stereoselectivity, consistent with a mechanism involving selective closure of reversibly formed diradical intermediates to the less strained cycloadducts. Finally, this method provides an important complement to the recently reported nickel-mediated cycloaddition[4a] in servicing problems in bicyclo[6.n.0]alkane synthesis.

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Supplementary Material Available: Analytical data for compounds **2**, **3**, **6**–**9**, **11**, **12**, **15**, and **16** (5 pages). Ordering information is given on any current masthead page.

Unusual Asymmetry of Methyl ^{2}H EFG in Thymine: A Solid State Deuterium NMR and ab Initio MO Study

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Solid-state ^{2}H NMR spectroscopy is a powerful method of studying molecular motion in the solid state.[1-4] The power of this technique derives from the facts that quadrupole coupling is the dominant interaction and the electric field gradient (EFG) tensor is usually axially symmetric for a deuteron bonded to carbon, with the unique axis along the C–D bond. In the case of a methyl group, rapid 3-fold rotation yields an averaged EFG whose symmetry axis is along the rotation axis, and the corresponding powder pattern is axially symmetric ($\eta \leq 0.01$) with a quadrupole splitting of ca. 40 kHz.[5]

We are interested in obtaining spectra of thymidine and ribothymidine, deuteriated at the methyl positions, to study motion of nucleotide bases in DNA and tRNA, respectively. In our initial work we are studying the dynamics of the model compound, thymine-*methyl*-d_3.[6] Inversion–recovery ^{2}H NMR spectra of this compound clearly showed the T_1 anisotropy predicted for 3-fold methyl jumps.[5,7] The linear Arrhenius plot of correlation time, τ_c, against $1/T$ (where $\tau_c = \tau_0 \exp(E/RT)$) yielded an apparent activation energy of 6.9 kJ/mol and a preexponential factor, τ_0, of 2×10^{-13} s. These results show that the ^{2}H spin–lattice relaxation is determined by the 3-fold methyl motion. However, this motion does not account for the asymmetry in the observed line shape, Figure 1. A computer simulation of this lineshape showed that the asymmetry parameter was 0.07–0.08, unusually large for a methyl deuteron, while the splitting, 36 kHz, was several kilohertz less than expected. The goal of the work reported herein was to determine the cause of this unusual methyl line shape.

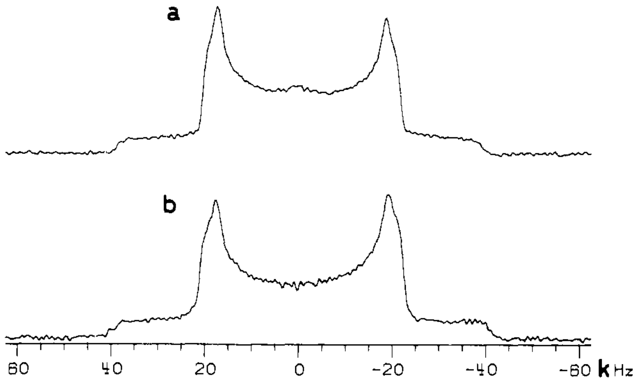

Figure 1. Powder ^{2}H NMR spectra, 38.45 MHz, of methyl deuteriated thymine: (a) at 295 K; (b) at 148 K. No line broadening is added.

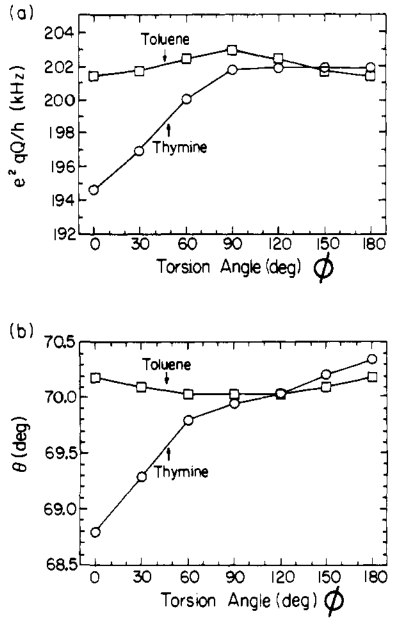

Figure 2. Calculated deuterium electric field gradient tensor for C–^{2}H in methyl group of thymine (○) and toluene (□). Torsion angle, ϕ, is defined by the atoms $C_{carbonyl}$–C_{ring}–C_{methyl}–D. (a) Deuterium coupling constant vs. ϕ; (b) the orientation of the z-axis, θ, with respect to the C_3 rotation axis.

Although the thymine-*methyl*-d_3 T_1 data are completely accounted for by the 3-fold rotation of the methy group, an additional rapid ($\tau_c < 10^{-11}$ s), small amplitude (rms angle <15°) motion cannot be excluded, since it would not significantly affect the ^{2}H spin–lattice relaxation. Such a small amplitude motion could explain the observed 7% asymmetry parameter and the 36-kHz splitting. For example, an excellent computer simulation of the observed line shape is obtained assuming that a Pake pattern ($\eta = 0$) with 40-kHz splitting is averaged by a 12° (rms) libration of the C_5–C_{methyl} bond axis.

If such a small-amplitude motion occurs at the C_5–C_{methyl} site, then it should also occur at the N–H sites, because the aromatic ring is rigid and neutron and X-ray diffraction studies of thymine moieties have shown that thermal parameters of methyl carbons are no larger than those of ring carbons.[8] The measured ^{2}H T_1 of N–^{2}H sites in (NH-d_2, methyl protonated) thymine was about 4000 s at 295 K. The ^{2}H relaxation is mostly determined by

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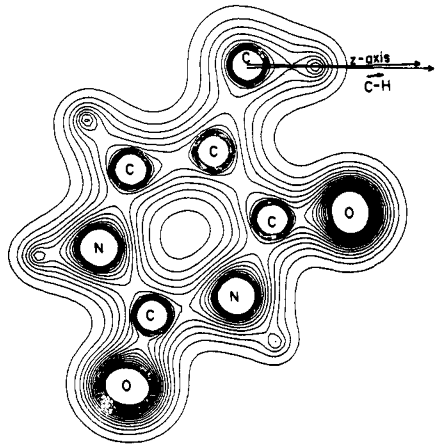

Figure 3. Electron density map of thymine from the ab initio MO calculation. Note that the z-axis is about 2° out of the C–H bond direction when $\phi = 0°$. Contours at 0.05 e$^-$ Å^{-3}; maximum contour at 1.0 e$^-$ Å^{-3}.

dipolar interactions with protons on the reorientating methyl group ($\tau_c = 3 \times 10^{-12}$ s at 295 K). Therefore, if motion occurs at an N–H site, it must have a correlation time of less than 2×10^{-15} s (rms angle 12°) to yield a T_1 value of greater than 4000s.

Because this correlation time is implausible, we performed ab initio molecular orbital calculations[9] to see if the calculated static ^{2}H EFG tensors of thymine-*methyl-d*$_3$ could explain the large asymmetry parameter. The static EFG tensors of toluene-*methyl-d*$_3$ were also calculated, because the methyl group is also adjacent to an aromatic ring, but the observed asymmetry parameter, in contrast to that of thymine, is very small (less than 0.02).[10]

Figure 2a shows the calculated angular dependence of the deuterium quadrupole coupling constant (QCC) with respect to methyl group orientation for thymine and toluene. We note that for thymine with a dihedral angle of zero, the deuteron–exocyclic oxygen internuclear distance is only 2.436 Å. The atomic charge (Mulliken) on the exocyclic oxygen is 0.59 e$^-$. This value is in good agreement with UPS result[11] and other ab initio calculations.[12] From a point charge model, the charge at the oxygen site creates an EFG component of −2.5 kHz along the C–H bond vector of thymine methyl group. As seen in electron density map shown in Figure 3, a point charge model does not fully account for the electron density in the oxygen p-orbitals that lie close to the methyl deuteron site. A more exact calculation involving integration over all occupied molecular orbitals of the thymine molecule gives the deuterium QCCs shown in Figure 2a. The 8-kHz reduction in QCC is noteworthy for the deuterium closest to the exocyclic oxygen site, i.e., $\phi = 0°$. The effect of the exocyclic oxygen on the EFG is also seen in the orientation of z-axis, as shown in Figure 2b. We note that the aromatic π-electrons do not affect the deuterium QCC or the z-axis orientation in toluene to nearly the same extent as the exocyclic oxygen of thymine. The calculated asymmetry parameters of the static EFG tensors of both thymine and toluene are about 0.05. Following the convention $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$, the calculations showed, for both molecules, that the y-axis of the deuterium EFG is normal to the C_{ring}–C_{methyl}–D plane while the x-axis lies in the C_{ring}–C_{methyl}–D plane.

Since the hydrogen positions of the methyl group are unknown in the thymine crystal,[15] the space-averaged (C_3 jumps) ^{2}H EFG tensor is calculated based upon the ab initio results (Figure 2), varying the dihedral angle ϕ from 0° to 60°. At ϕ = 0°, 20°, 40°, and 60°, the calculated values of the asymmetry parameter are 7%, 5%, 4%, and 3%, respectively. So a dihedral angle of less than 20° in thymine explains the experimentally obtained asymmetry parameter. On the other hand the calculated asymmetry parameters of the space-averaged ^{2}H EFG tensor for toluene are always less than 1% because the static EFG is nearly independent of ϕ. We believe that because a large asymmetry parameter is calculated over a large range of dihedral angle, that axially asymmetric spectra of the thymine moiety will be commonly seen.[18]

This study illustrates that reliable analysis of ^{2}H line shapes requires careful consideration of both the dynamic and static factors that affect the EFG tensor. In case of thymine-*methyl-d*$_3$, the large ^{2}H methyl asymmetry parameter is caused by the negative charge density on the exocyclic oxygen, rather than motional narrowing.

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(9) Gaussian-82 and the associated properties package was used to calculate the ^{2}H EFG in molecular and principal axis systems.[16] An interactive matrice manipulation program (Speakeasy) was used for determining the orientation of the EFG tensor. A Gaussian basis set (6-31G) was used for the results reported here. One calculation of toluene was done with p- and d-orbitals on the methyl hydrogen atoms; relative to (6-31G) basis set results, all electric field gradients were reduced by roughly the same factor, 0.9, while the orientation of the EFG tensor was unchanged. No corrections were made for C–H stretching vibrational effects.[17]

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Di-π-methane-like Photorearrangement of Dimesityl(mesitylethynyl)borane: Synthesis, Structure, and Aromaticity of Trimesitylborirene[1]

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The capacity of tricoordinate boron to engage in π-bonding with adjacent unsaturated carbon is evident in the properties of boracyclopolyenes. The heightened chemical reactivity of pentaarylboroles[2] and the relative chemical stability of heptaarylborepins[3] can be ascribed to the Hückel antiaromaticity of the former[4] and the Hückel aromaticity of the latter.[5] In addition, aromatic anions have been generated from both the boracyclo-

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