

Hyperfine Coupling Constants of the Cyclohexadienyl Radical in Benzene and Dilute Aqueous Solution

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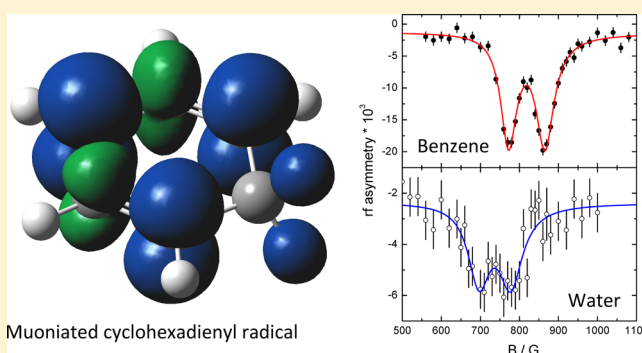
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ABSTRACT: The muon hyperfine coupling constant (A_μ) of the muoniated cyclohexadienyl radical ($C_6H_6\text{Mu}$) has been directly measured in a 5 mM solution of benzene in water by the radio-frequency muon spin resonance (RF- μ SR) technique. The relative shift of A_μ in aqueous solution compared with the value in neat benzene ($\Delta A_\mu/A_\mu = +0.98(5)\%$ at 293 K) can now be compared directly with theoretical predictions. Application of the RF- μ SR method to other dilute systems will provide extremely important information on understanding solvent effects.



INTRODUCTION

Muoniated spin probes have been recently used to study the partitioning of small amphiphiles in lamellar phase systems^{1–4} and a chiral nematic liquid crystal.⁵ Conventional spectroscopic techniques are not sensitive enough to study cosurfactant molecules that are present in low concentrations, whereas labeling the molecules with spin-polarized positive muons and characterizing the resulting radicals with muon spectroscopic techniques provides the necessary sensitivity for such studies. Muoniated spin probes are like conventional radicals except that one proton has been replaced with a spin-polarized muon and they are formed in situ by the reaction of muonium (Mu), a light isotope of hydrogen, with an unsaturated bond or an aromatic π system.^{6–8} Many of these spin probes are related to the muoniated cyclohexadienyl radical, which is formed by the addition of muonium to benzene (Figure 1). Information about the structure, dynamics, and local environment of the muoniated radical can be obtained by measuring the isotropic hyperfine coupling constants (hfccs) to the nuclei with $I > 0$,

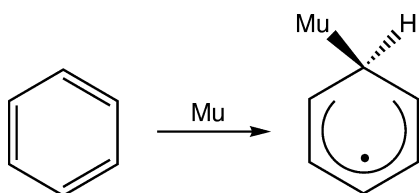


Figure 1. Formation of the muoniated cyclohexadienyl radical by Mu addition to benzene.

which maps out the distribution of the unpaired electron spin density.

The ‘standard’ method to measure muon hfcc of a radical is using the transverse-field muon spin rotation (TF- μ SR) technique, where a transverse magnetic field high enough to resolve the line splitting of the two ENDOR frequencies and to decouple the muon spin from all other surrounding nuclei with spin is applied.^{6,7} This method cannot be used for dilute solutions because the polarization of the Mu precursor dephases prior to the formation of the muoniated radicals. The lower concentration limit for TF- μ SR measurements is ~ 100 mM for a diffusion-controlled Mu addition. (The rate for Mu addition to benzene in aqueous solution is $k_{\text{Mu}} \approx (1.9 \text{ to } 3.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.^{9,10})

TF- μ SR could not be used to study cosurfactants in the lamellar phase systems and chiral nematic liquid crystal described above as the concentrations of cosurfactants are well below 100 mM. These experiments used avoided level crossing muon spin resonance (ALC- μ SR). 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, so there is no problem with dephasing. The asymmetry parameter is defined as $(n_B - n_F)/(n_B + n_F)$, where n_F is the total number of positrons detected in the forward counters and n_B is the total number of positrons detected in the backward counters and is proportional to the

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muon polarization, P_z . The lower concentration limit for ALC- μ SR is ~ 0.1 mM in aromatic systems and maybe one order of magnitude less for alkenes assuming a diffusion-controlled process.¹¹ This limit occurs when the rate of Mu addition to the cosurfactant is comparable to the rate of abstraction reactions with the solvent.

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 mix, which leads to a loss of time-integrated asymmetry. In a nonviscous liquid, only resonances characterized by the selection rule $\Delta M = 0$ are observed, where M is the sum of the m_z quantum numbers of the muon, electron, and proton spins. These are commonly referred to as Δ_0 resonances. The Δ_0 resonance field is given by

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

where A_μ is the muon hfcc, A_p is the proton hfcc, γ_μ is the muon gyromagnetic ratio, γ_p is the proton gyromagnetic ratio, and γ_e is the electron gyromagnetic ratio.^{6,7} The proton hfccs can be determined by measuring the Δ_0 resonance fields, as long as A_μ is known.

In the case of cyclohexadienyl radicals, it was assumed that the muon and methylene proton hfccs are proportional to each other, which means that both hfccs can be calculated from methylene proton Δ_0 resonance field. This approximation is certainly not accurate over a wide temperature range, and it would be useful to be able to measure A_μ directly in the dilute solution.

We report the direct measurement of the muoniated cyclohexadienyl radical ($\text{C}_6\text{H}_6\text{Mu}$) in aqueous solution using the radio-frequency muon spin resonance (RF- μ SR) technique. The main reason to apply this method for studying the $\text{C}_6\text{H}_6\text{Mu}$ radical was because its derivatives were used in the previously mentioned partitioning studies and because this radical and its protonated isotopomer (C_6H_7) are well-characterized both experimentally and theoretically.^{12,13} The solubility limit for benzene in water is 22.8 mM at 298 K, which is well below the minimum required concentration for TF- μ SR studies.¹⁴ Isotopic substitution can have a large effect on the vibrationally-averaged structure of a radical and calculations have shown that the hfccs of the cyclohexadienyl radical depend substantially on the geometry.¹³ The reduced muon hfcc ($A'_\mu = A_\mu \gamma_p / \gamma_\mu$) of $\text{C}_6\text{H}_6\text{Mu}$ is 28% larger than the methylene proton hfcc of $\text{C}_6\text{H}_6\text{Mu}$ and 20% larger than the methylene proton hfcc of C_6H_7 , while the methylene proton hfcc of $\text{C}_6\text{H}_6\text{Mu}$ is reduced by 6% compared with C_6H_7 .¹⁵ Lopes de Magalhães and Ramos used a diatomic Morse potential to calculate average bond lengths of 1.141 Å for C–H and 1.197 Å for C–Mu, an increase of 4.9%.¹⁶ They then reoptimized the structure with one methylene bond length fixed at a value 4.9% longer than for the optimized structure and found that the methylene C–H bond in $\text{C}_6\text{H}_6\text{Mu}$ is reduced by 0.3%. Hudson and Chafetz disagreed with this procedure because they consider this to be treating Mu as if it was a very heavy atom. They calculated the average over the stretching, out-of-plane bend, and in-plane bend degrees of freedom and found both the C–Mu and methylene C–H bonds are increased and that the change in range of the stretching motion has the largest effect on the hfccs.

Vujošević et al. measured the Δ_0 resonance field of the $\text{C}_6\text{H}_6\text{Mu}$ radical in a range of solvents and mixtures and were able to explain the solvent shifts in terms of a dipole–dipole reaction field model.¹⁷ An extension of the model that includes the dipole–quadrupole interaction can account for the larger hfcc in benzene compared with that in octadecane and the variation of the hfccs in mixtures of benzene and cyclohexane.¹⁸ Straka et al. used ab initio calculations with polarizable continuum models (PCMs) and explicit inclusion of water molecules into supermolecular complexes to better understand solvent effects on the hfccs of the $\text{C}_6\text{H}_6\text{Mu}$ radical.¹² Their conclusion was that changes in the muon and methylene proton hfccs are due to solvent-induced structural changes and a direct electronic polarization of the spin density within the radical by the solvent. The hfccs depend on whether the solvent effects are accounted for by the inclusion of PCM or explicit solvent molecules or both, but in general the hfccs are largest in water and smallest in the gas phase, with benzene falling in between.

The RF- μ SR technique is extensively described in several comprehensive articles, so we shall not provide extensive details but refer the reader to these previous publications.^{19–21} The Hamiltonian for the 3-spin $1/2$ system of the muon, electron, and methylene proton with isotropic hyperfine couplings in an externally applied magnetic field B_0 is given by

$$\hat{H} = A_\mu \hat{S}_e \cdot \hat{I}_\mu + A_p \hat{S}_e \cdot \hat{I}_p - \gamma_\mu \vec{B}_0 \cdot \hat{I}_\mu - \gamma_p \vec{B}_0 \cdot \hat{I}_p \quad (2)$$

where \hat{S}_e , \hat{I}_μ , and \hat{I}_p are the spin operators for the electron, muon, and proton, respectively. The Breit–Rabi diagram for a system with hfccs of $A_\mu = 515$ MHz and $A_p = 124$ MHz, typical values for the $\text{C}_6\text{H}_6\text{Mu}$ radical, is shown in Figure 2. A linearly

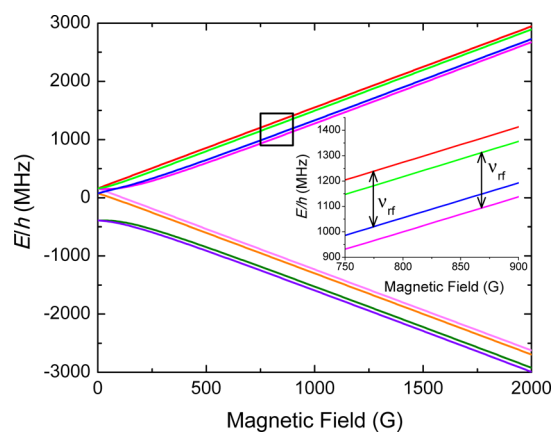


Figure 2. Breit–Rabi diagram for an isotropic electron-muon-proton system with $A_\mu = 515$ MHz and $A_p = 124$ MHz. One set of RF transitions is indicated in the insert, while a second RF transition occurs at ~ 2.1 kG but with a much smaller line splitting. The line positions are dependent on the RF frequency, which was 218.5 MHz in this experiment.

polarized radio frequency field $B_1(t) = B_1 \cos(2\pi\nu_{\text{RF}}t)\vec{x}$ perpendicular to the external field induces transitions between energy levels with opposite muon spin polarization if the frequency matches the energy splitting at the resonance fields. This is seen as a reduction of the time-integrated muon spin asymmetry at a resonance field in the high-field limit given by

$$B_{\text{res}} = \frac{\nu_{\text{RF}} \pm \frac{1}{2}A_{\mu}}{\gamma_{\mu}} \quad (3)$$

where ν_{RF} is the RF frequency. The RF transitions are indicated in the insert of Figure 2. In this simplified picture the center position of these two resonances is determined by the muon hfcc (RF transitions in a hypothetical muonium system neglecting the proton hfcc), and the splitting is determined by the proton hfcc. However, simple perturbation theory fails in an accurate determination of the hfcc values for the relatively low fields used for RF experiments (typically only a few kG for frequencies up to ~ 500 MHz; for a description of the microwave μ SR technique working at high fields and frequencies, see Kreitzman et al.²²). Thus, for the analysis of the experimental results, a numerical treatment of the RF Hamiltonian with $\vec{B} = B_0\vec{z} + \vec{B}_1(t)$ is required.

EXPERIMENTAL SECTION

The RF- μ SR experiments were carried out using the DEVA spectrometer at the ISIS pulsed muon facility. Spectrophotometric-grade benzene was obtained from Sigma Aldrich and used without further purification. The benzene and water were deoxygenated separately by several freeze–pump–thaw cycles, and the 5 mM aqueous solution was prepared under a nitrogen atmosphere in a plastic glovebag. The deoxygenation process is extremely important because residual oxygen would lead to line broadening or even the disappearance of the μ SR signal due to muon spin depolarization by Heisenberg spin exchange.

The RF- μ SR sample cell was made of Shapal ceramic and had a 25 mm \times 25 mm window made of 50 μ m Mylar, which is sufficiently thin to allow surface muons to penetrate into the liquid. The volume of solution exposed to the muon beam was ~ 1.5 mL, and the sample was loaded into the cell in situ via 1/16 in stainless-steel capillaries. To ensure that the sample cell in the cryostat was properly filled, we performed a transverse-field muon spin rotation experiment at 20 G before the actual RF- μ SR measurement. Changes in α , a parameter that corrects for different solid-angle counting efficiencies from the forward and backward detector arrays, served as an indicator for filling the cell. α is a function of the sample thickness and its exact position within the spectrometer. Filling the sample cell with liquid caused α to increase due to the change in the muon stopping distribution within the spectrometer. All measurements were carried out at 293.0 ± 0.1 K with the sample mounted in an exchange gas flow cryostat. The temperature stability is important as the muon and methylene proton hfccs of the $\text{C}_6\text{H}_6\mu$ radical change dramatically with temperature.¹⁵ The concentration of benzene in the solution was checked by UV–vis spectroscopy after recovering the sample from the liquid cell.

The RF coil around the sample cell could only be tuned and matched over a limited frequency range, so a frequency of 218.5 MHz was used for all experiments to bring the resonances within the magnetic field range of the DEVA spectrometer (2 kG).²³ The RF power was set at 60 W, which was chosen to give the optimum balance between resonance amplitude and line width and to prevent breakdown of the RF coil. The RF- μ SR spectra were fit using the Quantum muon spin simulation program developed by Lord.²⁴

RESULTS AND DISCUSSION

The RF- μ SR spectra of the $\text{C}_6\text{H}_6\mu$ radical in benzene and in the aqueous solution are shown in Figure 3. The line widths are

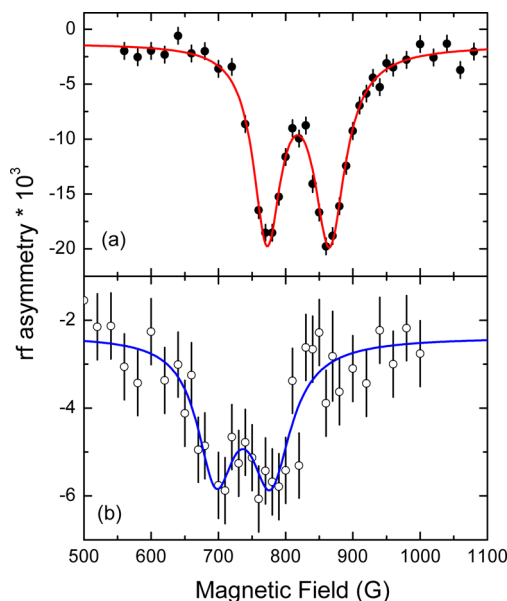


Figure 3. RF- μ SR spectra of $\text{C}_6\text{H}_6\mu$ in (a) liquid benzene and (b) a 5 mM solution of benzene in water. The solid lines represent the results of fits of the full Hamiltonian using the Quantum muon spin simulation program (ref 24).

slightly larger in the aqueous solution, even though both spectra were obtained under the same experimental conditions. In the present version of the analysis software the line width is described phenomenologically by B_1 , whose value was 3 G for water and 1.7 G for bulk benzene. The larger line width in water is most likely due to the viscosity dependence of the spin relaxation rates and the viscosity of water (0.890 cP at 298 K) being larger than that of benzene (0.604 cP at 298 K).²⁵ The amplitudes of the resonances in the aqueous solution are approximately one-third of those measured for benzene, the difference arising from the amount of precursor muonium formed in each liquid. Percival et al. found that 20% of muons in water form μ ,²⁶ whereas it is estimated that 65% of the muons in benzene form μ , prior to their rapid reaction with benzene and the formation of the $\text{C}_6\text{H}_6\mu$ radical.²⁷

The muon and proton hfccs determined for each system by RF- μ SR are listed in Table 1 along with the values determined by TF- μ SR and ALC- μ SR. Measurements not performed at 293 K have been corrected using the temperature dependence of the muon and proton hfccs calculated from the data reported in refs 15 and 17. A_{μ} of the $\text{C}_6\text{H}_6\mu$ radical in aqueous solution is 0.98(5)% larger than that in benzene, which agrees with the ALC- μ SR measurements by Vujošević et al., where A_{μ} was found to be 0.99% larger in the aqueous solution than in benzene. However, values from RF- μ SR measurements could be obtained without requiring any additional assumptions. Straka et al. calculated A_{μ} in water to be 3.39% larger than that in benzene using the CPCM model, which is significantly larger than what we have measured.

The RF- μ SR technique provides accurate measurement of A_{μ} but the error in the fitted value of A_p is very large. It was necessary to include A_p to get accurate values for A_{μ} , but in practice one should use RF- μ SR to only measure A_{μ} and

Table 1. Summary of the Measured Muon and Methylene Proton Hyperfine Coupling Constants of the Muoniated Cyclohexadienyl Radical in Benzene and Dilute Aqueous Benzene Solutions at 293 K

sample	method	A_{μ}/MHz	A_p/MHz	reference
C_6H_6	RF- μSR	514.78(4)	124.6(14)	this work
	TF- μSR + ALC- μSR	514.807(11) ^a	126.133(16) ^a	15
	ALC- μSR	514.29 ^{b,c,d}	126.01 ^{b,c,d}	17
5 mM $\text{C}_6\text{H}_6/\text{H}_2\text{O}$	RF- μSR	519.8(3)	124(7)	this work
20 mM $\text{C}_6\text{H}_6/\text{H}_2\text{O}$	ALC- μSR	519.39 ^{b,c,e}	127.26 ^{b,c,e}	17

^aCalculated from least-squares fit of data reported in ref 15. ^bCalculated assuming a A_{μ}/A_p ratio of 4.0815(5), which was calculated from the fitted values of the hfccs at 293 K using the data in ref 15. ^cNo errors were reported in the resonance field position, so the error in the hyperfine coupling constants has not been calculated. ^dCalculated given $B_{\text{res}}^{\Delta_0} = 20\,716\text{ G}$ at 308 K and $\Delta B_{\text{res}}^{\Delta_0}/\Delta T = -3.60\text{ G K}^{-1}$. ^eCalculated given $B_{\text{res}}^{\Delta_0} = 20\,931\text{ G}$ at 308 K and $\Delta B_{\text{res}}^{\Delta_0}/\Delta T = -3.00\text{ G K}^{-1}$.¹⁷

determine A_p from the ALC- μSR resonance field. These experiments could be improved by performing the measurements in high magnetic fields (i.e., greater than $\sim 2\text{ kG}$), where the splitting due to the methylene proton is negligible. The ISIS Muon Facility has recently replaced the DEVA spectrometer with a spectrometer known as HiFi²⁸ that has a maximum field of 50 kG, and a new RF apparatus has been developed for this spectrometer.

Our measurements show that it is reasonable to calculate the muon and methylene proton hfccs of the position of the methylene proton resonance with the assumption that the A_{μ}/A_p ratio = 4.0815(5), the value determined from the data of Yu et al. ALC- μSR measurements are much less time-consuming than RF- μSR measurements, so the verification that reasonable values can be obtained using ALC- μSR is important. This method for determining hfccs is possibly valid over only a limited temperature range, as Fleming et al. found that the A_{μ}/A_p ratio decreases from 4.063 at 313 K to 4.058 at 353 K for the $\text{C}_6\text{H}_6\text{Mu}$ radical in the gas phase.²⁹

CONCLUSIONS

RF- μSR has been used to measure the muon hfcc of the muoniated cyclohexadienyl radical in benzene and a dilute aqueous solution of benzene. Compared with neat benzene, values for A_{μ} in a 5 mM aqueous solution at 293 K were found to increase by $\sim 5\text{ MHz}$. This shift in A_{μ} corresponds to a fraction change ($\Delta A_{\mu}/A_{\mu}$) of +0.98(5)% and agrees well with the values previously reported by Vujošević et al. hfccs obtained from the RF- μSR measurements suggest that the calculations performed by Straka et al. using a CPCM solvation model overestimate the solvent shift in these systems. The procedure used by Vujošević et al. in analyzing ALC- μSR spectra, specifically assuming $A_{\mu}/A_p = 4.0815(5)$, leads to reasonably accurate values of the muon hfcc.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Scheuermann, R.; Tucker, I. M.; Creeth, A. M.; Dilger, H.; Beck, B.; Roduner, E. Towards the Determination of Partition Coefficients of Cosurfactants at Surfactant Bilayer Interfaces by Muon Spin Resonance Spectroscopy. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1510–1512.
- (2) Scheuermann, R.; Tucker, I. M.; Dilger, H.; Staples, E. J.; Ford, G.; Fraser, S. J.; Beck, B.; Roduner, E. Partitioning of Small Amphiphiles at Surfactant Bilayer/ Water Interfaces: An Avoided Level Crossing Muon Spin Resonance Study. *Langmuir* **2004**, *20*, 2652–2659.
- (3) Martyniak, A.; Dilger, H.; Scheuermann, R.; Tucker, I. M.; McKenzie, I.; Vujošević, D.; Roduner, E. Using Spin Polarised Positive Muons for Studying Guest Molecule Partitioning in Soft Matter Structures. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4723–4740.
- (4) Martyniak, A.; Dilger, H.; McKenzie, I.; Scheuermann, R.; Lagerwall, J.; Roduner, E. Partitioning and Reorientational Dynamics of Phenylalcohols in SDS Lyotropic Liquid Crystalline Mesophases: An ALC- μSR Study. *Colloids Surf., A* **2007**, *309*, 224–230.
- (5) Dawin, U. C.; Dilger, H.; Roduner, E.; Scheuermann, R.; Stoykov, A.; Giesselmann, F. Chiral Induction in Lyotropic Liquid Crystals: New Insight into the Role of Dopant Location and Dynamics. *Angew. Chem., Int. Ed.* **2010**, *49*, 2427–2430.
- (6) Roduner, E. *The Positive Muon as a Probe in Free Radical Chemistry - Potential and Limitations of the μSR Techniques*; Lecture Notes in Chemistry 49; Springer: New York, 1988; Vol. 49.
- (7) McKenzie, I.; Roduner, E. Using Polarized Muons as Ultra-sensitive Spin Labels in Free Radical Chemistry. *Naturwissenschaften* **2009**, *96*, 873–887.
- (8) McKenzie, I. The Positive Muon and μSR Spectroscopy: Powerful Tools for Investigating the Structure and Dynamics of Free Radicals and Spin Probes in Complex Systems. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2013**, *109*, 65–112.
- (9) Stadlbauer, J. M.; Ng, B. W.; Ganti, R.; Walker, D. C. Muonium Addition Reactions to Aromatic Solutes. *J. Am. Chem. Soc.* **1984**, *106*, 3151–3153.
- (10) Roduner, E.; Louwrier, P. W. F.; Brinkman, G. A.; Garnet, D. M.; Reid, I. D.; Arseneau, D. J.; Senba, M.; Fleming, D. G. Quantum Phenomena and Solvent Effects on Addition of Hydrogen Isotopes to Benzene and to Dimethylbutadiene. *Ber. Bunsen-Ges.* **1990**, *90*, 1224–1230.
- (11) Heming, M.; Roduner, E.; B. D. Patterson, W. O.; Schneider, J.; Baumeler, H.; Keller, H.; Savić, I. M. Detection of Muonated Free Radicals through the Effects of Avoided Level Crossing. Theory and Analysis of Spectra. *Chem. Phys. Lett.* **1986**, *128*, 100–106.
- (12) Straka, M.; Kaupp, M.; Roduner, E. Understanding Solvent Effects on Hyperfine Coupling Constants of Cyclohexadienyl Radicals. *Theor. Chem. Acc.* **2005**, *114*, 318–326.
- (13) Hudson, B.; Chafetz, S. Zero-Point Corrections for Isotropic Coupling Constants for Cyclohexadienyl Radical, C_6H_7 and $\text{C}_6\text{H}_6\text{Mu}$: Beyond the Bond Length Change Approximation. *Molecules* **2013**, *18*, 4906–4916.
- (14) Shiu, W.-Y.; Ma, K.-C. Temperature Dependence of Physical-Chemical Properties of Selected Chemicals of Environmental Interest.

I. Mononuclear and Polynuclear Aromatic Hydrocarbons. *J. Phys. Chem. Ref. Data* **2000**, *29*, 41–130.

(15) Yu, D.; Percival, P. W.; Brodovitch, J.-C.; Leung, S.-K.; Kiefl, R. F.; Venkateswaran, K.; Cox, S. F. J. Structure and Intramolecular Motion of Muonium-substituted Cyclohexadienyl Radicals. *Chem. Phys.* **1990**, *142*, 229–236.

(16) de Magalhães, A. L.; Ramos, M. Calculation of Hyperfine Coupling Constants of Muonated Radicals. *Chem. Phys. Lett.* **1990**, *165*, 528–534.

(17) Vujošević, D.; Dilger, H.; McKenzie, I.; Martyniak, A.; Scheuermann, R.; Roduner, E. Local Ordering in Liquids: Solvent Effects on the Hyperfine Couplings of the Cyclohexadienyl Radical. *J. Phys. Chem. B* **2007**, *111*, 199–208.

(18) Dilger, H.; Hess, S.; Scheuermann, R.; Vujošević, D.; McKenzie, I.; Roduner, E. Local Ordering in Quadrupolar Liquids Observed by the Hyperfine Couplings of the Cyclohexadienyl Radical. *Physica B* **2009**, *404*, 927–929.

(19) Scheuermann, R.; Schimmele, L.; Schmidt, J.; Major, J.; Herlach, D.; Scott, C. A. Radio-frequency Muon Spin Resonance (RF- μ SR) Experiments on Condensed Matter. *Appl. Magn. Reson.* **1997**, *13*, 195–217.

(20) Cottrell, S. P.; Cox, S. F. J.; Lord, J. S.; Scott, C. A. Radio-frequency μ SR Experiments at the ISIS Pulsed Muon Facility. *Appl. Magn. Reson.* **1998**, *15*, 469–476.

(21) Percival, P. W.; Addison-Jones, B.; Brodovitch, J.-C.; Sun-Mack, S. Radio-frequency Muon Spin Resonance Studies of Endohedral and Exohedral Muonium Adducts of Fullerenes. *Appl. Magn. Reson.* **1996**, *11*, 315–323.

(22) Kreitzman, S. R.; Estle, T. L.; Hitti, B.; Schneider, J. W.; Chow, K. H.; Lichti, R. L. A Microwave μ SR Spectrometer. *Hyperfine Interact.* **1994**, *87*, 1063–1068.

(23) Cottrell, S. P.; Cox, S. F. J.; Scott, C. A.; Lord, J. S. The Commissioning of a Spectrometer Optimised for Radio-frequency Measurements at a Pulsed Muon Source. *Physica B* **2000**, *289*–290, 693.

(24) Lord, J. S. Computer Simulation of Muon Spin Evolution. *Physica B* **2006**, *374*, 472–474.

(25) *CRC Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2005.

(26) Percival, P. W.; Roduner, E.; Fischer, H. Radiolysis Effects in Muonium Chemistry. *Chem. Phys.* **1978**, *32*, 353–367.

(27) Roduner, E.; Brinkman, G. A.; Louwrier, P. W. F. Muonium-substituted Organic Free Radicals in Liquids. Isomer Distribution and End-of-track Radiolytical Processes Determined from Studies of Cyclohexadienyl Radicals Derived from Substituted Benzenes. *Chem. Phys.* **1984**, *88*, 143–153.

(28) Lord, J. S.; et al. Design and Commissioning of a High Magnetic Field Muon Spin Relaxation Spectrometer at the ISIS Pulsed Neutron and Muon Source. *Rev. Sci. Instrum.* **2011**, *82*, 073904.

(29) Fleming, D. G.; Arseneau, D. J.; Pan, J. J.; Shelley, M. Y.; Senba, M.; Percival, P. W. Hyperfine Coupling Constants of Muonium-substituted Cyclohexadienyl Radicals in the Gas Phase: $C_6H_6\text{Mu}$, $C_6D_6\text{Mu}$, $C_6F_6\text{Mu}$. *Appl. Magn. Reson.* **1997**, *13*, 181–194.