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. **1a**PF$_6$,**1b**PF$_6$ (isomer I), 119638-12-9; **1a**PF$_6$,**1b**PF$_6$ (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, $\omega_\Delta^{\mathrm{iso}} = n\omega_r$, 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 $\omega_\Delta^{\mathrm{iso}}$ 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.

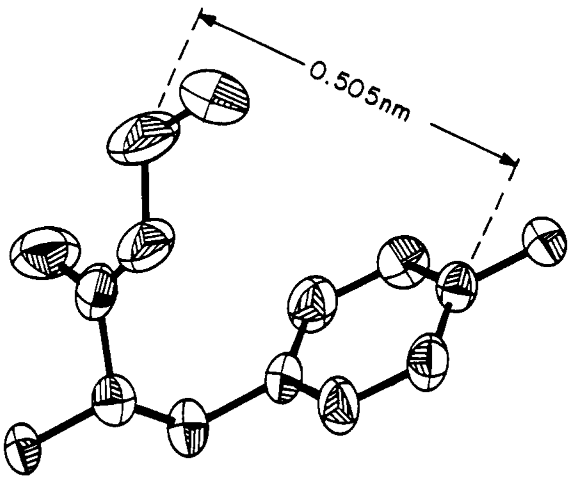

Figure 1. The structure of tyrosine ethyl ester,[14] showing the 0.505-nm separation between the labeled carbons.

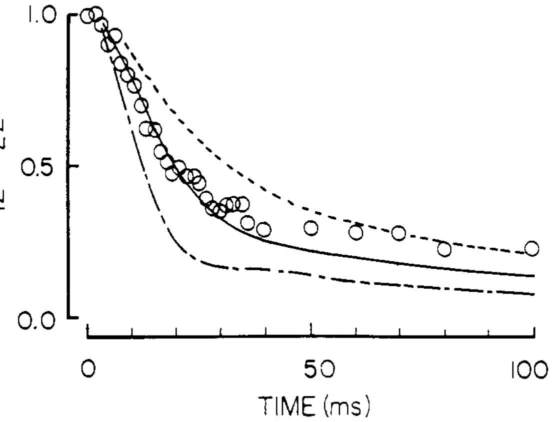

Figure 2. Calculated and experimental evolution of the difference polarization for the $n = 1$ rotational resonance in tyrosine ethyl ester at $\omega_r/2\pi = 9.400$ kHz and a field of 9.4 T. Experimental points, (○); curve calculated for 0.555 nm, (--); curve calculated for 0.505 nm, (—); curve calculated 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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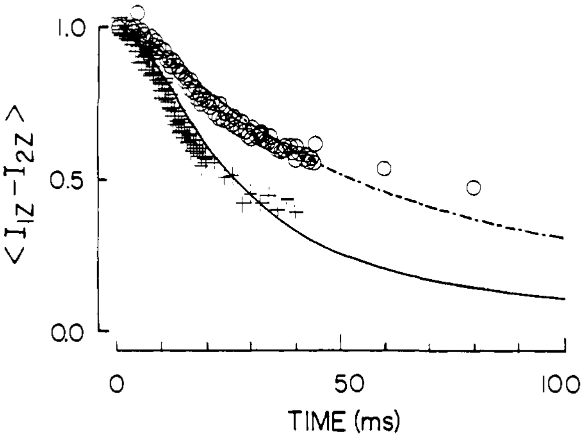

Figure 3. Calculated and experimental evolution of the difference polarization for (a) the $n = 2$ rotational resonance (+, —) and (b) the $n = 3$ rotational resonance (O, —·—) in TEE. Both results were obtained at a field of 7.5 T. Calculations assumed an internuclear separation of 0.505 nm. Other parameters are given in the caption to Figure 2.

TEE crystallizes in a "scorpion"-like conformation where the chain is bent back over the plane of the aromatic ring (Figure 1) and the separation between labeled carbons is 0.505 nm.[15] The magnetization transfer is followed using a simple technique:[13,16] a nonequilibrium initial condition is established by selectively inverting the Zeeman magnetization of one site. After evolution for a variable mixing time τ_m, a nonselective $\pi/2$ pulse is applied to measure the new distribution of magnetization between the two sites. The exchange process is conveniently described as a decay of difference magnetization. Figure 2 displays experimental and calculated curves of the normalized difference magnetization for the $n = 1$ rotational resonance in TEE, and the line for 0.505 nm clearly provides the best fit. In Figure 3, experimental and calculated curves are shown for the $n = 2$ and $n = 3$ resonances. Again, there is good agreement, especially at short times, for a 0.505-nm internuclear separation.

The numerical calculations used to derive the curves (Figures 2 and 3) will be described elsewhere.[17] They differ from previous calculations[13] in that the simultaneous influence of coherent fields and relaxation is incorporated by an integration of the Liouville superoperator over one rotational period. The parameters required, in addition to the internuclear distance, are the isotropic shifts, the principal values of the shift tensors, which are known for many functional groups,[18] and the mutual orientation of the two tensors.[19]

The decay time constant of the zero-quantum coherence of the two spins, T_2^{ZQ}, must also be estimated. Zero-quantum decay influences the magnetization transfer, since the difference polarization is continuously exchanged with zero-quantum coherence under the influence of the dipolar coupling. The zero-quantum relaxation rate is difficult to measure experimentally, but, under the assumption of dephasing by uncorrelated random fields, it may be estimated as the sum of the single-quantum transverse relaxation rates of the two spins.[10] These may be obtained from the spectral line widths, after correcting for magnet inhomogeneity. For the present simulations, the value $T_2^{ZQ} = 6.3$ ms was used.

It is necessary to comment on the sensitivity of the results to errors in the tensor orientations and T_2^{ZQ}. Our calculations suggest that when the sideband intensities are small, as is the case for the TEE $n = 1$ resonance, the results are insensitive to the tensor orientations within 15°. However, the higher order resonances ($n = 2, 3...$) are dependent on the relative tensor orientations and thus can potentially provide information on the relative orientation of molecular groups as well as further constraints on the bond distance. As mentioned above, T_2^{ZQ} was estimated as the sum of the single-quantum T_2's, correcting for the small contribution from the inhomogeneous applied magnetic field. The *conservative* error margin of ±0.05 nm on the measured distance of 0.5 nm reflects an uncertainty of ±1.4 ms in the value of T_2^{ZQ}. The simultaneous fitting of the data for the $n = 1$, 2, and 3 resonances with the same parameters raises confidence in the values used.

The results presented here demonstrate that rotationally enhanced magnetization transfer can be used to measure specific internuclear separations up to at least 0.5 nm for ^{13}C–^{13}C spin pairs. The main requirement for quantitative experiments is an isolated two-spin system, which can be achieved with isotopic labeling.[20] The technique is expected to be most useful for distinguishing among a set of possible distances and conformations in biochemical systems, where the menu of labeling schemes is expanding rapidly.[21-23]

Acknowledgment. F.C. is the recipient of an MIT Bantrell Fellowship. We thank the Los Alamos Stable Isotope Laboratory for the [4'-^{13}C$_1$]tyrosine from which TEE was synthesized. This research was supported by the National Institutes of Health (GM-23403, GM-25505, GM-36920, and RR-00995).

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[16] The experiments described in this note were performed on two home-built spectrometers with fields of 9.4 and 7.5 T. Sample spinning was performed in rotors and stators purchased from Doty Scientific (Columbia, SC). In all cases the spinning speed was stabilized within ±0.05% (see: de Groot, H. J. M.; Copié, V.; Smith, S. O.; Winkel, C.; Lugtenburg, J.; Herzfeld, J.; Allen, P. J.; Griffin, R. G. *J. Magn. Reson.* **1988**, *77*, 251). Double ^{13}C-labeled TEE was prepared by esterifying [4'-^{13}C$_1$]Tyr with [1'-^{13}C$_1$]-ethanol. Data were collected on two samples containing 100% doubly labeled TEE, diluted to either 5% or 20% in nonlabeled material. The results were indistinguishable, suggesting that the ^{13}C spin pairs were effectively well isolated from one another in both cases.

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[20] Rotational resonance is also possible between naturally occuring spin pairs—^{31}P–^{31}P, ^{19}F–^{19}F—thus circumventing the requirement of labeling. Moreover, since these nuclei have larger γ's, it should be possible to measure distances which are correspondingly larger than 0.5 nm.

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Intramolecular Catalysis of Enolization: A Probe for Stereoelectronic Effects at Carboxyl Oxygen

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Catalysis by neighboring carboxylate has been examined in a number of contexts, and the results have been summarized by Kirby.[1] The behavior of carboxylate in such systems is frequently expressed as "effective molarity" (EM), in which the rate for an intramolecular reaction is compared to that of an appropriate bimolecular case. The usefulness of EM for reactions of carboxylates has been criticized by Gandour[2] since the less basic anti lone pair (eq 1) is invariably involved in the intramolecular cases, whereas the more basic syn lone pair is likely to be involved in the bimolecular cases. Such stereoelectronic effects at carboxylate oxygen may be responsible for the low EM's observed in intramolecular general base catalyzed (igbc) processes, e.g., **1** and **2**.[2] It has not been possible to assess the importance of lone pair

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