Muon spin spectroscopy of the rod-like liquid crystal 4-\(n\)-octyl-4′-cyanobiphenyl (8CB)

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Abstract. Avoided level crossing muon spin resonance (ALC-μSR) spectroscopy has been used to study the four cyclohexadienyl-type radicals produced by the addition of muonium (Mu) to the rod-like liquid crystal 4-\(n\)-octyl-4′-cyanobiphenyl (8CB). ALC-μSR spectra have been obtained over a wide temperature range in the isotropic (I), nematic (N), smectic-A (Sm-A) and crystalline (Cr) phases. The ALC-μSR spectra of the Mu adducts of 8CB are very similar to those of the Mu adducts of 4-\(n\)-pentyl-4′-cyanobiphenyl (5CB). Four \(\Delta_0\) resonances were observed in the ALC-μSR spectra in the I, N and super-cooled Sm-A phases, from which the methylene proton hyperfine coupling constants (hfcs) of the Mu adducts of 8CB were determined as a function of temperature. The methylene proton hfcs of two of the radicals have unusual temperature dependence in the N and Sm-A phases and have smaller values than would be predicted from extrapolating the data in the isotropic phase. The shift of the hfcs is due to the dipolar hyperfine coupling, the ordering of the molecules along the applied magnetic field and the fluctuations of the molecules about the director. \(\Delta_1\) resonances appear just below the Cr–Sm-A phase transition, which indicates that this transition is associated with cessation of rotation around the long molecular axes.

1. Introduction

A liquid crystal (LC) is a material that exhibits phases in a temperature region between the solid or crystalline (Cr) phase and the liquid or isotropic (I) phase that possess some properties of both liquids and solids [1-2]. The mesophases can flow like a liquid but have anisotropic optical and electromagnetic characteristics. LCs are characterized by the shape of the molecules with calamitic LC made up of long, rod-like molecules. Calamitic LC can form a large number of mesophases with the most common being the nematic (N) phase. In the N phase the material gains an amount of orientational order but no positional order. This reordering is thought to be due to the packing constraints of the rod-like molecules. The molecules in the N phase order along a preferred direction known as the director (\(n\)). Below the N phase the LC can form smectic phases where the molecules, although still forming a fluid, prefer to lie on average in layers, with each layer being essentially a 2-D nematic LC. In the smectic-A (Sm-A) phase the director of each layer is parallel to the layer normal.
The physical and chemical properties of the rod-like cyanobiphenyl (nCB) LC have been extensively studied, partly because several members of this family can exhibit mesophases near room temperature and have potential commercial applications. 4-\textit{n}-octyl-4′-cyanobiphenyl (8CB) is the first member of this series to exhibit both N and Sm-A phases. The phase transition temperatures depend on the heating or cooling rate (\(T_{NI} = 312.2\ \text{K},\ T_{Sm-A-N} = 305.3\ \text{K}\) and \(T_{CrSm-A} = 267.0\ \text{K}\) with a cooling rate of 10 K min\(^{-1}\) [3]).

It is a longstanding goal to better understand the behaviour of the molecules within the LC. Many of the common techniques for characterizing LCs, such as polarizing optical microscopy, only provide information about the bulk properties. Magnetic resonance techniques such as nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) has been used to provide information about the dynamics and ordering of the 8CB molecules at the molecular level. Both NMR and EPR have studied small probe molecules, such as substituted benzenes, alkanes or stable nitroxide radicals like tempo, that become orientationally ordered due to the anisotropic environment in 8CB [4-14]. NMR has also been used to study molecular dynamics of pure 8CB [15,16].

Spin labelling involves attaching a paramagnetic group to a molecule in order to probe the molecular dynamics and local environment. Spin labels can be introduced into LC with unsaturated bonds by the addition of muonium (Mu), a light isotope of hydrogen [17]. The result is a radical, known as a muoniated radical, in which a proton has been replaced with a positive muon. Muons are sensitive probes because they are produced with spin polarisation close to 100%, the parity-violating decay of the muon provides a convenient way to monitor the evolution of their spin, and its lifetime (2.2 \(\mu\text{s}\)) is comparable to the lifetimes of many organic radicals. There are a series of experimental techniques collectively known as muon spin rotation, resonance and relaxation or \(\mu\)SR that are powerful tools for studying the structure and dynamics of muoniated radicals in soft matter, solids, liquids, and gases [18]. Avoided level crossing muon spin resonance (ALC-\(\mu\)SR) has been used extensively to study soft matter systems, particularly the partitioning of cosurfactants in lamellar phase dispersions [19-21].

The ALC-\(\mu\)SR technique involves measuring the asymmetry of the muon decay, which is proportional to the muon polarization, as a function of a magnetic field applied parallel to the initial direction of the muon spin. In high magnetic fields, the eigenstates of the radical can be approximated by pure Zeeman states, so there is no evolution of the muon’s spin with time, and the asymmetry is independent of the magnetic field. At specific values of the applied magnetic field, nearly degenerate pairs of spin states can be mixed through the isotropic and anisotropic components of the hyperfine interaction. The muon polarization oscillates between the two mixing states, and this leads to a loss of time-integrated asymmetry. There are three types of ALC resonances, which are referred to as \(\Delta_0\), \(\Delta_1\) and \(\Delta_2\). The subscript refers to the difference in the total spin number between the two mixing states. The \(\Delta_2\) resonance is extremely weak and narrow and rarely observed.

The \(\Delta_1\) resonance field is given by

\[
B_{\text{res}}^{\Delta_1} = \frac{A_\mu}{2\gamma_\mu} - \frac{A_\mu}{2\gamma_e} \tag{1}
\]

where \(A_\mu\) is the muon hfc, \(\gamma_\mu\) is the muon gyromagnetic ratio, and \(\gamma_e\) is the electron ratio. The \(\Delta_1\) resonance arises from mixing between spin states with the same electron and proton spins but different muon spin directions. These spin states are mixed only in the presence of anisotropy, so the \(\Delta_1\) resonance can be considered to be diagnostic of a frozen state or anisotropic motion.

The \(\Delta_0\) resonance is due to mixing between spin states that have the same electron spin but opposite muon and proton spins and is observed for muoniated radicals in the solid, liquid, or gas phases. The \(\Delta_0\) resonance field depends on both the muon hfc and the proton hfc, \(A_p\), and is given by

\[
B_{\text{res}}^{\Delta_0} = \frac{1}{2} \left[ \frac{A_\mu - A_p}{\gamma_\mu - \gamma_p} - \frac{A_\mu + A_p}{\gamma_e} \right] \tag{2}
\]
where $\gamma$ is the proton gyromagnetic ratio.

The muon and methylene proton hfcs of muoniated cyclohexadienyl-type are approximately proportional to each other.

$$A_\mu = K \cdot A_p$$ (3)

The main contribution to $K$ is the $\gamma_\mu/\gamma_p$ ratio, which is 3.183, and the rest results from the mass dependence of the molecule’s vibrational modes. $K$ was found to be 4.123 for the cyclohexadienyl radical in benzene at 298 K [22]. This approximation allows to determine $A_p$ from the $\Delta_0$ resonance field by combining equations (2) and (3) to give

$$B_{\text{res}}^{\Delta_0} = \Theta \cdot A_p$$ (4)

where $\Theta = 1.67 \times 10^{-2}$ T MHz$^{-1}$ around room temperature.

The only LC to have been studied by $\mu$SR is 4-\text{n-}pentyl-4$'$-cyanobiphenyl (5CB) [23-25]. Four types of substituted cyclohexadienyl radical were formed by Mu addition to the biphenyl moiety of 5CB, and their proton hfcs were measured using ALC-$\mu$SR. The proton hfcs of two of the muoniated isomers shift from their isotropic value in the N phase and this was demonstrated to result from the ordering of the molecules, alignment of the molecules with the magnetic field and fluctuations of the molecules about the director. 8CB is the first LC to be studied by $\mu$SR that exhibits a Sm-$A$ phase.

2. Experimental

8CB was purchased from Sigma-Aldrich and was used without further purification. Oxygen was removed by melting the sample in a nitrogen atmosphere and bubbling with nitrogen gas for approximately two hours. The degassed samples were sealed in brass cells with an internal volume of 17 ml and 50 $\mu$m brass foil windows.

The ALC-$\mu$SR experiments were performed using the ALC spectrometer at the $\pi$E3 beamline of the Paul Scherrer Institute in Villigen, Switzerland. The sample was initially melted, and the ALC-$\mu$SR spectra were obtained at several temperatures as the sample was slowly cooled (~0.2 K min$^{-1}$). The magnetic field was always greater than 1.4 T while the sample was cooling in order to produce an oriented monodomain with the director aligned along the magnetic field [1,16]. The samples were left for 15-30 min to equilibrate at a given temperature before measurements were made, and several scans were performed at each temperature (each taking at least 45 min) to obtain a sufficient signal-to-noise ratio. No changes were observed in the ALC-$\mu$SR spectra as a function of time at a given temperature, so we conclude that the sample was at thermal equilibrium at all times when the measurements were made. The ALC-$\mu$SR spectra of 8CB in the I, N and Sm-$A$ phases were obtained between 1.65 and 2.15 T with a step size of 1 mT, while the ALC-$\mu$SR spectra in the Cr phase were obtained between 1.2 and 2.2 T with a step size of 2 mT.

ALC-$\mu$SR spectra have a large field-dependent background that is very sensitive to the stopping position of the muons. Each resonance was fit with a single Lorentzian function, and a fifth-order polynomial was used to model the background. The fitting was performed with the MINUIT function minimization library in the ROOT package from CERN [26]. All of the ALC-$\mu$SR spectra in the I, N and Sm-$A$ phases were fit between 1.7 and 2.1 T. The corrected asymmetry is the asymmetry after the subtraction of the background.

3. Results and Discussion

3.1. ALC-$\mu$SR spectra of the isotropic, nematic and smectic $A$ phases

Representative ALC-$\mu$SR spectra of the Mu adducts of 8CB in the Sm-$A$, N and I phases are shown in figure 1. Four resonances were observed between 1.8 and 2.0 T, which are the methylene proton $\Delta_0$ resonances of the radicals shown in figure 2. They are known to be $\Delta_0$ resonances as they are present in the I phase and assignment is based on a comparison of the experimental hfcs with the DFT
calculated hfcs reported for the Mu adducts of 4-\textit{n}-methyl-4'\textquoteleft-cyanobiphenyl (1CB) [25]. Such a comparison is valid because the hfcs should be independent of the length of the alkyl chain.

No \(\Delta_1\) resonances were observed at any temperature in the Sm-A, N and I phases, which indicates that all of the radicals have very small dipolar hfcs. The small dipolar hfcs arise from the rapid rotation of the molecules about the long axis. The rapid rotation results in the hyperfine tensor having axial symmetry with one component parallel to the rotation axis \(D_\parallel\) and two components perpendicular to the rotation axis \(D_\perp\), with \(D_\parallel = -2D_\perp\). The angle between the principal components of the hyperfine tensor and the axis of rotation results in a very small \(D_\parallel\).

3.2. Temperature dependence of the proton hyperfine coupling constants in the isotropic, nematic and smectic-A phases

The four \(\Delta_0\) resonances broadened and shifted to higher fields as the temperature was lowered. The methylene proton hfcs of the four Mu adducts of 8CB are shown as a function of temperature in figure 3, and these increased linearly with decreasing temperature in the I phase, although \(dA_p/dT\) in Mu-2-8CB \((-7.8\pm0.9) \times 10^{-3}\text{ MHz K}^{-1}\) and Mu-3-8CB \((-3.9\pm0.7) \times 10^{-3}\text{ MHz K}^{-1}\) is less than that of Mu-1-8CB \((-2.06\pm0.14)\times 10^{-2}\text{ MHz K}^{-1}\) and Mu-4-8CB \((-1.40\pm0.09)\times 10^{-2}\text{ MHz K}^{-1}\). The \(dA_p/dT\) values for the Mu adducts of 8CB are similar to the values of the corresponding values of the Mu adducts of 5CB [25]. The muon and methylene proton hfcs of cyclohexadienyl-type radicals are known to increase linearly with decreasing temperature due to the vibrational motion of the CHMu group [22]. The methylene proton hfcs of Mu-1-8CB and Mu-4-8CB increased approximately linearly with decreasing temperature in the N and Sm-A phases, while the methylene proton hfcs of Mu-2-8CB and Mu-3-8CB deviate from linearity below \(T_{NI}\) and are lower in the N and Sm-A phases than one would predict based on an extrapolation of the values measured in the I phase. The shift of the hfcs,
ΔA_p, is defined to be the difference between the measured hfc and the extrapolated isotropic hfc. The temperature dependence of ΔA_p is shown in figure 4. The shift of A_p is given empirically by

$$\Delta A_p = C(T_{NI} - T)^\beta$$

(5)

The critical exponent, β, has values of 0.22±0.07 for Mu-2-8CB and 0.22±0.03 for Mu-3-8CB while the N—I phase transition temperature was determined to be 313.5±1.5 K from Mu-2-8CB and 310.2±0.9 K from Mu-3-8CB. No shift of the proton hfc was observed in Mu-1-8CB or Mu-4-8CB because the dipolar hfcs in these molecules are further averaged by torsional motion of the biphenyl moieties. The torsional barriers of Mu-1-1CB and Mu-4-1CB were shown to be much lower than those of Mu-2-1CB and Mu-3-1CB [25].

**Figure 3.** Temperature dependence of the methylene proton hyperfine coupling constants of the Mu adducts of 8CB: Mu-1-8CB (△), Mu-2-8CB (●), Mu-3-8CB (□), and Mu-4-8CB (▼). The dotted vertical lines show the I—N, N—Sm-A and Sm-A—Cr phase transitions. The solid lines are the fits in the nematic and smectic-A phases.

**Figure 4.** Temperature dependence of the hyperfine coupling constant shift, ΔA_p, for two of the Mu adducts of 8CB: Mu-2-8CB (●) and Mu-3-8CB (□). The dotted vertical lines show the I—N, N—Sm-A and Sm-A—Cr phase transitions. The solid lines are the best fits to the data using equation (5).

The hfcs of Mu-2-8CB and Mu-3-8CB shift from their isotropic values because of the ordering of the molecules, the alignment of the molecules with the magnetic field and the dipolar hyperfine interaction. We have assumed that the angular distribution of 8CB molecules in the N and Sm-A phases can be obtained using the Maier-Saupe (MS) theory. The normalized distribution of molecules as a function of angle, f(θ), according to the MS theory is given by [1]

$$f(\theta) = \frac{\exp(m \cdot \cos^2 \theta)}{4\pi Z}$$

(6)

where the normalization constant, Z, is given by...
\[ Z = \int_0^1 \exp\left(mx^2\right) dx \] (7)

The angular distribution depends on the order parameter (S), the interaction energy between molecules (U), the Boltzmann constant (kB) and the temperature (T) since [1]

\[ m = \frac{3U \cdot S}{2kB^2} \] (8)

It has been previously demonstrated that for radicals with a small axially symmetric dipolar coupling aligned along the rotation axis and an angular distribution given by the MS theory the shift of the proton hfc is given by [25]

\[ \Delta A_p = D_{p||} \left[ 1 - \frac{k_BT}{2U \cdot S} \right] \] (9)

The proton hfc of Mu-2-8CB and Mu-3-8CB in the N and Sm-A phases are lower than expected based on the isotropic values because \( k_BT/(2U \cdot S) > 1 \) in this temperature region. This can be demonstrated just below \( T_{NI} \), where according to the MS model the order parameter is 0.44 and \( k_BT_{NI}/U(T_{NI}) = 4.55 \) [1]. The shift approaches \( D_{p||} \) as the temperature goes to zero, which is the expected value for static molecules that are aligned along the magnetic field. The temperature dependence of \( \Delta A_p \) indicates that \( D_{p||} \) is also temperature dependent and goes to zero near the phase transition. \( D_{p||} \) can be calculated from \( \Delta A_p \) assuming that the order parameter is known. The temperature dependence of \( S(T) \) for cyanobiphenyl LC can be approximated to within one percent with the following expression.

\[ S(T) = 0.1 + 0.9 \left[ 1 - 0.99(T/T_{NI}) \right]^{0.25} \] (10)

The decrease of \( D_{p||} \) as the temperature is lowered is due to the fluctuations of the radicals about the local director and the fluctuations of the director decreasing in amplitude. This is responsible for the broadening of the \( \Delta_0 \) resonances with decreasing temperature. The rate of change of \( D_{p||} \) appears to be greater in the N phase than in the Sm-A phase. The dipolar coupling constant of Mu-2-8CB is consistently larger than that of Mu-3-8CB and this is in agreement with the calculated \( D_{p||} \) values for the molecules only undergoing fast uniaxial rotation [25].

Figure 5. Temperature dependence of the dipolar hyperfine coupling constants (\( D_{p||} \)) of two of the Mu adducts of 8CB in the nematic phase: Mu-2-8CB (●) and Mu-3-8CB (□). The solid lines are a guide for the eyes.
3.3. ALC-μSR spectra of the crystalline phase

There was a large change in the ALC-μSR spectra when the sample was cooled below 279.2 K. This was determined to be the phase transition temperature based on the observation of a temperature spike due to the release of latent heat. This was not observed in 5CB because the crystallization enthalpy of 5CB (-3.77 kJ mol⁻¹) is much smaller than that of 8CB (-24.33 kJ mol⁻¹) [27]. The ALC-μSR spectra of the Cr phase of 8CB are very different from that of 5CB, although both contain large and broad overlapping resonances. The assignment of the resonances is based on the theoretical calculations on 1CB [25]. The resonance at 1.67 T is due to overlapping Δ₁ resonances of Mu-2-8CB and Mu-3-8CB. The resonance at 1.82 T is due to overlapping Δ₀ resonances of Mu-2-8CB and Mu-3-8CB and Δ₁ resonances of Mu-1-8CB and Mu-4-8CB. The resonance at 2.01 T is due to overlapping Δ₀ resonances of Mu-1-8CB and Mu-4-8CB. The appearance of Δ₁ resonances indicates that the magnitude of the dipolar hfcs has increased considerably, which suggests that the molecules are no longer rotating rapidly about their long axis. The large amplitude of the resonances in the Cr phase compared with those in the higher temperature phases is consistent with the larger dipolar hfcs in the Cr phase.

Figure 6. ALC-μSR spectrum of the Mu adducts of 8CB in the smectic-A phase (● – 282 K) and the crystalline phase (○ – 277 K). The solid lines represent the best fit to the data.

4. Conclusions

Four types of substituted muoniated cyclohexadienyl radical were formed by the addition of muonium to the calamitic LC 8CB. The methylene proton hfcs were measured by ALC-μSR over a wide temperature range that encompassed the I, N, Sm-A and Cr phases. The proton hfcs of two muoniated radical isomers shift from the isotropic values in the N and Sm-A phases due to the alignment of the molecules along the magnetic field, the ordering of the molecules and fluctuations of the molecules about the director. The dipolar hyperfine coupling constant is approximately zero at the N–I phase transition due to large amplitude fluctuations of the radicals about the director. The dipolar coupling increase as the temperature is lowered due to this vibrational motion decreasing in amplitude. The rate of decrease in the amplitude of the fluctuations about the director is larger in the N phase than in the Sm-A phase. The appearance of Δ₁ resonance below the Cr–Sm-A phase transition indicates that the molecules no longer rotate rapidly around the long axis in the Cr phase.
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6. References

[1] de Gennes P G and Prost J 1993 The Physics of Liquid Crystals (Oxford: Oxford University Press)
[2] Collings P J and Hird M 1997 Introduction to Liquid Crystals: Chemistry and Physics (London: Taylor and Francis Ltd.)
[3] Sharma D, MacDonald J C and Iannachione G S 2006 J. Phys. Chem. B 110 16679
[4] Yethiraj A, Sun Z, Dong R Y and Burnell E E 2004 Chem. Phys. Lett. 398 517
[5] Yethiraj A, Weber A C J, Dong R Y and Burnell E E 2007 J. Phys. Chem. B 111 1632
[6] Polnaszek C F and Freed J H 1975 J. Phys. Chem. 79 2283
[7] Brooks S A, Luckhurst G R, Pedulli G F and Roberts J 1976 J. Chem. Soc., Faraday Trans. 2 72 651
[8] Rao K V S, Polnaszek C F and Freed J H 1977 J. Phys. Chem. 81 449
[9] Lin W J and Freed J H 1979 J. Phys. Chem. 83 379
[10] Meirovitch E, Igner D, Igner E, Moro G and Freed J H 1982 J. Chem. Phys. 77 3915
[11] Nayeem A and Freed J H 1989 J. Phys. Chem. 93 6539
[12] Morsy M A, Hwang J S and Oweimreen G A 1997 J. Phys. Chem. B 101 2120
[13] Morsy M A, Oweimreen G A and Al-Tawfiq A M 1998 J. Phys. Chem. B 102 3684
[14] Oweimreen G A and Hwang J S 2001 Chem. Phys. Lett. 334 83
[15] Magnuson M L and Fung B M 1994 J. Chem. Phys. 100 1470
[16] Emsley J W, Long J E, Luckhurst G R, Pedrielli P 1999 Phys. Rev. E 60 1831
[17] Roduner, E. 2005 Muonium - an ultra-light isotope of hydrogen. Isotope Effects in Chemistry and Biology ed A Kohen and H H Limbach (New York: CRC Press) pp 433-450
[18] McKenzie I and Roduner E 2009 Naturwissenschaften 96 873
[19] Scheuermann R, Tucker I M, Creeth A M, Dilger H, Beck B and Roduner E 2002 Phys. Chem. Chem. Phys. 4 1510
[20] Scheuermann R, Tucker I M, Dilger H, Staples E J, Ford G, Fraser S B, Beck B and Roduner E 2004 Langmuir 20 2652
[21] Martyniak A, Dilger H, Scheuermann R, Tucker I M, McKenzie I, Vujosevic D and Roduner E 2006 Phys. Chem. Chem. Phys. 8 4723
[22] Yu D, Percival P W, Brodovitch J C, Leung S K, Kief R F, Venkateswaran K, Cox S F J 1990 Chem. Phys. 142 229
[23] Lovett B W, Stießerberger J S, Blundell S J, Jestädth Th, Ardavan A, Marshall I M, Pratt F L and Reid I D 2000 Physica B 289-290 612
[24] Lovett B W, Blundell S J, Stießerberger J S, Pratt F L, Jestädth Th, Hayes W, Cottrell, S. P and Reid I D 2001 Phys. Rev. B 63 054204
[25] McKenzie I, Dilger H, Stoykov A and Scheuermann R 2009 J. Phys. Chem. B 113 10135
[26] http://root.cern.ch (accessed October 22, 2009)
[27] Oweimreen G A and Morsy M A 2000 Thermochimica Acta 346 37