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Molecular Dynamics in the Rod-like Liquid Crystal 4-(*trans*-4-Pentylcyclohexyl)benzotrile (PCH5) Probed by Muon Spin Resonance Spectroscopy

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Abstract

Two types of muoniated spin probes were produced by the addition of muonium (Mu) to the phenyl ring of the rod-like liquid crystal 4-(*trans*-4-pentylcyclohexyl)benzotrile (PCH5). Avoided level crossing muon spin resonance spectroscopy was used to characterize the muoniated spin probes and to probe dynamics of PCH5 at the molecular level. The methylene proton hyperfine coupling constant (hfcc) of one of the muoniated spin probes shift in the nematic phase due to the dipolar hyperfine coupling, the ordering of the molecules along the applied magnetic field and fluctuations about the local director. The amplitude of these fluctuations in PCH5 is determined from the temperature dependence of the methylene proton hfcc.

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1. Introduction

Liquid crystals (LC) are materials that form phases with a degree of order between the disorder of a liquid or isotropic (I) phase and the regular structure of crystalline (Cr) phases [1, 2]. The molecules that make up a LC have anisotropic shapes, such as rods (calamitic LC) or disks (discotic LC). Rod-like molecules can form a wide range of mesophases but the most common is the nematic phase (N), where the molecules' positions are disordered but the long molecular axes on average point along a preferred direction known as the director (\hat{n}). The order in a LC is quantified using the order parameter, S , which is defined by

$$S = \int \frac{1}{2} (3 \cos^2 \theta - 1) f(\theta) d\Omega \quad (1)$$

where θ is the angle between the rotation axis of a rod-like molecule and the director, and $f(\theta)d\Omega$ is the fraction of molecules in a solid angle $d\Omega$ that are oriented at an angle θ [1].

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4-(*trans*-4-Pentylcyclohexyl)benzonitrile (PCH5) is a rod-like LC with a N–I transition at 327.6 K and a Cr–N transition at 303 K. Its structure is very similar to that of 5CB (4-*n*-pentyl-4'-cyanobiphenyl) except that a phenyl ring has been replaced by a cyclohexane ring. Paramagnetic spin probes can be produced by the reaction of muonium (Mu), a light hydrogen isotope [3], with the phenyl ring of PCH5. In these muoniated radicals the unpaired electron interacts with the muon and with any nuclei in the radical with non-zero spin and the strength of the interaction between the unpaired electron and the nucleus 'X' is the hyperfine coupling constant (hfcc), A_X . The hfccs are the sum of an isotropic component due to the Fermi contact interaction (A_X^{iso}) and an anisotropic component due to dipolar coupling between the electron and nuclear spins (denoted D_X if the hyperfine tensor has axial symmetry). The hfccs of the muoniated radicals provide information on the structure of the radical but also about the local environment, the orientation and molecular dynamics.

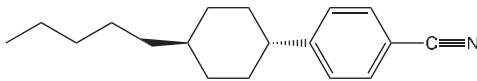


Fig. 1. Structure of 4-(*trans*-4-pentylcyclohexyl)benzonitrile.

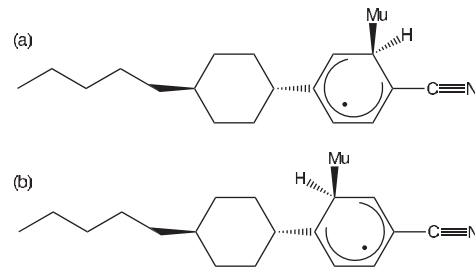


Fig. 2. Structures of the two types of Mu adducts: (a) Mu-2-PCH5 and (b) Mu-3-PCH5.

Muoniated radicals can be characterized by the avoided level crossing muon spin resonance (ALC- μ SR) spectroscopic technique. This technique has been applied to study a range of soft matter systems [4, 5, 6, 7, 8]. The ALC- μ SR technique involves measuring the asymmetry of the muon decay as a function of a magnetic field applied parallel to the initial direction of the muon spin. Resonances occur at specific values of the applied magnetic field due to mixing of nearly degenerate pairs of spin states through the isotropic and anisotropic components of the hyperfine interaction. There are three types of resonances, which are characterized by the selection rule $\Delta M = 0, \pm 1$ and ± 2 , where M is the sum of the m_z quantum numbers of the muon, electron and proton spins. The resonances are referred to as Δ_0 , Δ_1 and Δ_2 resonances, respectively. The Δ_2 resonance is extremely weak and is rarely observed. The Δ_1 resonance field is given by:

$$B_{\text{res}}^{\Delta_1} = \frac{A_\mu}{2\gamma_\mu} - \frac{A_\mu}{2\gamma_e} \quad (2)$$

where A_μ is the muon hfcc, γ_μ is the muon gyromagnetic ratio and γ_e is the electron gyromagnetic ratio [3]. The Δ_1 resonance is considered to be diagnostic of a frozen state, anisotropic motion or slow isotropic reorientation. The shape of the resonance is sensitive to the motion of the radical and depends on the sign and magnitude of D_μ . The Δ_0 resonance is observed for muoniated radicals undergoing both isotropic or anisotropic reorientational motion. The Δ_0 resonance field depends on both the muon hfcc and the proton hfcc, A_p , and is given by:

$$B_{\text{res}}^{\Delta_0} = \frac{1}{2} \left[\frac{A_\mu - A_p}{\gamma_\mu - \gamma_p} - \frac{A_\mu + A_p}{\gamma_e} \right] \quad (3)$$

where γ_p is the proton gyromagnetic ratio [3].

The isotropic and dipolar muon and methylene proton hfccs of cyclohexadienyl radicals are proportional to each other.

$$A_\mu = K \cdot A_p \quad (4)$$

The main contribution to K is the γ_μ/γ_p ratio, which has a value of 3.183, and the rest results from the mass

dependence of the molecule's vibrational modes. K was chosen to be 4.123, which is the value determined for the $C_6H_6\mu$ radical [9]. This approximation makes it possible to determine A_μ and A_p solely from $B_{res}^{\Delta_0}$.

2. Experimental

PCH5 was purchased from Sigma Aldrich. Oxygen was removed by melting the samples in a nitrogen atmosphere and bubbling with nitrogen gas for approximately two hours. It is necessary to remove O_2 from the samples because the Heisenberg spin-exchange reaction can broaden the resonances in the ALC- μ SR spectra [10]. The degassed samples were sealed in aluminum cells with an internal volume of 3 mL and 20 μ m titanium foil windows. The ALC- μ SR experiments were performed using the ALC spectrometer at the π E3 beam line of the Paul Scherrer Institute in Villigen, Switzerland.

The sample was melted and the ALC- μ SR spectra were obtained at several temperatures as the sample was slowly cooled. No changes were observed in the ALC- μ SR spectra as a function of time at a given temperature, so we conclude that the sample was at thermal equilibrium when the measurements were made. All the ALC- μ SR spectra of PCH5 were measured between 1.6 and 2.1 T with a step size of 2 mT, except at several temperatures in the I phase (330.6, 334.5, 339.4, 344.3 and 349.1 K) where the ALC- μ SR spectra were obtained from 1.8 to 2.1 T with a step size of 2 mT. The magnetic field was always greater than 1.6 T in order to produce an oriented mono-domain with the \hat{n} aligned along the magnetic field. Each resonance was fit with a single Lorentzian function and a 5th order polynomial was used to model the background. The fitting was performed with the MINUIT function minimization library in the ROOT package from CERN [11].

All ab initio calculations were performed using the Gaussian 03 package [12]. The DFT calculations were performed on 4-methylbenzotrile (MBN), a model for the phenyl ring moiety of PCH5, in order to save computational resources. The geometries of the μ adducts of MBN were optimized with the unrestricted B3LYP density functional and the 6-311G(d,p) basis set and the hfccs were calculated using the unrestricted PBE0 functional and the EPR-II basis set. These theoretical methods have been demonstrated to give hfccs close to the experimental values [13]. μ is almost chemically identical to H but its lower mass means that the vibrationally averaged C- μ bond is approximately 4.9 % longer than the corresponding C-H bond and the methylene C-H bond is reduced by approximately 0.3 % [14]. The hfccs were calculated for a structure with these bonds altered by the appropriate amount from their optimized value. The muon hfccs were calculated by including a factor of 3.183 to account for the larger gyromagnetic ratio of the muon.

3. Results and Discussion

Representative ALC- μ SR spectra of PCH5 are shown in Fig. 3. There are two intense and narrow resonances in both the N and I phases at \sim 1.95 and 2.03 T and an additional broad resonance at \sim 1.81 T in the N phase. The narrow resonances that are present in both the N and I phases are the methylene proton Δ_0 resonances of the radicals shown in Fig. 2. A_p was calculated using Eq. 3 and Eq. 4 and it decreases linearly with increasing temperature in the I phase due to the vibrational motion of the CH μ group. The broad resonance is the superposition of the two Δ_1 resonances and they appear below the N-I phase transition indicating anisotropic reorientational motion. DFT calculations on the model compound MBN (Table 1) suggest that the lower field Δ_0 resonance is due to the Mu-3-PCH5 radical and the higher field Δ_0 resonance is due to the Mu-2-PCH5 radical.

Table 1. Calculated muon and methylene proton hyperfine coupling constants for the μ adducts of MBN (UPBE0/EPR-II/UB3LYP/6-311G(d,p)).

	A_μ / MHz	A_p / MHz
Mu-2-MBN	531.2	130.7
Mu-3-MBN	525.6	129.4

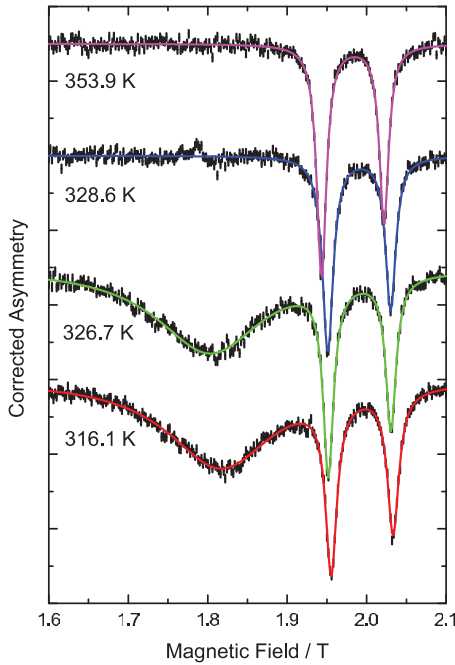


Fig. 3. ALC- μ SR spectra of PCH5 in the N and I phases.

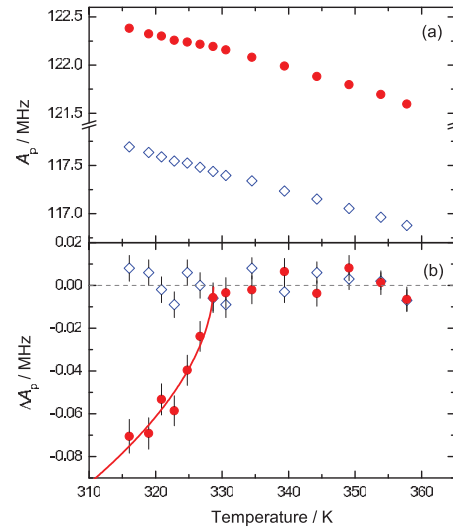


Fig. 4. (a) Temperature dependence of the methylene proton hfccs and (b) shifts of the methylene proton hfccs of the Mu adduct of PCH5 in the N and I phases.

A_p of Mu-2-PCH5 shifts from the isotropic value at T_{N-I} . This shift arises from the ordering of the molecules along the applied magnetic field and fluctuations of the molecules about the local \hat{n} . The Mu adducts of PCH5 have axially symmetric muon and methylene proton hyperfine tensors due to rapid rotation around the “long” molecular axis; one component (D_X^{\parallel}) is parallel to the axis of rotation and two components are perpendicular (D_X^{\perp}). The dipolar tensor is by definition traceless so

$$D_X^{\parallel} = -2D_X^{\perp} \quad (5)$$

The values of A_μ and A_p depend on the angle between the rotation axis of the molecule and the applied magnetic field, θ :

$$A_X = A_X^{\text{iso}} + \frac{1}{2}D_X^{\parallel} (3 \cos^2 \theta - 1) \quad (6)$$

We define the hfcc shift, ΔA_X , to be the difference between the orientationally averaged hfcc, $\langle A_X \rangle$, and A_X^{iso} , which is obtained by extrapolation from the I phase. In the case of a macroscopically aligned liquid crystal with \hat{n} oriented along the magnetic field ΔA_X is given by

$$\Delta A_X = \langle A_X \rangle - A_X^{\text{iso}} = \langle D_X^{\parallel} \rangle S \quad (7)$$

where $\langle D_X^{\parallel} \rangle$ is the motionally-averaged muon dipolar hfcc. S has been calculated from the dielectric anisotropy reported by Schad et al. [15]. $\langle D_p^{\parallel} \rangle$ has been calculated using Eq. 7 and decreases with increasing temperature in the N phase due to the fluctuations of the radical about its average orientation and goes to zero at T_{N-I} . We have assumed a simple “wobbling in a cone” model where there is equal probability for $0 < \phi < \phi_c$ and $\pi - \phi_c < \phi < \pi$ and zero probability for $\phi_c < \phi < \pi - \phi_c$ (ϕ is the angle between the instantaneous long axis of the radical and the cone axis). Israelachvili et al. have derived expressions for the hyperfine parameters of a spin probe rotating rapidly about the long molecular axes and simultaneously wobbling within a cone [16]. It can be shown that this motion leads to

$$\langle D_X^{\parallel} \rangle = D_X^{\parallel} \left(\frac{\cos \phi_c + \cos^2 \phi_c}{2} \right) \quad (8)$$

The value of D_p^{\parallel} , i.e. for pure uniaxial rotation, can be estimated by extrapolating to T_{Cr-N} and this has a value of -0.17 MHz. It is the estimation of D_p^{\parallel} that introduces the largest systematic error in determining the amplitude of the fluctuations. The behavior of PCH5 is similar to that of 5CB in that $\langle D_p^{\parallel} \rangle$ goes to zero at T_{N-I} . This indicates the molecules are undergoing large amplitude fluctuations as they approach the phase transition. $\langle D_p^{\parallel} \rangle$ is used to calculate ϕ_c from equation 8 and hence $\langle \phi^2 \rangle$, the mean-squared fluctuation amplitude.

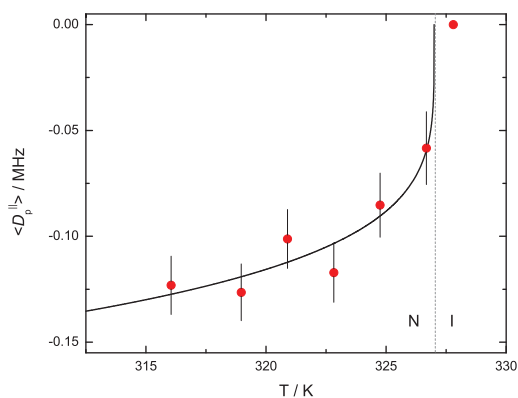


Fig. 5. Temperature dependence of the orientationally-averaged dipolar proton hfcc. The solid line is a guide for the eyes.

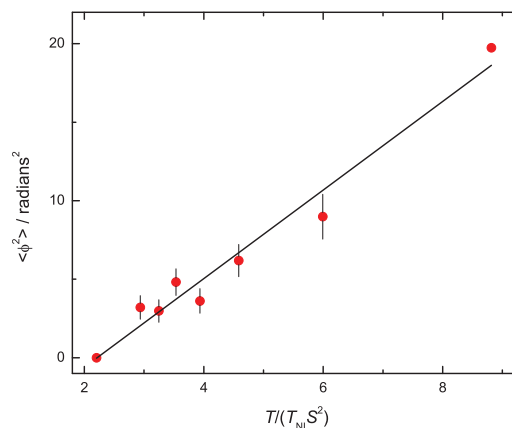


Fig. 6. Dependence of the mean-squared fluctuation amplitude on reduced temperature and the order parameter.

De Gennes and Prost estimated that for a rod-like molecule $\langle \phi^2 \rangle$ is given by

$$\langle \phi^2 \rangle \approx \frac{k_B T q_c}{\pi^2 K} \quad (9)$$

where k_B is the Boltzmann constant, T is the temperature, q_c is an upper cutoff wave vector and K is the average Frank elasticity constant [1]. K depends strongly on temperature and de Gennes and Prost noted that $K \sim S^2$ [1]. We find that $\langle \phi^2 \rangle$ increases approximately linearly with T/S^2 , which is unlike other LC such as MBBA or cholesteryl nonanoate, where $\langle \phi^2 \rangle$ increases approximately linearly with T [17]. The linear dependence of $\langle \phi^2 \rangle$ with T/S^2 for PCH5 suggests that the wobbling-in-a-cone model is an appropriate description of the molecular motion. We have no explanation for why the hfccs of Mu-3-PCH5 do not shift in the mesophase.

4. Conclusions

ALC- μ SR spectroscopy has been used to probe the dynamics of muoniated spin probes in the rod-like LC PCH5. The methylene proton hfcc of one of the Mu adducts of the phenyl ring of PCH5 shifts in the nematic phase and the amplitude of the fluctuation about its average position has been determined from this shift.

References

- [1] P. G. de Gennes, J. Prost, The Physics of Liquid Crystals, 2nd Edition, Oxford University Press, 1993.
- [2] P. J. Collings, M. Hird, Introduction to Liquid Crystals: Chemistry and Physics, Taylor and Francis Ltd., 1997.
- [3] I. McKenzie, E. Roduner, Naturwissenschaften 96 (2009) 873–887.
- [4] B. W. Lovett, S. J. Blundell, J. S. Stieberger, F. L. Pratt, T. Jestädt, W. Hayes, I. D. Reid, Phys. Rev. B 63 (2001) 054204.
- [5] R. Scheuermann, I. M. Tucker, A. M. Creeth, H. Dilger, B. Beck, E. Roduner, Phys. Chem. Chem. Phys. 4 (2002) 1510–1512.
- [6] R. Scheuermann, I. M. Tucker, H. Dilger, E. J. Staples, G. Ford, S. B. Fraser, B. Beck, E. Roduner, Langmuir 20 (2004) 2652–2659.

- [7] A. Martyniak, H. Dilger, R. Scheuermann, I. M. Tucker, I. McKenzie, D. Vujosevic, E. Roduner, *Phys. Chem. Chem. Phys.* 8 (2006) 4723–4740.
- [8] I. McKenzie, H. Dilger, A. Stoykov, R. Scheuermann, *J. Phys. Chem. B* 113 (2009) 10135–10142.
- [9] D. Yu, P. W. Percival, J.-C. Brodovitch, S.-K. Leung, R. F. Kiefl, K. Venkateswaran, S. F. J. Cox, *Chem. Phys.* 142 (1990) 229–236.
- [10] H. Dilger, A. Martyniak, R. Scheuermann, D. Vujosevic, I. M. Tucker, I. McKenzie, E. Roduner, *Physica B* 374–375 (2006) 317–320.
- [11] <http://root.cern.ch>[online, cited 12/01/2011].
- [12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision B.05.
- [13] R. Improta, V. Barone, *Chem. Rev.* 104 (2004) 1231–1253.
- [14] E. Roduner, *The Positive Muon as a Probe in Free Radical Chemistry - Potential and Limitations of the μ SR Techniques* (Lecture Notes in Chemistry), Vol. 49, Springer, Berlin, 1988.
- [15] H. Schad, G. Baur, G. Meier, *J. Chem. Phys.* 71 (1979) 3174–3181.
- [16] J. Israelachvili, J. Sjösten, L. E. G. Eriksson, M. Ehrström, A. Gräslund, A. Ehrenberg, *Biochimica et Biophysica Acta* 382 (1975) 125–141.
- [17] I. McKenzie, R. Scheuermann, K. Sedlak, A. Stoykov, *J. Phys. Chem. B* 115 (2011) 9360–9368.