new reaction; and (iii) the difference in the thermal and photochemical reaction pathways is both remarkable and curious and contrasts our previous report[4] on the formation of a stable methylidene under photochemical conditions only. Mechanistic studies[12] are in progress.

Acknowledgment. Financial support was provided by NSERC in the form of an operating grant to M.D.F. We also thank Johnson Matthey for the generous loan of $IrCl_3$.

Supplementary Material Available: NMR and analytical data for $Ir(\eta^2\text{-}CH_2PR_2)H[N(SiMe_2CH_2PPh_2)_2]$ (R = Ph, **2a**; R = Me, **2b**) (1 page). Ordering information is given on any current masthead page.

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(12) Preliminary kinetic investigations have established that both **1a** and **1b** rearrange via a first-order process; monitoring the disappearance of **1a**-d_3, $Ir(CD_3)PPh_2[N(SiMe_2CH_2PPh_2)_2]$, established that k_H/k_D is 1.42 (2). The thermolysis of the monodeuterated derivative $Ir(CDH_2)PPh_2[N(SiMe_2CH_2PPh_2)_2]$, **1a**-$d_1$, gives the corresponding hydride *fac*-$Ir(\eta^2\text{-}CHDPPh_2)H[N(SiMe_2CH_2PPh_2)_2]$ and the deuteride *fac*-$Ir(\eta^2\text{-}CH_2PPh_2)D[N(SiMe_2CH_2PPh_2)_2]$ in a ratio of 84 ± 2:16 ± 2, which corresponds to k_H/k_D = 2.7 (4) for the C–H cleavage step after correction for statistical effects and isotopic purity.

Stereomemory within a Formally Unsaturated Chiral Tungstenocene Methyl Complex

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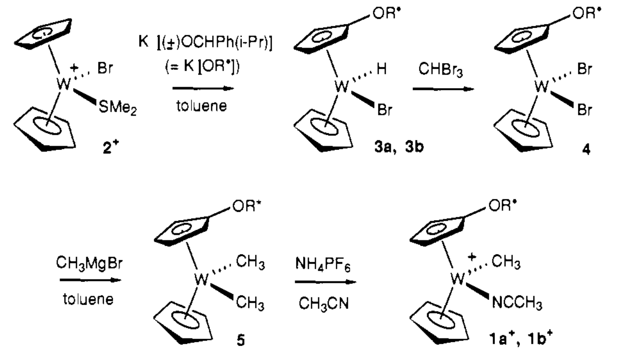
Chiral metal centers are important as stereochemical probes in mechanistic organometallic chemistry[3] and are of particular current interest because of the dramatic advances in chiral induction with organometallic reagents and catalysts.[4] When chiral centers are tetrahedrally coordinated they are usually stereochemically stable, and, when racemization occurs, it is dissociative and involves unsaturated intermediates.[3] Racemization does not, however, necessarily follow dissociation, and our understanding of chiral tetrahedral complexes would be advanced by elucidation of the factors controlling the stereochemistry of their unsaturated derivatives.[5] Alkyl complexes are particularly intriguing since they can achieve effective saturation via agostic interactions[6] or via α- or β-hydride elimination.[7] We recently developed a route to tungstenocene complexes with chiral metal centers,[8] and we now report how these may be used to determine the stereochemical stability of a formally unsaturated tungstenocene methyl complex.

Scheme I



The chiral tungstenocene methyl complex $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}(CH_3)(NCCH_3)]PF_6$ was prepared as an enantiomeric mixture of diastereomers (**1a**PF$_6$, **1b**PF$_6$)[9,10] from $[W(\eta\text{-}C_5H_5)_2(SMe_2)Br]PF_6$ (**2**PF$_6$) in four steps as shown in Scheme I. Crude $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}HBr]$ (**3a**, **3b**)[8,9] (prepared from 3.0 g, 5.0 mmol of **2**PF$_6$) was treated with bromoform (5 mL, 57 mmol) to precipitate analytically pure grey green crystals of $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}Br_2]$ (**4**,[11] 1.90 g, 3.05 mmol ≡ 61% from **2**PF$_6$) over 8 h. Methylation of **4** (0.225 g, 0.36 mmol) in toluene (45 mL) with 3.1 M MeMgBr in Et_2O (1.2 mL, 3.7 mmol) gave $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}Me_2]$ (**5**) after 12 h. Pure **5**[12] (0.125 g, 0.25 mmol ≡ 71%) was isolated as orange needles by crystallization from pentane after ethanolysis. Protonolysis of **5** (0.085 g, 0.17 mmol) with NH_4PF_6 (0.080 g, 0.49 mmol) in CH_3CN (25 mL) for 5 h gave a 3:2 mixture (^{1}H NMR) of **1a**PF$_6$ and **1b**PF$_6$ (0.087 g, 0.13 mmol) in 77% yield after recrystallization (acetone/H_2O).

The less soluble diastereomer was separated from the mixture (1.5:1, 0.050 g, 0.075 mmol) by vigorously stirring (8 h) the oily orange brown solid in benzene (12 mL) to give a fine amber powder (>98% **1a**PF$_6$, 0.016 g, 0.024 mmol ≡ 53% of starting **1a**PF$_6$) under a red brown solution (0.72:1 **1a**$^+$ to **1b**$^+$).[13] Pure **1b**PF$_6$ could not be isolated by chromatography, fractional crystallization, or preferential extraction.

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(9) In the case of complexes prepared as diastereomeric mixtures the "a" diastereomer is that with the downfield resonance for the C_5H_5 ligand in acetone-d_6. The absolute stereochemistries of the "a" and "b" diastereomers reported in this paper have not been determined and are not required for the present work.

(10) ^{1}H NMR $\{(CD_3)_2CO$, 500 MHz$\}$: **1a**PF$_6$ δ 7.3–7.5 (*c*, 5 H, C_6H_5), 5.32 (s, 5 H, C_5H_5), 5.29, 4.63, 4.51, 4.41 (m, 1 H each, C_5H_4), 4.92 (d, J = 5.9 Hz, 1 H, OC*H*), 2.68 (s, 3 H, $NCCH_3$), 2.25 (octet, J = 6.3 Hz, 1 H, C*H*$(CH_3)_2$), 1.00 (d, J = 6.9 Hz, 3 H, $CHCH_3$), 0.83 (d, J = 6.8 Hz, 3 H, $CHCH'_3$), 0.23 (s, satellites $J_{W\text{-}H}$ = 5.5 Hz, 3 H, W–CH_3); **1b**PF$_6$ δ 7.3–7.5 (c, 5 H, C_6H_5), 5.29 (s, 5 H, C_5H_5), 5.02 (d, J = 6.0 Hz, 1 H, OC*H*), 4.95, 4.87, 4.79, 4.61 (m, 1 H each, C_5H_4), 2.62 (s, 3 H, $NCCH_3$), 2.25 (m, 1 H, C*H*$(CH_3)_2$), 1.02 (d, J = 6.9 Hz, 3 H, $CHCH_3$), 0.80 (d, J = 7.0 Hz, 3 H, $CHCH'_3$), 0.19 (s, satellites $J_{W\text{-}H}$ = 5.5 Hz, 3 H, WCH_3). Anal. Calcd for $C_{23}H_{28}ONWPF_6$: C, 41.65; H, 4.26; N, 2.11. Found (Multichem, Lowell MA): C, 41.68; H, 4.22; N, 2.00.

(11) ^{1}H NMR $\{(CD_3)_2SO$, 250 MHz$\}$ δ 7.2–7.5 (c, 5 H, C_6H_5), 5.51 (s, 5 H, C_5H_5), 5.32, 5.08, 4.80, 4.40 (m, 1 H each, C_5H_4), 4.92 (d, J = 6.0 Hz, 1 H, OC*H*), 2.22 (m, 1 H, C*H*CH_3), 0.85 (d, J = 7.2 Hz, 3 H, $CHCH_3$), 0.72 (d, J = 7.2 Hz, 3 H, $CHCH'_3$); mass spectrum, parent ion: WBr_2 isotope envelope at m/e = 624 ($^{187}W^{81}Br_2$). Anal. Calcd for $C_{20}H_{22}OBr_2W$: C, 38.61; H, 3.57. Found (Multichem, Lowell MA): C, 38.56; H, 3.62.

(12) ^{1}H NMR $\{(CD_3)_2CO$, 250 MHz$\}$ δ 7.25–7.45 (c, 5 H, C_6H_5), 4.65 (d, J = 6.8 Hz, 1 H, OC*H*), 4.44 (s, 5 H, C_5H_5), 4.17, 3.87, 3.73, 3.64 (m, 1 H each, C_5H_4), 2.11 (octet, J = 7.0 Hz, 1 H, C*H*$(CH_3)_2$), 0.95 (d, J = 7.2 Hz, 3 H, $CHCH_3$), 0.79 (d, J = 7.2 Hz, 3 H, $CHCH'_3$), −0.15 (s, satellites $J_{W\text{-}H}$ = 6.0 Hz, 3 H, W-CH_3), −0.16 (s, satellites $J_{W\text{-}H}$ = 6.0 Hz, 3 H, W-CH'_3); $^{13}C\{^1H\}$ NMR $\{(CD_3)_2CO$, 75.5 MHz, DEFT sequence$\}$ δ 128.98, 128.53, 128.30 C_6H_5, non-ipso carbons), 87.83 (OCH), 87.02 (C_5H_5), 83.35 (C_5H_4, substituted carbon), 76.77, 71.30, 70.88, 69.36 (C_5H_4, nonsubstituted carbons), 35.49 ($CHCH_3$), 19.32 ($CHCH_3$), 18.48 ($CHC'H_3$), −17.20 (W–CH_3 satellites $J_{W\text{-}C}$ = 68 Hz), −19.14 (W–$C'H_3$ satellites $J_{W\text{-}C}$ = 74 Hz), mass spectrum, parent ion: W isotope envelope at m/e = 492 (^{184}W). Anal. Calcd for $C_{22}H_{28}OW$: C, 53.67; H, 5.74. Found (Multichem, Lowell MA): C, 53.42; H, 5.82.

(13) Further crops of **1a** could be obtained from the benzene extract by epimerization in CH_3CN at 60 °C for several hours followed by a further benzene extraction.

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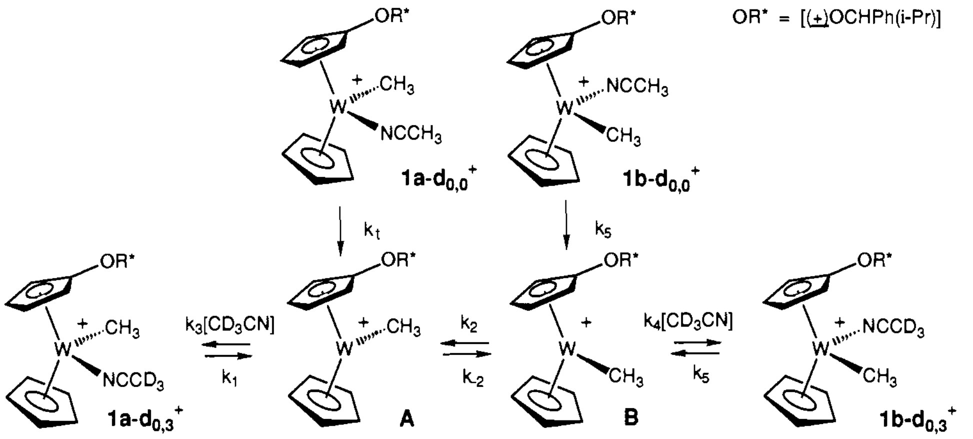
Scheme II



The stereochemical stability of the formally unsaturated tungstenocene methyl complex $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}Me]^+$ was determined by ^{1}H NMR observation of thermal (42 °C) substitution of **1**$^+$ in CD_3CN. This leads cleanly to **1-*d***$_{0,3}^{+}$,[14] and it was immediately apparent, despite some epimerization, that substitution of pure **1a-*d***$_{0,0}^{+}$ primarily gave **1a-*d***$_{0,3}^{+}$, i.e., there was predominant retention of configuration.

Stereomemory in the substitution was quantified by a kinetic study interpreted in terms of Scheme II. Two assumptions incorporated here were derived from experimental observations as follows:[15] (1) consumption of **1a-*d***$_{0,0}^{+}$ and **1b-*d***$_{0,0}^{+}$ in CD_3CN is first order for 4 half-lives with rate constants $k_1 = 9.20\ (6) \times 10^{-5}\ s^{-1}$ and $k_5 = 1.17\ (2) \times 10^{-4}\ s^{-1}$, and consumption is also first order with essentially the same rate constants ($k_1 = 9.74\ (15) \times 10^{-5}\ s^{-1}$ and $k_5 = 1.24\ (4) \times 10^{-4}\ s^{-1}$) in 1:16 CD_3CN:$(CD_3)_2CO$, establishing unimolecular kinetics;[16] (2) no **1b-*d***$_{0,0}^{+}$ is formed from **1a-*d***$_{0,0}^{+}$ in acetonitrile-d_3, eliminating any possibility of nondissociative epimerization of **1**$^+$.

The stereochemical stability of A and B is most directly described by k_2 and k_{-2}, but these cannot be evaluated. An alternative description of the stereomemory of A and B involves the ratios of the rates of formation of **1a-*d***$_{0,3}^{+}$ and **1b-*d***$_{0,3}^{+}$ from pure **1a-*d***$_{0,0}^{+}$ and from pure **1b-*d***$_{0,0}^{+}$, but direct measurement of these rates is complicated since they must be evaluated at zero conversion to eliminate epimerization between **1a-*d***$_{0,3}^{+}$ and **1b-*d***$_{0,3}^{+}$. This problem can, however, be circumvented by a detailed analysis (based on application of the steady-state approximation to [A] and [B]—Supplementary Material) which establishes that these time dependent ratios are given at $t = 0$ by:

$$R_a = \frac{d[\mathbf{1a}\text{-}d_{0,3}{}^+]}{d[\mathbf{1b}\text{-}d_{0,3}{}^+]} = \frac{k_1(K_{eq} + 1) - A_o}{A_o} \qquad (1)$$

and

$$R_b = \frac{d[\mathbf{1b}\text{-}d_{0,3}{}^+]}{d[\mathbf{1a}\text{-}d_{0,3}{}^+]} = \frac{k_5(1/K_{eq} + 1) - A_o}{A_o} \qquad (2)$$

where K_{eq} is the equilibrium constant for the conversion of **1b**$^+$ to **1a**$^+$, and A_o is the first-order rate constant for this conversion.[17] These were conveniently determined to be 1.46 (7) and 6.0 (2) $\times 10^{-5}\ s^{-1}$ at 42 °C from the intensities of the WCH_3 resonances in a solution prepared from pure **1a-*d***$_{0,0}^{+}$, leading to $R_a = 2.7$ (±0.2) and $R_b = 2.3$ (±0.3).

The magnitudes of R_a and R_b establish that the formally unsaturated cations produced by acetonitrile loss from **1a**$^+$ and **1b**$^+$ possess significant stereomemory. The most obvious interpretations are that $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}(CH_3)]^+$ has a pyramidal ground state,[18] with an inversion rate slower than the trapping reaction, or that the pseudotetrahedral environment is preserved by interaction of a methyl C–H bond with the metal. The latter seems the more likely explanation for two reasons: (1) experiments exploring dissociative CD_3CN substitution for Br$^-$ in **3a** and **3b** (under conditions under which CD_3CN substitution of $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}(NCCH_3)H]^+$ is slow, and at temperatures from 25 to 75 °C) failed to provide evidence for stereomemory, suggesting that the hydride intermediate $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}H]^+$ (lacking an α-C–H bond) epimerizes rapidly; (2) comparison of the rate of the first order loss of CH_3CN from **1a-*d***$_{3,0}^{+}$[21] and **1b-*d***$_{3,0}^{+}$[21] at 42 °C with that from the undeuterated species establishes kinetic isotope effects (k_H/k_D) of 1.26 (3) and 1.22 (2), respectively, for dissociation from **1a**$^+$ and **1b**$^+$, and implies weakening of a WCH_2–H bond in the transition state for dissociation, consistent with a significant α-interaction in the subsequent intermediate.[22] This could involve either an agostic interaction[6] or α-elimination to an intermediate alkyidene hydride, as suggested previously by Green in the case of related tungstenocene alkyls[25] and as established by Bercaw in the case of isoelectronic peralkyltantalocene alkyls.[26] α-elimination is, however, essentially one extreme of agostic interaction,

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(14) This nomenclature indicates that the acetonitrile methyl is deuterated while the W-methyl is not.

(15) We also assume that secondary kinetic isotope effects for acetonitrile dissociation from **1-*d***$_{0,0}^{+}$ and **1-*d***$_{0,3}^{+}$ are negligible.

(16) The high concentration of CD_3CN ensures that back reaction with the released CH_3CN is negligible.

(17) Equilibration of any mixture of **1a**$^+$ (= **1a-*d***$_{0,3}^{+}$ + **1a-*d***$_{0,0}^{+}$) and **1b**$^+$ (= **1b-*d***$_{0,3}^{+}$ + **1b-*d***$_{0,0}^{+}$) should obey first-order kinetics, and this has been confirmed experimentally over 4 half-lives.

(18) d^2 bent metallocenes should be either pyramidal with a singlet ground state or pseudoplanar (achiral) with a triplet ground state,[19] and calculations have indicated that $[W(\eta\text{-}C_5H_5)_2CH_3]^+$ "might have a high-spin ground state".[20]

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(21) This nomenclature indicates that the W-methyl is deuterated, while the acetonitrile methyl is not.

(22) Similar kinetic isotope effects in solvolyses of β-deuterated organic reactants are interpreted as consequences of hyperconjugation in intermediate carbocations.[23] There is clearly an interesting analogy between inorganic agostic interactions and organic hyperconjugative interactions, but there are also many distinctions between them. Agostic interactions are, for example, well established as strong ground-state effects,[6] while hyperconjugation is a transition-state phenomenon which does not result in stereoretention during solvolyses.[24]

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and the distinction cannot be addressed experimentally with the available data.[27] Since in its earliest recorded use αγοστος means "the flat of the hand", it would be particularly apposite if agostic interactions stabilize the chirality (handedness) of this and other formally unsaturated transition-metal centers.[28]

Acknowledgment. We thank the National Science Foundation for financial support and Karen Bowden for translations from the Greek. The Bruker AM-500 used for these experiments was purchased with the assistance of NSF Grant no. CHE-84-10774 to Harvard University.

Registry No. **1aPF$_6$,1bPF$_6$** (isomer I), 119638-12-9; **1aPF$_6$,1bPF$_6$** (isomer II), 119717-50-9; **3a,3b** (isomer I), 114860-17-2; **3a,3b** (isomer II), 114925-24-5; **4**, 119638-10-7; **5**, 119638-13-0; CHBr$_3$, 75-25-2.

Supplementary Material Available: Derivation of eq 1 and 2 (4 pages). Ordering information is given on any current masthead page.

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(27) Interpretation of the first-order kinetics of the thermal conversion of $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H]^+$ to $[W(\eta\text{-}C_5H_5)_2(CH_3)(PMe_2Ph)]^+$ is subject to similar ambiguities.[25g]

(28) *ο δ'εν κονιησι πεσων ελε γαιαν αγοστω.* (*Illiad* 11.425) "And falling in the dust he grasped the earth with his hand".

Measurement of Internuclear Distances in Polycrystalline Solids: Rotationally Enhanced Transfer of Nuclear Spin Magnetization

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In this communication we demonstrate a magic angle spinning (MAS) NMR technique for measurement of the distance between two homonuclear sites separated by as much as 0.5 nm. In solution NMR distance determinations via the nuclear Overhauser effect are widely employed to determine molecular structure.[1-3] However, analogous experiments in solids, based on spin diffusion, have been only partially successful because of the complexity of the abundant spin dipolar coupling networks.[4-10] The approach described here is based on the simplification which results when this multispin problem is reduced to one of two spins, coupled weakly to the environment. Experimentally, this is achieved by (i) proton decoupling during the magnetization exchange process, greatly attenuating the influence of abundant nuclear spins; (ii) selective isotopic labeling of both sites of interest, so that the system may be approximated as a set of magnetically dilute coupled spin pairs; (iii) MAS with matching of the *rotational resonance* condition, $\omega_\Delta^{\text{iso}} = n\omega_r$, for the spin pairs of interest, ensuring that the magnetization transfer is driven in an efficient and predictable fashion by the sample rotation.[11-14] Here $\omega_\Delta^{\text{iso}}$ is the difference between the isotropic shift frequencies of the two sites, ω_r is the spinning frequency, and n is a small integer. Under these conditions the dynamics of magnetization exchange are predictable by numerical simulation, if the parameters characterizing the spin pair system are known. The dipolar coupling and therefore the internuclear separation may be measured by matching experimental results with numerical simulations. We demonstrate the measurement of an internuclear distance of 0.50 ± 0.05 nm (corresponding to a coupling of ~50 Hz) on a sample of tyrosine ethyl ester (TEE), ^{13}C-labeled at both the -CH$_2$- of the ester moiety and at the 4'-OH aromatic carbon.

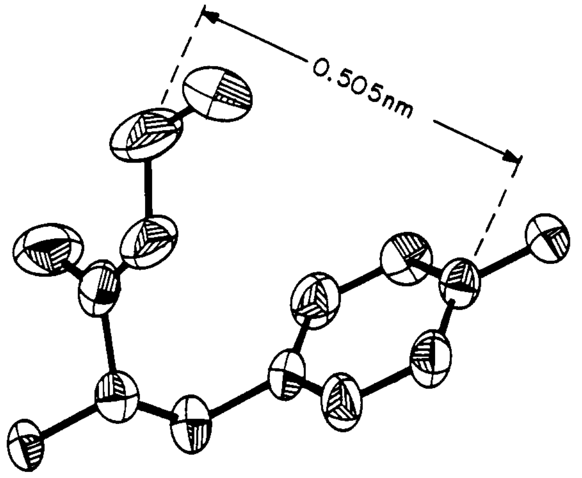

Figure 1. The structure of tyrosine ethyl ester,[14] showing the 0.505-nm separation between the labeled carbons.

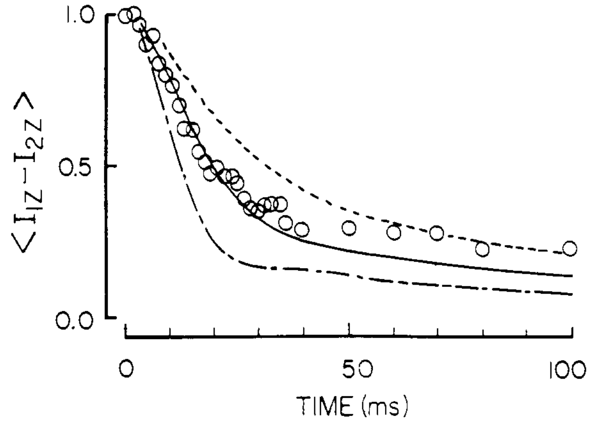

Figure 2. Calculated and experimental evolution of the difference polarization for the $n = 1$ rotational resonance in tyrosine ethyl ester at $\omega_r/2\pi = 9.400$ kHz and a field of 9.4 T. Experimental points, (○); curve calculated for 0.555 nm, (-‍-); curve calculated for 0.505 nm, (—); curve calculated for 0.455 nm, (—-—). Aromatic shielding tensors $\sigma_{11} = -92$ ppm, $\sigma_{22} = -4$ ppm, $\sigma_{33} = 96$ ppm, with the most shielded axis (σ_{11}) perpendicular to the ring, least shielded axis (σ_{33}) along the C–O bond; methylene shielding tensor $\sigma_{11} = -46$ ppm, $\sigma_{22} = \sigma_{33} = 23$ ppm, with the most shielded axis (σ_{11}) along the C–O bond. The results from 5000 randomly oriented crystallites were averaged. $T_2^{ZQ} = 6.3$ ms.

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