chiral conformers. © 2001 Published by Elsevier Science Ltd.

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Investigation of the Enantioselectivity of Three Polypeptide Liquid-Crystalline Solvents Using NMR Spectroscopy

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ABSTRACT The enantioselective potentials of three polypeptide liquid-crystalline molecules made of poly-γ-benzyl-l-glutamate (PBLG), poly-γ-ethyl-l-glutamate (PELG) or poly-ε-carbobenzyloxy-l-lysine (PCBL) are investigated and compared using proton, carbon-13 and deuterium NMR spectroscopy. From a practical point of view, we propose an efficient alternative to the PBLG system, which is essential when chiral homopolymer fails in distinguishing between enantiomers or enantiotopic elements. From a theoretical point of view, this study provides new information on the role of the lateral side chain of the polypeptide in the mechanisms of enantiodiscrimination. The various experimental results reported show the extraordinary adaptability of this methodology, and so enlighten the very large potential of NMR in chiral liquid crystals in the field of enantionic and enantiotopic analysis.

KEYWORDS chiral liquid crystal, enantioselectivity, enantiotopic differentiation, NMR spectroscopy, poly-γ-benzyl-l-glutamate, poly-ε-carbobenzyloxy-l-lysine, poly-γ-ethyl-l-glutamate

NMR Experimental Evidence of the Differentiation of Enantiotopic Directions in C₅ and C₂ᵥ Molecules Using Partially Oriented, Chiral Media

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Abstract: We report new and explicit experimental evidence of the differentiation of ¹H−H, ¹³C−H, and ¹³C−¹³C enantiotopic directions in prochiral molecules with C₅ and C₂ᵥ symmetry dissolved in a chiral liquid-crystalline phase using ¹³C and ²H{¹H} NMR spectroscopy at the natural abundance level. The case of endo-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride, bicyclo[2.2.1]hepta-2,5-diene, and ethyl alcohol oriented in organic solutions of poly-γ-benzyl-l-glutamate (PBLG) or poly-ε-carbobenzyloxy-l-lysine (PCBL) is investigated and discussed. Next, we describe the first NMR differentiation of enantiotropic directions in a C₂ᵥ molecule with no stereogenic carbon using malononitrile as a model. The various results presented in this work experimentally validate our recent theoretical arguments which predict that NMR spectra of nonplanar C₅ and C₂ᵥ components embedded in a chiral oriented solvent should differ from those recorded in nonchiral oriented media, because their effective molecular symmetry point group (interacting molecule) is different from their molecular point group (isolated molecule). In addition, the differentiation of enantiotropic directions in C₂ᵥ molecules exhibiting no stereogenic tetrahedral center illustrates for the first time an old stereochemical hypothesis which speculates that “for molecules of the type CXXY... the two X groups as well as the Y groups are equivalent and cannot be distinguished in chiral or achiral circumstances. However, the relationships between X and Y groups are not all equivalent. The four X−Y relationships may be ordered into two enantiotopic sets of two equivalent relationships” (Mislow, K.; Raban, M. Top. Stereochem. 1967, 1, 1) and validate the stereogenicity concepts proposed more recently by Fujita (Fujita, S. J. Am. Chem. Soc. 1990, 112, 3390).
2002 (7)

Routine Use of Natural Abundance Deuterium NMR in a Polypeptidic Chiral Oriented Solvent for determination of the Enantiomeric Composition of Chiral Building Blocks

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Chiral Liquid Crystal NMR: A Tool for Enantiomeric Analysis

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Enantiomeric and Enantiotopic Analysis of Cone-shaped Compounds with C₃ and C₃ᵥ Symmetry Using NMR Spectroscopy in Chiral Anisotropic Solvents

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Enantiomeric and Enantiotopic Analysis of Cone-Shaped Compounds with C₃ and C₃ᵥ Symmetry Using NMR Spectroscopy in Chiral Anisotropic Solvents

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Abstract: We describe the enantiomeric and enantiotopic analysis of the NMR spectra of compounds derived from the functionalized cone-shaped core, cyclohexenylbenzylamines (C-HT), dissolved in weakly oriented isotropic chiral liquid crystals (C-LC) based on organic solutes of poly-γ-phenylpropionamide. The C-HT core lacks prochirality, as well as stereogenic intramolecular centers. However, depending on the pattern of substitution, chiral and achiral compounds with different symmetries can be obtained. Thus, symmetrically unsubstituted (C₃ᵥ symmetry) derivatives are prochiral and possess enantiotropic elements. In the first part we use 1H- and 13C-NMR to study two unsubstituted (−OH or −OCH₃) CHTs, where the ring methylene protons are fully deuterated, and show for the first time that the observation of enantiomeric discrimination of chiral molecules with a C₃ᵥ symmetry axis is possible in a GLC. It is argued that this discrimination reflects different orientational ordering of the M and P isomers, rather than specific chiral short-range solute-solute interactions that may affect differently the magnetic parameters of the enantiomers or even their geometry. In the second part we present similar measurements on hexafluorinated CHT with flexible side groups (−OC(O)CH₃ and the, partially deuterated bisalcohols, −OC(O)CH₂(−)), having on the average C₃ᵥ symmetry. No spectral discrimination of enantiotropic sites was detected for the −OC(O)CH₃ derivative. This is consistent with a recent theoretical work (J. Chem. Phys. 1999, 111, 6850) that indicates that in C₃ᵥ molecules no chiral discrimination between enantiotopic elements, based on ordering, is possible. In contrast, a clear splitting was observed in the 1H spectra of the enantiomeric deuterons of the side groups in the tri(dioxysilane)−C-HT. It is argued that this discrimination reflects different ordering characteristics of the various, rapidly on the NMR time scale interconverting forms of this compound. Assuming two twisted structures for each of the dioxysilane side groups, four different conformers are expected, comprising two sets of enantiomeric pairs with, respectively, C₃ and C₁ symmetry. Differential ordering and/or fractional population imbalance of these enantiomeric pairs leads to the observed spectral discrimination of sites in the side chains that on average form enantiotopic pairs.

Investigation of SmI₂ Mediated Cyclisation Process of δ-iodo-α,β-Unsaturated Esters by Deuterium 2D NMR in Oriented Solvents

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Investigation of SmI₂-mediated cyclisation of δ-iodo-α,β-unsaturated esters by deuterium 2D NMR in oriented solvents

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Abstract—We have investigated the mechanism of the SmI₂-mediated cyclisation of δ-iodo-α,β-unsaturated esters using proton-decoupled deuterium 1D and 2D NMR in weakly ordered polypeptide liquid crystal solvents. Analysis of the spectroscopic results demonstrates that the cyclisation reaction takes place with concomitant and extensive racemization at the γ-position and the reason for this racemisation is discussed. We also report an efficient 2D NMR strategy for distinguishing meso- from d- and l-diastereoisomers based on the introduction of a CD₃ probe in the molecules to be studied. This approach allows determination of the diastereoisomeric and enantiomeric composition of a mixture. © 2002 Elsevier Science Ltd. All rights reserved.

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L’art de discriminer des énantiomères

Une molécule est chirale (du grec kheir, main) si elle existe sous deux formes images l'une de l'autre dans un miroir, mais non superposables ; comme le sont nos deux mains. Du point de vue de la pharmacologie, ces formes dites énantiomères peuvent présenter une activité biologique différente, voire même radicalement opposée. Comme le principe actif d'un médicament est très souvent une molécule chirale, il est crucial d'en déterminer la pureté enantiomérique.

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Enantiomeric Excess Measurements in Weakly Oriented Chiral Liquid Crystal Solvents through 2D $^1$H Selective Refocusing Experiments

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Enantiomeric excess measurements in weakly oriented chiral liquid crystal solvents through 2D $^1$H selective refocusing experiments

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Abstract

In this article, a simple and robust method is proposed for simplifying the analysis of proton spectra of molecules dissolved in weakly oriented chiral media. The NMR approach investigated is based on the use of proton selective refocusing 2D experiments (SERF) to measure proton proton dipolar couplings from unresolved lines. This technique is applied to the case of enantiomers dissolved in chiral polypeptide liquid crystals. It is shown that an accurate determination of enantiomeric excess is possible within a short experimental time.

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Keywords: NMR; Chiral liquid crystal; SERF; Enantiomeric excess; Orientation

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Résonance magnétique nucléaire du deutérium en abondance naturelle dans les cristaux liquides chiraux: Franchir une nouvelle frontière dans l’analyse de la chiralité

La mesure de la pureté enantiomérique est devenue une priorité analytique associée au développement incontournable de la synthèse asymétrique. Pour répondre aux attentes et exigences croissantes des chimistes organisateurs dans ce domaine, nous proposons une méthodologie originale fondée sur l’utilisation de la RMN. 1D ou 2D du deutérium en abondance naturelle dans les milieux orientés chiraux polypeptidiques. Le champ d’applications étendu et la flexibilité de cette approche en font un nouvel outil compétitif dans l’analyse de la chiralité, offrant une véritable alternative aux méthodes utilisées habituellement dans les laboratoires.

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Natural Abundance Deuterium NMR Spectroscopy in Polypeptide Liquid Crystals as a New and Incisive Means for Enantiodifferentiation of Chiral Hydrocarbons

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FULL PAPER

Natural Abundance Deuterium NMR Spectroscopy in Polypeptide Liquid Crystals as a New and Incisive Means for the Enantiodifferentiation of Chiral Hydrocarbons

Philippe Lesot, Muriel Sarfati, and Jacques Courtieu

Abstract: Polymeric chiral liquid-crystalline solvents based on homopolymeras are of interest with the view to discriminate between enantiomeric pairs of chiral hydrocarbons using proton-decoupled deuterium one- and two-dimensional NMR spectroscopy at natural abundance level. This method offers the major advantage that neither chemical modification nor isotopic labelling of the solutes to be studied is required. Chiral differentiation between optical isomers is observed through a difference in residual deuteron quadrupolar splittings. The spectroscopic separations and the S/N ratio from the spectra are usually large enough to measure the enantiomeric excess with an accuracy varying between 5 to 10%. This analytical approach is successfully applied to a large collection of chiral, rigid or flexible unsaturated as well as saturated hydrocarbons, including cases of axial chirality, atropoisomerism, and moieties existing as a mixture of enantiomers interconverting by ring inversion. Using the results reported in literature, a systematic comparison with other analytical strategies (NMR, GC, HPLC, VCD) is made and discussed. Also, a tentative proposal to rationalise the various results in terms of chiral differentiation and enantioselective shape recognition is presented. We show that this original tool provides an attractive and incisive alternative to the existing analytical techniques for studying nonfunctionalised chiral materials.

Keywords: deuterium • enantioselectivity • hydrocarbons • liquid crystals • NMR spectroscopy

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Efficient enantiodiscrimination of chiral monophosphine oxides and boranes by phosphorus coupled $^{13}$C NMR spectroscopy in the presence of chiral ordering agents

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Abstract—The synthesis of new chiral phosphoranes via the corresponding oxides or boranes is reported and the analytical potential of $^{13}$C-$^1$H NMR spectroscopy in weakly ordering polyamide liquid crystalline phases in view to differentiate between enantiomers of these chiral phosphoranes precursors is explored. In particular results involving organic solutions of poly-$\gamma$-benzyl-$\gamma$-glutamates (PBGL) and poly-$\epsilon$-carboxy-benzyl-$\gamma$-lysine (PCBLL) are described. This NMR approach allows determination of the enantiomeric composition, and provides therefore a new efficient alternative to classical methods usually used to analyze this class of compounds. A description of various spectral enantiodifferentiations patterns expected to be observed using $^{13}$C-$^1$H NMR of enantiomers having a spin-$\frac{1}{2}$ heteroatomic nucleus, embedded in a chiral liquid crystal is presented. © 2003 Elsevier Science Ltd. All rights reserved.

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2D-NMR Strategy Dedicated to the Analysis of Perdeuterated Enantiomer Solutes in Weakly Ordered Chiral Liquid Crystals

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Abstract: Methods for the assignment of the quadrupolar doublets in the deuterium NMR spectra of weakly ordered, perdeuterated or partially deuterated chiral compounds dissolved in chiral liquid crystals are described which use robust 2D correlation NMR experiments. To overcome a lack of resolution in deuterium labelled COSY 2D spectra in such materials, we propose and explore a correlation 2D sequence which is based on deuterium−carbon 2D correlation spectroscopy. The technique results in a $^{13}$C−$^1$H contour plot and allows the full resonance assignment of overcrowded deuterium-1H spectra using carbon−deuterium correlations. The $^1$H auto-correlation and $^{13}$C−$^1$H correlation experiments are applied in the case of a racemic mixture of 2-ethylhexanoic acid-$d_{10}$ dissolved in a polyamide chiral oriented solvent. The performance and the limits of both techniques are presented and discussed. For the last step of the assignment procedure, we propose a simple method for obtaining two coherent sets of quadrupolar splittings, one for each enantiomer.

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Structural Ambiguities Revisited in Two Bridged Ring Systems Exhibiting Enantiotopic Elements, Using Natural Abundance Deuterium NMR in Chiral Liquid Crystals

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The natural abundance deuterium 2D Q-COSY NMR spectra of two apolar bridged ring systems, norbornene (C_2 symmetry) and quadracyclane (C_5symmetry), oriented in a chiral liquid crystal made of an organic solution of poly-γ-benzyl-ε-glutamate (PBLG), are analyzed. In such a chiral oriented solvent, enantiotopic nuclei or directions are nonequivalent. Consequently, it is possible to measure many more anisotropic interactions compared to those obtained from NMR spectra in nonchiral nematogenic solvents. From the measurement of all residual quadrupolar splittings, ΔQQ, and one bond carbon–proton residual dipolar couplings, D(C–H), all the elements of the second rank order tensor, S_{ij}, were calculated. Knowledge of the S_{ij} values allows all deuterons and subsequently proton NMR resonances to be assigned unambiguously. The reason is that there exists a one-to-one mathematical relationship linking the orientational order parameters of a solute molecule, the molecular geometry, and the anisotropic interactions measured on oriented spectra. In the case of norbornene, it was possible to assign nuclei to each enantiotopic face in this prochiral molecule. Such an analytical approach yields original stereochemical information probing the diastereotopicity and/or enantiotopicity of molecules, and is revealed to be a very useful alternative to conventional 2D-NMR experiments in isotropic solvents.

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The orientational order and conformational distributions of the two enantiomers in a racemic mixture of a chiral, flexible molecule dissolved in a chiral nematic liquid crystalline solvent

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The orientational order and conformational distributions of the two enantiomers of (±)-α-ethyl/hexanoic acid-d_{15}, a flexible chiral molecule, dissolved in a chiral nematic liquid crystalline solvent made of PBLG in an organic co-solvent are obtained by analysis of NMR data. The anisotropic, NMR parameters are obtained from the separated analysis of the two enantiomers using carbon–deuterium, deuterium–deuterium 2D correlation experiments and proton-coupled carbon-13 1D experiments. The analysis of conformational distributions, and the conformationality depend on orientational order parameters are derived using the additive potential, AP, model.
Exploring the Analytical Potential of NMR Spectroscopy in Chiral Anisotropic Media for the Study of the Natural Abundance Deuterium Distribution in Organic Molecules

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DOI: 10.1021/ac030385e

Exploring the Analytical Potential of NMR Spectroscopy in Chiral Anisotropic Media for the Study of the Natural Abundance Deuterium Distribution in Organic Molecules

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The deuterium/hydrogen (D/H) ratio measurement by quantitative 2H NMR spectroscopy in a method of choice for the analysis of kinetic isotopic effects associated with enzyme-catalyzed reactions during a biosynthetic pathway. However, the efficiency of the current isotopic 2H (2H) NMR can be limited by the rather small chemical shift dispersion of deuterium nuclei. In addition, this method does not allow the enantiomeric deuterons in prochiral molecules to be spectrally discriminated, hence precluding the quantification of isotopic fractionation on methyl proestereogenic sites. In this work, we explore another analytical strategy able to circumvent these disadvantages. This approach is based on the use of natural abundance 2H2 D NMR experiments on solutes embedded in polyepitidie, chiral liquid crystalline solvent. Thus, we show that NMR in these oriented phases is a powerful way to separate deuterium signals on the basis of the quadrupolar interactions, providing a promising alternative to overcrowded 2H NMR spectra obtained in liquid state. To illustrate our purpose, we have experimentally investigated the case of 1,1′-bis(phenylthio)hexane derived by cleavage from methyl linolate of safflower. The 2H NMR results in chiral liquid crystals is presented and discussed. We show, for the first time, that (D/H)hyper and (D/H)deuterated can be measured at the same methyl position of a fatty acid chain.

New Amino Acid based on Anionic Surfactants and their Use as Enantiodiscriminating Lyotropic Liquid Crystalline NMR Solvent

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New amino acid-based anionic surfactants and their use as enantiodiscriminating lyotropic liquid crystalline NMR solvents

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Abstract—New amino acid-based anionic surfactants have been synthesized and their use as chiral oriented NMR solvents studied. A series of sulfonated amphiphilic L-Ph or L-Ala derivatives with pentyl to tetradecyl tails were prepared by reacting the corresponding amino acid esters with o-sulfo-benzoic anhydride. Their critical micelle concentrations (CMC) range from 1.6×10^{-2} to 1.4×10^{-2} mol/L and depend on the alkyl chain length as well as on the nature of the amino acid block. These values are comparatively lower than those of classical surfactants such as alkylbenzenesulfonates and N-acyl-L-amino-carboxylates. Their use as chiral liquid crystals (CLC) for analytical purposes is reported. In particular, it is shown that aqueous solutions of these chiral surfonates in the presence of chlorinated solvents (CHCl_3, C_2H_5Cl, C_2H_4Cl_2, or CCl_4) provide homogeneous oriented NMR solvents able to differentiate between enantiomers of d,l-alanine-2,4-f using proton and deuterium NMR spectroscopy.

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Use of Two-dimensional Correlation between $^2$H quadrupolar splittings and $^{13}$C CSA’s for Assignment of NMR Spectra in Chiral Nematics

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DOI: 10.1039/b316488h

Use of two-dimensional correlation between $^2$H quadrupolar splittings and $^{13}$C CSA’s for assignment of NMR spectra in chiral nematics

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The possibility of correlating visible spectral enantiodiscriminations in a single 2D map using simultaneously both quadrupolar and dipolar nuclei is presented and experimentally demonstrated.

The method uses deuterium-carbon-13 heteronuclear 2D experiments with $^{13}$C in natural abundance applied to deuterated compounds oriented in chiral, nematic liquid crystals (PBLG/CHCl$_3$). Illustrative examples involving chiral and prochiral solute molecules are analysed and discussed. We show that this approach provides an efficient and elegant way to assign deuterium resonances for each enantiomer or enantiotopic directions in prochiral molecules.

Heteronuclear Selective Refocusing 2D-NMR Experiments for the Spectral analysis in Chiral Oriented Solvents

DOI: 10.1002/mrc.1399

Heteronuclear selective refocusing 2D NMR experiments for the spectral analysis of enantiomers in chiral oriented solvents

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We report the use of carbon–proton heteronuclear selective refocusing 2D NMR experiments dedicated to the spectral analysis of enantiomers dissolved in weakly ordering chiral liquid crystalline solvents.

The method permits the extraction of carbon–proton residual dipolar couplings for each enantiomer from a complex or unresolved proton-coupled $^1$C spectral patterns. Illustrative examples are analysed and discussed. It is shown that an accurate determination of enantiomeric excess is possible. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: NMR; $^{13}$C NMR; chiral liquid crystal; selective pulses; enantiomeric excess

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Analysis of the $^{13}$C NMR Spectra of Molecules, Chiral by Isotopic Substitution, Dissolved in a Chiral Oriented Environment: Toward the Absolute Assignment of the pro-R/pro-S Character of Enantiotopic Ligands in Prochiral Molecules

P. LESOT*, O. LAFON, J. COURTIEU, P. BERDAGUÉ
DOI: 10.1002/chem.200400065

Abstract: We examined and discuss the proton- and deuterium-decoupled carbon-13 2D spectrum of a molecule, chiral by virtue of the isotopic substitution, dissolved in a chiral oriented medium which simultaneously exhibits chiral discrimination, enantioemic enrichment and isotopic effect. Using the 1-deutero-(2,3,4,5,6-pentadeutero-phenyl)phenylmethanol orientationally ordered in a chiral nematic liquid crystalline as illustrative example, we point out three important features. First, we demonstrate that the absolute assignment of the pro-R/pro-S character may be derived from the absolute configuration of the isotopically chiral analog. Second, we report evidence that isotopic effect on $^{13}$C chemical shift anisotropy is negligible in a weakly orienting solvent. Third, we definitely establish that the molecular orientation of prochiral $C_2$ symmetry molecules and their parent compounds that are chiral by virtue of the isotopic substitution is the same.

Keywords: chirality - enantioselectivity - isotopic effect - liquid crystals - NMR spectroscopy

Modified z-gradient Filtering as a New Mean to Obtain Phased Deuterium Autocorrelation 2D NMR Spectra in Oriented Solvents

O. LAFON, P. LESOT*, D. MERLET, J. COURTIEU
DOI: 10.1016/j.jmr.2004.08.010

Abstract

We describe a modified z-gradient filter scheme specifically designed to obtain pure absorption mode deuterium 2D NMR spectra recorded in oriented solvents. The proposed technique is investigated by analyzing the evolution of the density operator for a spin $I = 1$. The method is applied to the recently designed $Q$-COSY and $Q$-resolved 2D experiments to simplify the analysis of chiral molecules dissolved in weakly orienting chiral liquid crystals. The efficiency of this z-gradient filtering technique is illustrated using the perdeuterated 1-butanol, a prochiral molecule of average $C_2$ symmetry, dissolved in an organic solution of poly-$\gamma$-benzyl-L-glutamate (PBLG). The experimental results as well as the advantages of the new experiments compared with the previous ones are described and discussed.

Keywords: $^2$H NMR spectroscopy; Quadrupolar splittings; Chiral liquid crystals; z-Gradient filter

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The Effect of a Chiral Nematic Solvent on the Orientational Order and Conformational Distribution of a Flexible Prochiral Molecule

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DOI: 10.1039/b411203b

The effect of a chiral nematic solvent on the orientational order and conformational distribution of a flexible prochiral solute

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Deuterium NMR spectroscopy is used to detect the reduction in symmetry which occurs when a flexible prochiral molecule, 4-pentyl-4′-cyanobiphenyl, is dissolved in a chiral nematic solvent produced by dissolving poly-γ-benzyl-l-glutamate in organic solvents. The quadrupolar splittings obtained are used to investigate whether this phenomenon is the result of a reduction in symmetry of the anisotropic, solute-solvent interaction potential or whether the conformational distribution is also affected. It is demonstrated that the first assumption explains the enantiomeric discrimination in chiral liquid crystals and it is possible in this chiral medium to determine the relative configuration of the deuteriums in the methylene groups.

2005 (4)

Développement et Applications de la RMN du Deutérium en Abondance Naturelle dans les Cristaux Liquides Chiraux: Une autre Approche de l'Analyse en Chimie Organique

P. LESOT*

49. (A.R.)

Deuterium Three-dimensional NMR Experiments for Analysing Weakly Aligned, Isotopically Enriched Molecules

O. LAFON, P. LESOT*

DOI:10.1016/j.cplett.2005.01.040

Deuterium 3D NMR experiments for analysing weakly aligned, isotopically enriched solutes

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Abstract

In this contribution we report three new pure absorption mode deuterium 3D NMR experiments to analyse spectra of isotopically enriched solutions dissolved in weakly orienting liquid crystals. The potentialities of these 3D strategies are illustrated using the perdeuterated-l-butanol, a prochiral molecule of C2 symmetry in average, dissolved in a chiral mesophase made of poly-g-benzyl-l-glutamate. The experimental results obtained for the three different experiments are discussed and compared.

50. (A.R.)

Theoretical and Experimental Investigation of 13C Relayed 2H-2H-COSY 2D Experiments: Application to the Analysis of Weakly Aligned Solutes

O. LAFON, P. LESOT*

DOI:10.1016/j.jmr.2005.02.011

Theoretical and experimental investigation of 13C relayed 2H-2H-COSY 2D experiments: Application to the analysis of weakly aligned solutes

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Received 1 December 2004; revised 8 December 2004
Available online 15 March 2005

Abstract

We describe new NMR 2D experiments denoted DECADENCY for DEuterium Carbox DEuterium Nuclear Correlation spectroscopy, dedicated to the analysis of anisotropic deuterium spectra. They belong to the class of X-relayed Y,Y-COSY 2D experiments that was initially explored in the case of a 1H-X-2H fragment (Ix = 1/2) in isotropic medium. DECADENCY 2D experiments permit to correlate the quadrupolar doublets associated with two inequivalent deuterium nuclei in an oriented CD2 fragment through heteronuclear polarization transfers. Two kinds of pulse sequences are described here using either a double INEPT-type or DEPT-type process. DECADENCY 2D experiments provide an interesting alternative to 2H-2H COSY experiments when the geminal 1H-2H total coupling (scalar and dipolar) is null or too small to provide visible cross-correlation peaks. Such a situation is typically observed for geminal deuteriums in prochiral or chiral molecules dissolved in chiral liquid crystals. The efficiency of these techniques is illustrated using deuterated prochiral molecules, the phenyl[1H]methanol and the l-chloro-I-H

Keywords: 2H NMR spectroscopy; Quadrupolar splittings; Chiral liquid crystals; C-D polarization transfers

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Enantiomeric Analysis of Planar Chiral (η⁶-Arene) Chromium Tricarbonyl Complexes using NMR in Oriented Solvents

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DOI: 10.1021/om050239u

We investigate the analytical potential of proton-decoupled and proton-coupled carbon-13 NMR spectroscopy in chiral polypeptide liquid crystals for the enantiomeric discrimination of planar chiral (η⁶-arene)chromium tricarbonyl complexes. Experimental results obtained for chiral β-hydroxynamino alcohol and a series of chiral aldehydic complexes are reported and discussed in detail.

52.

Study of Molecular Rotational Isomerism using Deuterium NMR in Chiral Oriented Solvents

P. LESOT*, O. LAFO, H.B. KAGAN, P. FAN

DOI: 10.1039/b514694a

Deuterium NMR in polypeptide chiral liquid crystals is used for the first time to investigate the internal rotational isomerism phenomenon, illustrated by the interconversion between conformers of 1-(2′,6′-dideuterio-4′-methylphenyl)naphthalene.
53. (A.C.)

Assignment of Absolute Configuration of Natural Abundance Deuterium Signals Associated with (R)- and (S)-Enantioisotopomers in a Fatty Acid Aligned in a Chiral Liquid Crystal: Enantioselective Synthesis and NMR Analysis
V. BAILLIF, R. ROBINS, I. BILLAULT*, P. LESOT*
DOI: 10.1021/ja0617892

54. (A.C.)

Enantioselective Synthesis of Methyl-5-(R)-fluorohept-6-ynoate
V.L. MANTHATI, A.S.K. MURTHY, F. CAIJO, D. DROUIN, P. LESOT, D. GREE, R. GREE*
DOI: 10.1016/j.tetasy.2006.08.010
55. (A.C.)

Structure, Formation, and Dynamics of Mo\textsubscript{12} and Mo\textsubscript{16} Oxothio Molybdenum Rings Containing Terephtalate Derivatives

J.-F. LEMONNIER, S. FLOQUET* J. MARROT, E. TERAZZI, C. PIGUET, P. LESOT, A. PINTO, E. CADOT*

DOI: 10.1002/chem.200601369

Abstract: The influence of rigid or semirigid decahydroxylated anions, terephthalate (Ter\textsuperscript{4}\textsuperscript{+}), isophthalate (Iso\textsuperscript{4}\textsuperscript{+}), and phenylenehexaolate (PDA\textsuperscript{2}\textsuperscript{-}) on the self-condensation process of the [Mo\textsubscript{6}S\textsubscript{6}H\textsubscript{4}\textsuperscript{3+}]\textsuperscript{2+} dithiohathiocyanurate anion has been investigated. Three new molybdenum rings, \([\text{Mo}_{5}O_{6}S_{6}(OH)(Ter)^{3+}]^{-}\) ([\text{Mo}_{5}O_{5}S_{6}(OH)(Iso)^{3+}]^{-}), \([\text{Mo}_{5}O_{5}S_{6}(OH)(Ter)^{3+}]^{-}\) and \([\text{Mo}_{5}O_{6}S_{6}(OH)(Ter)^{3+}]^{-}\) ([\text{Mo}_{5}O_{6}S_{6}(OH)(Iso)^{3+}]^{-}) have been isolated and unambiguously characterized in the solid state by single-crystal X-ray studies and in solution by various NMR methods and especially by diffusion-correlated NMR (D\textsuperscript{H} DOSY) spectroscopy, which was shown to be a powerful tool for the characterization and speciation of templated molybdenum ring systems in solution. Characterization by FT-IR and elemental analysis are also reported. The dynamic and thermodynamic properties of both the sixteen-membered rings were studied in aqueous medium. Specific and distinct behaviors were revealed for each system. The Iso\textsuperscript{4}\textsuperscript{-} / Mo\textsubscript{6} S\textsubscript{6}H\textsubscript{4}\textsuperscript{3+} system gave rise to equilibrium, involving mono-templated \([\text{Mo}_{5}O_{6}(Iso)^{3+}]^{-}\) and bio-templated \([\text{Mo}_{5}O_{6}(Iso)^{3+}]^{-}\) ions.

Keywords: carboxylate ligands - molybdenum - NMR spectroscopy - polyoxometallates - solution

56. (A.R.)

Analysis of Intramolecular Dynamic Processes in Enantiomeric Diaryl Atropisomers and Related Derivatives through \textsuperscript{2}H NMR in Polypeptide Liquid Crystals

O. LAFON, P. LESOT*, C.A. FAN, H.B. KAGAN

DOI: 10.1002/chem.200601284

Analysis of Intramolecular Dynamic Processes in Enantiomeric Diaryl Atropisomers and Related Derivatives by \textsuperscript{2}H NMR Spectroscopy in Polypeptide Liquid Crystals

Olivier Lafon, [a] Philippe Lesot, [a, b] Chun-An Fan, [b] and Henri B. Kagan [b]

Abstract: We demonstrate the analytical potential of \textsuperscript{2}H (1H) NMR spectroscopy in weakly ordered, chiral hydrophobic liquid crystals made of poly(4-hexyl-2-phenyl-4H-benzopyran-4-yl) (PBLG) dissolved in chloroform or dichloromethane for investigating the intramolecular dynamic processes of four deuterated diaryl (derivatives of 1,4-dimethylphenyl) naphthalene. When the rotation of the aryl groups about the sp\textsuperscript{2}-sp\textsuperscript{3} bond is sufficiently slow relative to the NMR timescale, the method allows the spectral discrimination of enantiomeric atropisomers or enantiotropic directions in the prochiral derivatives. The effect of the position of substituents on the phenyl group on the conformational dynamics of these compounds has been examined as well as the nature of the organic co-solvent. When coalescence phenomena are observed, simulation of the experimental \textsuperscript{2}H-1H) NMR line shapes using a formalism tailored for two deuterons undergoing mutual exchange allows the rate constants and the activation parameters for the internal rotation processes to be calculated. Experimental values of \(\Delta H^\ddagger\) have been compared with data evaluated by molecular modelling calculations and the activation parameters are discussed for the various compounds. It is shown that these polypeptide mesophases have no significant impact on the interconversion dynamics of these compounds. In contrast with the nematic thermotropic phases, Helferich’s equation cannot be used to predict the evolution of the quadrupolar splittings (\(\Delta Q_0\) values), and hence the order parameters, versus \(T\) in the PBLG mesophases. For these particular lyotropic systems, it is shown that an exponential function of the form \(\Delta Q_0(\text{Hz}) = C \exp(-E RT/K)\) provides excellent agreement between the experimental and predicted \(\Delta Q_0\) values. Analysis of the results reported in this work suggests that orientation and chiral discrimination phenomena in these lyotropic solvents could be treated separately because they would involve different interaction mechanisms.

Keywords: atropisomerism - chirality - conformational analysis - exchange processes - kinetics and activation parameters - liquid crystals - NMR spectroscopy

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Synthetic Studies on Macrolactin A: Construction of C4-C27 fragment

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DOI: 10.1021/jo0701942

Homo- and Heteronuclear 2D NMR Approaches to Analyse a Mixture of Deuterated unlike/like Compounds using Weakly Ordering Chiral Liquid Crystals

K. BENALI, O. LAFON, H. ZIMMERMANN, E. GIUETT, P. LESOT*

DOI: 10.1016/j.jmr.2007.04.007

Abstract

We describe several homo- and heteronuclear 2D NMR strategies dedicated to the analysis of anisotropic nonaqueous H2O spectra of a mixture of deuterated unlike/like stereoisomers with two remote stereocenters, using weakly orienting chiral liquid crystals. To this end, we propose various 2D correlation experiments, denoted “DOH2O” or “DDH3C” (with n = 1, 2), that involve two heteronuclear polarization transfers of INEPT type with one or two proton relays. The analytical expressions of correlation signals for four pulse sequences reported here were calculated using the product-operator formalism for spin J = 1 and S = 3/2. The features and advantages of each scheme are presented and discussed. The efficiency of these 2D sequences is illustrated using various deuterated model molecules, dissolved in organic solutions of poly-L-lysine-based glutamate (PLBG) or poly-epsilon-lysylglycylglycine (PEGGLY) and NMR numerical simulations.

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Keywords: 2D quadrupolar splittings; 2D experiments; Chiral liquid crystals; INEPT transfer; Proton relay; aI Stereosomers

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59. (A.R.)

Chiral Discrimination in the $^{13}$C- and $^2$H-NMR of the Crown and Saddle Isomers of Nonamethoxy-Cyclotrimeratrylene in Chiral Liquid-Crystalline Solutions

O. LAFON, P. LESOT*, H. ZIMMERMANN, R. POUPKO, Z. LUZ *


DOI: 10.1021/jp070564q

60. (A.R.)

Empirical Determination of the absolute Configuration of Small Chiral Molecules using Natural Abundance $^2$H NMR in Chiral Liquid Crystals

L. ZIANI, P. LESOT*, A. MEDDOUR, J. COURTIEU


DOI: 10.1039/b711493a

**Empirical determination of the absolute configuration of small chiral molecules using natural abundance $^2$H NMR in chiral liquid crystals**

Latifa Ziani, Philippe Lesot, Abdelkrim Meddour and Jacques Courtieu

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Natural abundance deuterium 2D NMR spectroscopy in polypeptide liquid crystals is used for empirically determining the absolute configuration of small chiral molecules.
2008 (7)

61. (A.R.)

**2H NMR Studies of Two-homopolypeptide LyotropicMesophases: Toward the Quantification of Solute-FiberInteractions**

P. LESOT*, O. LAFON, C. AROULANDA, R. DONG


DOI: 10.1002/chem.200701543

**Abstract:** The analytical potential and enantioselective properties of lyotropic mesophases made by mixing two chemically different chiral polyammoniums are described. Here we examine the case of a mixture of poly-2-phenyl-5-lyctic acid (PBLG) and poly-ε-carboxylycylloxycalanine (PCBLX). We demonstrate that 2H NMR spectroscopy on these chiral oriented mixtures can discriminate both enantiomers and enantioselectic directions in prochiral molecules. Moreover, in such systems, degree of enantioselectivity, resolution, and sensitivity can be conveniently optimized by changing the relative proportion of the two polyammoniums. Therefore, these new enantioselective media provide a favorable alternative to single-polypeptide mesophases with respect to stereochimical applications. At a more fundamental level, the present work points out that sole distillation in the vicinity of each polypeptide partly governs the degree of enantioselectivity and NMR relaxation rates. To this end, the experimental trends of sole NMR observables (Δν0, T1) versus the fraction of peptide units of each polymer were analyzed by using a “mean-field” model derived from that proposed for mixture of thermosensitive, anisotropic, solvents, and based on the separation of intermolecular interactions between the sole and both polypeptides. This approach allows the relative sole-solute-affinity in these lyotropic systems to be determined. To identify the factors controlling sole-polypeptide affinities, we investigated various solutes (polar, apolar, rigid/flexible, chiral/achiral/prochiral/chiral molecules) using 2H NMR at natural abundance or on isotopically enriched solutes.

**Keywords:** enantioselectivity - liquid crystals - mesophases - NMR spectroscopy - polypeptides

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62. (A.V.) (invité)


P. LESOT*


**Résumé**

La quantification de la symétrie d’un cristal liquide chiral est un aspect primordial pour les Laboratoires Pharmaceutiques. Dans cet article, nous présentons les derniers développements technologiques et méthodologiques associés à la RMN du deutérium en abondance naturelle dans les solvants orientés chiraux. Nous montrons que l’affinité spatiale et temporelle de la RMN peut être modélisée par un spectromètre RMN de base équipée d’une sonde de détection cryogénique et utilisée dans des conditions isotopiques.

**Mots-clés**

RMN, deutérium, chiralité, cristaux liquides, configuration absolute, fractionnement isotopique
Combined Analysis of four C-18 Unsaturated Fatty Acids using Natural Abundance Deuterium 2D NMR Spectroscopy in Chiral Oriented Solvents

P. LESOT*, V. BAILLIF, I. BILLAULT

DOI: 10.1021/ac702443b

Combined Analysis of C-18 Unsaturated Fatty Acids Using Natural Abundance Deuterium 2D NMR Spectroscopy in Chiral Oriented Solvents

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The quantitative determination of isopropyl (3H/4H) ratios at natural abundance using the SNIF-NMR protocol is a well-known method for understanding the enzymatic biosynthesis of metabolites. However, this approach is not always successful for analyzing complex melanin fractions, and specifically, is inadequate for probing chromatic molecules such as complete essential unsaturated fatty acids. To overcome these analytical limitations, we use the natural abundance-deuterium 2D NMR (NAD 2D NMR) spectroscopy on solutes embedded in polyamide chiral liquid crystals. This approach, recently explored for measuring (3H/4H) ratios of small molecules (Lesot, F.; Baillif, V.; Billault, I. Anal. Chem. 2004, 76, 2827–2835), is a powerful way to separate the 3H signals of a non-identical enantiomer pair on the basis of the 3H quadrupolar interactions and of the 4H chemical shift. Two significant advances over our previous work are presented here and allow the complete isotopic analysis of four mono- and polyunsaturated fatty acid methyl ester methyl oleate (1), methyl linoleate (2), methyl linolenate (3), and methyl vernolate (4). The first consists of using NMR spectrometers operating at higher magnetic field strengths (14.1 T) and equipped with a selective cryoprobe optimized for deuterium nuclei. The second is the development of O-COSY Fz 2D NMR experiments able to reproduce phased 3H 2D maps after a double Fourier transformation. This combination of modern hardware and efficient NMR sequences provides a unique tool to analyze the (3H/4H) ratios of large chromatic molecules (C-18) dissolved in organic solutions of poly(ethylene glycol) and requires smaller amounts of solute than previous study on fatty acids. For each compound (1–4), all 3H quadrupolar doublets visible in the 2D spectra have been assigned on the basis of 3H chemical shifts, isotopic data obtained from isotropic quadrupolar NAD NMR, and by an interspectral comparison of the anisotropic NAD spectra of four fatty acids. The NMR results are discussed in terms of (3H/4H) isotopic distribution and molecular orientations in the mesophase. For the first time, we show that the investigation of natural isotopic fractionation of complete fatty acids is possible without the need for chemical modifications, hence providing an alternative method to probe the mechanisms of enzymes implied in the biosynthetic pathway of unsaturated fatty acids.

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A Comparison of Proton-detected 13C Local Field Experiments with Deuterium NMR at Natural Abundance for Studying Liquid Crystals


DOI:10.1080/02678290801935887

A comparison of proton-detected 13C local field experiments with deuterium NMR at natural abundance for studying liquid crystals

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(Accepted 22 January 2008)

A comparison is made between the information which can be derived on structure, conformation and orientational order of the molecules in a nematic liquid crystal 4-penty14-cyanobiphenyl (5CB) from the NMR spectra of the deuterium atoms at natural abundance (NAD NMR), and the two-dimensional proton-detected 13C local field experiment (PDFL). The nine residual quadrupolar splittings, δQ, obtained experimentally have been compared with quadrupolar tensors and a geometry and conformational potentials calculated by the DFT method B3LYP/6-311G**. The PDFL experiment yielded 42 scaled 13C–3H residual dipolar couplings, kDCH. The scaling factor, k, is determined experimentally by comparing unscaled and scaled residual dipolar couplings in a sample of fluorobenzene dissolved in a nematic liquid crystalline solvent. The corrected residual dipolar couplings, DCH, are used to investigate the structure and rotational potentials about each bond in the molecule.

Keywords: proton-detected 13C local field experiment; deuterium NMR at natural abundance

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Enantiomeric Analysis using Natural Abundance Deuterium 3D NMR Spectroscopy in Polypeptide Chiral Oriented Media

DOI: 10.1016/j.cplett.2008.04.065

Abstract
The use of natural abundance deuterium (NAD) three-dimensional (3D) NMR experiment in chiral liquid crystals (CLC) is reported and discussed. This homonuclear autocorrelation 3D experiment allows assigning deuterium signals of weakly aligned molecules at natural isotopic abundance. It provides an efficient strategy for identifying the spectral enantiomer-discriminations on NAD spectra. We demonstrate that 3D NMR is feasible within reasonable experimental times (14 h) using the 3D Quadrupole Double-Quantum NMR sequence [O. Lason, P. Lesot, Chem. Phys. Lett. 404 (2004) 90] and a 14.1 T NMR spectrometer equipped with a selective 5 mm-deuterium NMR cryoprobe. The analytical potentialities of this technique are illustrated in the case of (S)-but-2-yn-l-ol dissolved in poly-(o-benzyl-glutamate) (PCM) mesophase. © 2008 Elsevier B.V. All rights reserved.

Enantiodiscrimination in the Deuterium NMR Spectra of Flexible Chiral Molecules with Average Axial Symmetry Dissolved in Chiral Liquid Crystals. The Case of Tridioxyethylenetriphenylene

DOI: 10.1021/ja800957a

Abstract
Flexible chiral molecules undergoing fast interconversion (on the NMR time scale) between different conformational arrangements may yield "average" axial species with enantiotropically related sites. Contrary to this situation observed for rigid axial molecules, signals from these enantiomeric sites in NMR spectra recorded in chiral liquid-crystalline solutions can be resolved. In the present work, we studied the deuterium NMR spectra of tridioxyethylenetriphenylene (compound 4) statistically distributed to 10% in the flexible side chains and dissolved in chiral and achiral hydroxylic liquid crystals based on poly-2-phenylethanol. The fast chain-chain flipping of the side chains in 4 on average randomize the molecules axisymmetry (D_{2h}) with pairs of enantiotopic ethylene deuterons. These deuterons exhibit unusually large enantiodiscrimination. To explain this observation, we first describe how the average symmetry of flexible molecules can be changed from the symmetry of the "frozen" conformation and the nature of the averaging process. The procedure is then applied to 4 and used to analyze the NMR results. It is shown that the large enantiodiscrimination in the present case reflects a large difference in the orientational ordering of the conformational enantiomers participating in the interconversion processes as well as a large geometrical factor due to the special shape of the disphenylen side groups. The D_{2h} NMR spectra of 4 in the same hydroxylic liquid crystal solvent are analyzed to determine its orienting characteristics. Several related cases are also discussed.
Two aspects of the Desymmetrization of Selected Prochiral Aromatic or Vinylic Dihalides: Enantioselective Halogen-Lithium Exchange and Prochiral Recognition in Chiral Liquid Crystals

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DOI: 10.1016/j.tetasy.2008.12.003

Investigation of Fatty Acid Elongation and Desaturation Steps in Fusarium lateritium by Quantitative Two-dimensional Deuterium NMR Spectroscopy in Chiral Oriented Media

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The origin of hydrogen atoms during fatty acid biosynthesis in Fusarium lateritium has been quantified by isotope tracking close to natural abundance. Methyl linoleate was isolated from F. lateritium grown in natural abundance medium or in medium slightly enriched with labeled water, glucose, or acetate, and the 2H incorporation was determined by quantitative 2H-1H NMR in isotropic and chiral oriented solvents. Thus, the individual (2H1)H ratio at each pro-R and pro-S hydrogen position of the CH2 groups along the chain can be assessed. These values allow the isotope redistribution coefficients (a2H) that characterize the specific source of each hydrogen atom to be related to the non-exchangeable hydrogen atoms in glucose and to the medium water. In turn, these can be related to the stereoreactivity that operates during the introduction or removal of hydrogens along the fatty acid chain. First, at even CH3, the pro-S hydrogen comes only from water by protonation, whereas the pro-R hydrogen is introduced partly via acetate but principally from water. Second, the monosubstituted hydrogen of glucose (positions H-6,6 and H-1) are shown to be introduced to the odd CH2 via the NAD(P)H pool used by both reductases involved in the elongation steps of the fatty acid chain. Third, it is proved that hydrogens removed at sites 9,10 and 12,13 during desaturation by Δ9- and Δ12-desaturases are pro-R, and that during these desaturation steps α-secondary kinetic isotope effects occur at the 9 and 12 positions and not at the 10 and 13 positions.

1The on-line version of this article available at http://www.jbc.org contains supplemental Figs. S1–S4 and Table S1.
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The abbreviations used are: FAS, fatty acid synthase; PLSG, poly-y-benzyl-L-glutamate; KB, kinetic isotope effect; FAME, fatty acid methyl ester.
69. (A.F.) (Revue)

Natural Abundance Deuterium NMR Spectroscopy: Developments and Analytical Applications in Liquid, Liquid Crystalline and Solid Phase
P. LESOT*, J. COURTIEU
DOI: 10.1016/j.pnmrs.2009.01.001

70. (A.L.) (Article de Livre)

Analytical Potentials of Natural Abundance Deuterium NMR Spectroscopy In Achiral Thermotropics and Polypeptide Chiral Liquid Crystals
P. LESOT*, C. AROULANDA
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Chapter 2
Analytical Potentials of Natural Abundance Deuterium NMR Spectroscopy in Achiral Thermotropics and Polypeptide Chiral Oriented Solvents
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Deuterium NMR spectroscopy in oriented solvents is a powerful methodology that can be efficiently used for various analytical applications. The majority of studies involved isotopically enriched analytes so far. However as deuterium nuclei are naturally present at the level of ca. 0.011% on average in all (bio)organic compounds, the natural abundance deuterium NMR (NAD-NMR) is possible and has been explored very early in the NMR history. Actually this quadrupolar nucleus (I = 1) with a small nuclear electric quadrupole moment is a remarkable tracer that can be easily detected with modern high-field FT NMR spectrometers. This chapter presents fundamentals of NAD-NMR spectroscopy in achiral and chiral liquid-crystalline environments and its various possible contributions to the chemical analysis. This includes some theoretical aspects and a survey of the most useful applications. The potentialities of NAD-NMR using liquid crystals with low and high degree of ordering are reviewed. A special emphasis will be given on the development of NAD-NMR in polypeptide chiral liquid crystals that provides an original method for enantiomeric analysis and stereochemical investigations. Finally the most recent analytical progresses of anisotropic NAD-NMR using spectrometers equipped with deuterium cryogenically cooled probes will be presented.
71.
(A.R.)

Enantiodiscrimination of Flexible Cyclic Solutes using Deuterium NMR Spectroscopy in Polypeptide Chiral Mesophases: Investigation of cis-Decalin and THF
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The conformational dynamics and orientational behavior of two model cyclic solutes, cis-decalin (cis-dec) and tetrahydrofuran (THF), dissolved in weakly ordering, polypeptide chiral liquid crystals (CLCs) are theoretically discussed and experimentally investigated using deuterium and carbon-13 NMR spectroscopy. The analysis of enantiomeric and enantiotropic discriminations in these compounds is shown to depend on the rate of conformational exchange regime, slow or fast. The slow exchange regime is illustrated through the case of cis-dec at low temperature (243 K). We show that the deuterium NMR spectra in this regime can be qualitatively and quantitatively interpreted by restricting the conformational pathway of cis-dec to two enantiomeric conformers of C2 symmetry. The orientational order parameters of these two interconverting enantiomers are calculated by matching the 1H quadrupole splittings with calculated conformer structures.

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72.
(A.R.)

Analysis of the Enantiotopic Discrimination in the NMR Spectra of Prochiral Solutes Dissolved in Chiral Liquid Crystals
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The enantiotopic discrimination in the NMR spectrum of prochiral molecules dissolved in chiral liquid crystals (CLCs) is governed by the ordering of the solute molecules. The lifting of the spectral degeneracy of enantiotopic sites in such solvents stems from the nonequivalence in their effective ordering. This, in turn, is brought about by a change in the directions (or the equivalence) of the principal axes of their ordering tensor, relative to those in achiral liquid crystals. This discrimination mechanism can only occur for solute molecules belonging to a limited number of (“allowed”) improper point groups, viz., D∞h, C∞h, C∞v, and S∞[D. Merlet, J. W. Emsley, P. Lesot, and J. Courtoy, J. Chem. Phys., **III**, 6890 (1999)]. In this work it is shown that the ordering tensor of such prochiral solutes in CLC, SCLC, and likewise, the tensors, T, describing the anisotropic magnetic resonance interactions of enantiotopic pairs, can be partitioned into symmetric and antisymmetric (and irrelevant) parts. The NMR results in such solvents can be cast into separate sets of equations depending on either the symmetric or the antisymmetric parts of SCLC and T. The discrimination observed in such solvents depends only on the latter set of equation, while the former applies to the average splitting of enantiotopic pairs as well as to diastereotopic or homotopic sites in the prochiral molecules. The factorization procedure greatly facilitates the analysis of the ordering properties of prochiral solutes in CLC and provides new insight on the discrimination mechanism. In particular, it allows correlation between independent enantiotopic partners and the identification of NMR signals belonging to common prosterogenic faces in the molecule. Expressions relating NMR observables with the symmetric and antisymmetric parts of SCLC are derived for each of the four allowed groups. Model examples are presented and discussed. © 2009 American Institute of Physics.
The conformation and orientational order of a 1,2-disubstituted ethane nematogenic molecule (I22) in liquid crystalline and isotropic phases studied by NMR spectroscopy†

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The structure, conformation and orientational order of the mesogen I22 have been studied by proton, carbon-13 and deuterium 1D and 2D-NMR spectroscopies at natural abundance and at various magnetic fields when in the nematic phase, the isotropic phase close to the nematic-isotropic phase transition, and as a solute in the chiral nematic solution comprised of the polypeptide PBLG dissolved in chloroform. It is concluded that 95% of conformers have a trans arrangement about the central C–C bond of the ethane fragment in all phases.

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