

Chromatography with ether-hexane (10:90) gave 1,1-didemethylretinal (86 mg, 94% yield) in a 2:1 all-trans:13-cis ratio: UV (pentane)  $\lambda_{\max}$  384 nm ( $\epsilon$  23 200) (all-trans), 378 nm ( $\epsilon$ , 18 000) (13-cis);  $^1\text{H NMR}$   $\delta$  (all-trans) 1.63 (m, 4, 2-H, 3-H), 1.86 (s, 3, 18-H), 2.05 (s, 3, 19-H), 2.1-2.2 (m, 4, 1-H, 4-H), 2.3 (s, 3, 20-H), 5.98 (d,  $J = 8.1$ , 1, 14-H), 6.26 (d,  $J = 11.6$ , 1, 10-H), 6.30 (d,  $J = 15.7$ , 1, 8-H), 6.38 (d,  $J = 14.9$ , 1, 12-H), 6.91 (d,  $J = 15.7$ , 1, 7-H), 7.16 (dd,  $J_1 = 11.6$ ,  $J_2 = 14.9$ , 1, 11-H), 10.10 (d,  $J = 8.1$ , 1, 15-H); (13-cis) 1.63 (m, 4, 2-H, 3-H), 1.86 (s, 3, 18-H), 2.05 (s, 3, 19-H), 2.1-2.2 (m, 4, 1-H, 4-H), 2.16 (s, 3, 20-H), 5.84 (d,  $J = 8.0$ , 1, 14-H), 6.31 (d,  $J = 11.6$ , 1, 10-H), 6.32 (d,  $J = 15.7$ , 1, 8-H), 6.91 (d,  $J = 15.7$ , 1, 7-H), 7.05 (dd,  $J_1 = 11.6$ ,  $J_2 = 14.9$ , 1, 11-H), 7.28 (d,  $J = 14.9$ , 1, 12-H), 10.22 (d,  $J = 8.0$ , 1, 15-H); CI-MS 257 ( $\text{MH}^+$ ), 239 ( $\text{MH} - \text{H}_2\text{O}$ ), 161 ( $\text{MH} - \text{methylcyclohexene}$ ).

The Schiff bases were prepared by dissolving the aldehyde in dry ethanol followed by addition of the corresponding amine (1.5 equiv) at 25 °C. The reaction mixture was stirred for 30 min followed by evaporation of the ethanol and excess of amine under high vacuum. The Schiff bases were dissolved in the required solvent and were protonated with solution saturated with HCl. Immonium salt **5** was prepared by mixing (1.2 equiv) pyrrolidine perchlorate with the corresponding al-

dehyde in ethanol for 3 h at 25 °C. The ethanol was evaporated under high vacuum, and the residual oil was dissolved in the required solvent. Immonium salt **6** was prepared similarly by mixing the aldehyde with proline in trifluoroethanol for 10 h at 25 °C.

**Laser Photolysis.** Pulsed-laser photolysis experiments were carried out with a UV-14, DL-200 Molecron  $\text{N}_2/\text{dye}$  laser system (8 ns, 0.5-1 mJ). Use was also made (especially for the low-temperature measurements) of a Nd:YAG dye laser system (15 ms, 10-50 mJ) equipped with an appropriate cryostat. Actual exciting light intensities ( $\text{mJ}/\text{cm}^2$ ) were also controlled by the use of lenses and neutral density filters. Data were digitized with Biomation 8100 or Tektronix 7912 transient recorders, followed by computer averaging and analysis.

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## Deuterium Quadrupole Echo Study of Urea Motion in Urea/*n*-Alkane Inclusion Compounds

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**Abstract:** Urea molecules constituting the host lattice of the inclusion compound, urea- $d_4/n$ -nonadecane, have been found to undergo 180° flips about the C=O axis at the rate of  $2.0 \times 10^6 \text{ s}^{-1}$  at 303 K with an activation energy of  $23 \pm 2 \text{ kJ mol}^{-1}$ . The kinetic parameters for this process were obtained from simulations of the deuterium quadrupole echo spectra at a pulse spacing at 40  $\mu\text{s}$ . At longer pulse spacings the quadrupole echo line shapes reveal the presence of an additional dephasing process which is angle dependent and can be ascribed to unresolved dipolar interactions, in particular, the nitrogen-deuterium coupling.

Urea forms adducts with a variety of organic compounds such as unbranched alcohols, acids, and *n*-alkanes. In all cases, spirals of hydrogen-bonded urea molecules form the walls of hexagonal channels within which the guest molecules reside in extended conformations and undergo rapid rotation about their long axis. The urea molecules lie almost coplanar with the channel walls, with the carbonyl bonds oriented at 90° to the long axes of the channels. Although the structures are nonstoichiometric with respect to the urea/guest ratio, in almost all cases the repeat distance of the urea channel structure along the crystal *Z* axis is 11 Å and the channel diameter is about 5 Å.<sup>1-3</sup> The guest molecules exhibit considerable disorder along the crystal *Z* axis while being highly ordered in directions perpendicular to this axis.<sup>4</sup> At room temperature the unit cell of the channel structure is hexagonal and contains six urea molecules. The dimensions of the channels are such that they are able to accommodate only unbranched aliphatic compounds. On heating, the inclusion compounds decompose to give pure urea and the guest compound while at low temperatures (~160 K for  $\text{C}_{19}\text{H}_{40}$  adduct) the complexes undergo a phase transition from the hexagonal to an orthorhombic structure. Both the thermal stability and the phase transition temperature vary significantly with the length of the guest molecule.<sup>5-9</sup> A comprehensive review of the properties and

applications of urea inclusion compounds is available.<sup>10</sup>

The conformational and dynamic properties of these compounds have been investigated by several groups using  $^1\text{H}$ ,<sup>11</sup>  $^{13}\text{C}$ ,<sup>12-14</sup> and  $^2\text{H}$ <sup>15-17</sup> NMR techniques. Most of the studies to date have been concerned only with the dynamics of the guest molecules while the channel walls themselves have generally been regarded as rigid. The only reported studies of channel dynamics in urea inclusion compounds are those of Clement et al.<sup>18,19</sup> They observed that the lines in the  $^{14}\text{N}$  NQR spectrum of the urea/trioxane complex disappeared as the temperature was raised above 283 K and proposed that this might be the result of hindered rotation of the urea molecules about their C=O bonds although they did not characterize the nature of the motion in any detail. It would be unwise, however, to draw general conclusions concerning channel motion in urea adducts from these results since the urea/trioxane

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adduct is exceptional among urea inclusion compounds. Although the basic structure is similar to that of the *n*-alkane adducts in that it consists of hexagonal channels, the unit cell itself is rhombohedral rather than hexagonal. Furthermore, the urea/trioxane mole ratio is exactly 3, and there is a more rigid spatial relationship between the guest molecules and host lattice structure than for the nonstoichiometric urea/*n*-alkane adducts. In fact, the urea/trioxane complex more closely resembles the thiourea adducts<sup>10</sup> than other urea adducts. NQR studies of thiourea complexes have also been carried out and the results interpreted in terms of hindered rotation of the thiourea molecules about their C=S bonds.<sup>19,20</sup>

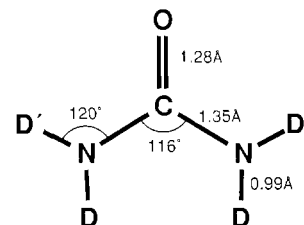
The question of large amplitude motion within the channel walls of urea and thiourea inclusion compounds is of considerable interest since any such motion would presumably be associated with the thermodynamic stability of the compounds. In view of the dimensions of the channels, the urea motion must interfere with the guest molecules, and it is intriguing to speculate whether motion of the urea molecules influences the guest dynamics in an observable manner. Accordingly, we have undertaken the present study of powdered *n*-nonadecane/urea-*d*<sub>4</sub> (UIC) using deuterium quadrupole echo spectroscopy.

Analysis of deuterium NMR powder line shapes has been used to study molecular motion in a wide range of solids including lipids,<sup>21</sup> proteins,<sup>22</sup> synthetic polymers,<sup>23</sup> and a variety of clathrates.<sup>15,24,25</sup> The line shapes are sensitive to motion occurring with rates between 10<sup>3</sup> and 10<sup>8</sup> s<sup>-1</sup>. In many cases the dominant motional processes which occur in this frequency regime are jump processes in which molecules or fragments of molecules undergo instantaneous exchange between two or more discrete sites. The effects of such motion on the line shape depend critically on the relative orientations of the exchange sites as well as on the jump rate. Consequently, the line shapes are highly characteristic of the jump motion. The formalism for describing the effects of molecular motion on deuterium powder line shapes has been described by several authors<sup>26-31</sup> and will not be discussed here. Here we show that the deuterium line shapes of UIC can be interpreted by assuming that the host molecules undergo 180° flips about their C=O bonds. Measurement of the line shapes over a range of temperatures enables us to determine an activation energy for the jump motion, which in turn provides an estimate of the strength of the hydrogen bonds between urea molecules in the channel walls. In addition, the line-shape analysis determines the orientations, relative to a molecular frame, of the quadrupole interaction tensors for two of the four urea deuterons. We also discuss the effect of unresolved dipolar couplings on the deuterium spectra and show how this can account for the loss of spectral intensity observed at long pulse spacings.

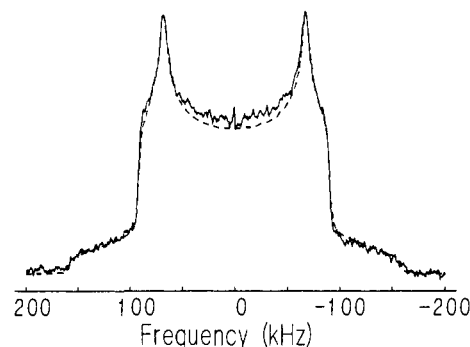
### Experimental Methods

**Materials.** Urea-*d*<sub>4</sub> and C<sub>19</sub>H<sub>40</sub> were purchased from Aldrich Chemicals and used as received. The urea-*d*<sub>4</sub>/C<sub>19</sub>H<sub>40</sub> complex was prepared by precipitation from an 2-propanol-*O-d* solution (Aldrich). The white needle crystals were filtered, washed with benzene, and allowed to dry in air. These were ground thoroughly and packed into 5-mm (o.d.) glass tubes for use in the NMR experiments.

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**Figure 1.** Geometry of urea in urea/*n*-alkane inclusion compounds from Smith.<sup>1</sup> All CND bond angles have been assumed to be 120° and N-D bond lengths are taken to be the same as those in pure urea.<sup>30</sup>



**Figure 2.** Deuterium quadrupole echo spectrum of urea-*d*<sub>4</sub> at 30 °C. The solid line refers to the experimental spectrum (256 scans, echo delay,  $\tau = 40 \mu\text{s}$ ) and the dashed line to a rigid lattice simulation with  $e^2qQ/h = 212 \text{ kHz}$  and  $\eta = 0.145$ . The apodization functions used for the experimental and calculated FID's are detailed in the Experimental Methods section of the text.

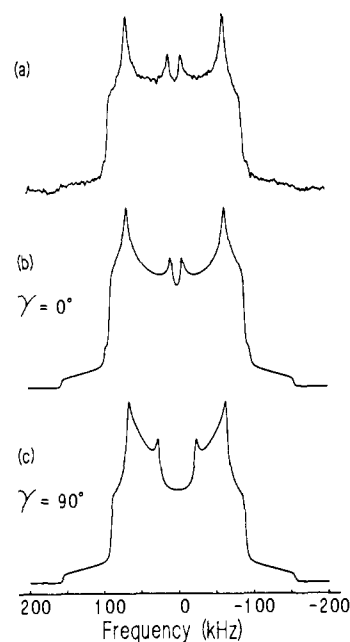
**NMR Experiments.** All deuterium NMR spectra were recorded at 38.4 MHz on a homebuilt spectrometer interfaced to a Nicolet 2090 digital oscilloscope and 1280 computer. The powder patterns were obtained using a quadrupole echo sequence with a 90° pulse length of 1.9  $\mu\text{s}$  and a dwell time of 500 ns. The second echo delay was adjusted at each temperature so that the resulting free induction decay (FID) was digitized close to the top of the echo maximum, but if necessary, the FID's were fractionally left shifted<sup>32</sup> so that the  $t = 0$  point for Fourier transformation came as close to the top of the echo maximum as possible. Recycle delays were chosen to be at least 10 times an average spin-lattice relaxation time,  $T_1$ , measured from the echo maximum using a saturation recovery sequence. More accurate values have been obtained for single crystals of UIC,<sup>33</sup> but the "powder average"  $T_1$  increases from about 25 ms at 338 K to 5 s at 258 K. For pure urea-*d*<sub>4</sub>  $T_1$  is much longer ( $\sim 30$  s at 303 K) and a recycle delay of 300 s was required. The number of acquisitions recorded varied from 768 (338 K) to 64 (258 K) for UIC and was 256 for urea-*d*<sub>4</sub>. The FID's were apodized with 2 kHz of Lorentzian line broadening prior to Fourier transformation.

**Line Shape Simulations.** Spectral simulations were performed using the FORTRAN program, MXQET.<sup>31</sup> The program calculates the FID's and powder patterns resulting from quadrupole echo sequences for deuterons which undergo exchange between specified sites, including corrections from finite pulse power and effects of exchange during pulses. The calculated FID's were apodized with 2 kHz of Lorentzian broadening and 2 kHz (for pure urea-*d*<sub>4</sub> line-shape simulation) or 1 kHz (for UIC simulations) of Gaussian broadening before Fourier transformation.

### Results and Discussion

**Adoption of a Model for the Motion.** Urea molecules are essentially planar with all bond angles being close to 120°. The precise geometry of urea in *n*-alkane adducts was determined by Smith<sup>1</sup> and is illustrated in Figure 1. We have assumed that the CND bond angles are 120° and the N-D bond lengths are taken to be the same as those found in pure urea.<sup>34</sup> There are minor differences between urea geometry in the pure compound and in the complex. In pure urea, which exhibits a tetragonal crystal structure,<sup>34</sup> the NCN bond angle is 118°. The C-N and C-O

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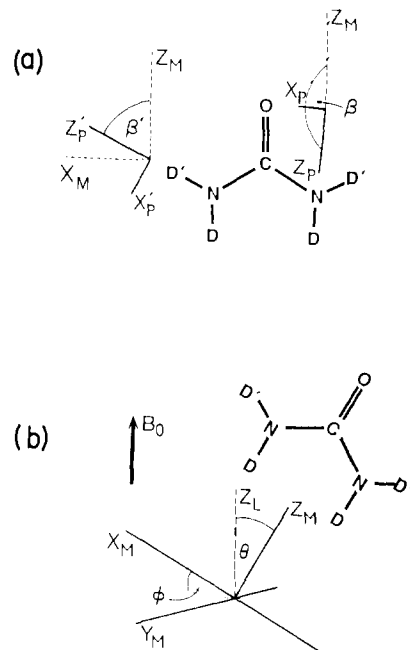


**Figure 3.** (a) Deuterium quadrupole echo spectrum of urea- $d_4$ /C $_{19}$ H $_{40}$  at 303 K obtained with a pulse spacing of 40  $\mu$ s. The line-shape simulations in (b) and (c) are for urea deuterons with  $e^2qQ/h = 212$  kHz and  $\eta = 0.145$  undergoing 180° jumps about the carbonyl axis at  $2.0 \times 10^6$  s $^{-1}$ . The principal  $Z$  components,  $q_{zz}$ , of the deuterium quadrupole coupling tensors are assumed to make angles of 60° and 180° with the jump axis. In (b) the angle  $\gamma = 0^\circ$  ( $q_{xx}$  in plane of urea molecule) while in (c)  $\gamma = 90^\circ$  ( $q_{xx}$  normal to urea plane).

bond lengths are 1.26 and 1.34 Å, respectively, although small variations in these values have been reported in the literature.<sup>34,35</sup> The most significant difference between tetragonal urea and urea in the complex, regarding molecular geometry, lies in the intermolecular C=O...N angles. In the complex these are 136° and 116°, respectively, for the H and H' (see Figure 1) hydrogen bonds, while in pure urea the equivalent bond angles are 99° and 129°.<sup>35</sup>

Figure 2 shows the spectrum of pure urea- $d_4$  recorded at 303 K. Superimposed on the experimental spectrum is a quadrupole echo spectrum calculated for deuterons in a rigid lattice. From a visual comparison of the experimental spectrum with several calculated, we obtained  $e^2qQ/h = 212 \pm 2$  kHz and  $\eta = 0.145 \pm 0.005$ . Few previous NMR studies of deuterium in ND $_2$  groups are available for comparison with these results. Recent NQR studies of ND and ND $_2$  groups<sup>36,37</sup> indicate that our values for  $e^2qQ/h$  and  $\eta$  for deuterium in urea are typical, although quadrupole interaction tensors for deuterium attached to nitrogen exhibit a substantial variation in magnitude and asymmetry, largely because of the strong influence of hydrogen bonding. It should be noted that, besides using a 2-kHz Gaussian apodization, the effects on the line shape from nitrogen-deuterium dipolar coupling have not been accounted for in the simulation. The  $^{14}\text{N}$ -D dipolar coupling constant,  $h\gamma_{\text{N}}\gamma_{\text{D}}/4\pi^2r^3$ , is about 1.33 kHz, assuming a value of 1 Å for the N-D bond length,  $r$ . Ignoring the  $^{14}\text{N}$ -D dipolar coupling may lead to an overestimation of  $e^2qQ/h$  for deuterium of between 2 and 3 kHz and a small (1-2%) error in  $\eta$ .

The powder spectrum of UIC, recorded at 303 K, is shown in Figure 3a. It is immediately apparent that this is not a rigid lattice spectrum although the total width and major splitting are comparable to those observed for pure urea. The smaller peaks (at  $\pm 8$  kHz) and the additional features which occur at  $\pm 95$  kHz indicate the existence of a mobile component in the spectrum. The



**Figure 4.** (a) Location of molecular ( $X_M, Y_M, Z_M$ ) and principal ( $X_P, Y_P, Z_P$ ) axes in urea. The single primes indicate reference to the D' deuterons. Note that  $X_M, Z_M$ , and  $X_P$  and  $Z_P$  for all deuterons lie in the urea plane. (b) The Euler angles ( $\theta, \phi$ ) which define the orientation of the laboratory axis,  $Z_L$  (defined by  $B_0$ ), relative to the molecular frame.

major splitting for UIC is 132 kHz (for pure urea it is 136 kHz), and the intensity of the outer wings of the spectrum is less than that in the spectrum of pure urea. These features suggest that the spectrum contains two distinguishable components: a rigid component that gives rise to the full width spectrum and a mobile component that produces the central peaks and extra shoulders. In other words, there are two types of deuterons which experience very different motional averaging of their quadrupole tensors.

The most likely explanation for the deuterium line shape is that the urea molecules rotate about their C=O bonds at rates faster than  $10^5$  s $^{-1}$ . This motion will result in significant averaging of  $T_2^{L_0}$  (i.e., the principal component of the interaction tensor in the laboratory frame) for the off-axis deuterons while leaving that for the parallel deuterons largely unaffected. Given the known crystal structure<sup>1,5</sup> which shows each urea molecule to be held by four hydrogen bonds nearly in the urea plane, the potential for rotation about the C=O bond must have two minima at rotation angles,  $\phi = 0^\circ$  and  $180^\circ$ . Thus it is probably a good approximation to model the C=O rotation as 180° jumps. Figure 3b shows a simulated powder pattern for urea deuterons undergoing 180° jumps about the carbonyl axis at a rate of  $2.0 \times 10^6$  s $^{-1}$ . All the essential features of the UIC spectrum (Figure 3a) are reproduced.

The UIC deuterium line shape could, in principle, also result from the existence of mobile and rigid urea molecules in the complex. For example, some urea molecules might be included in the channels and give rise to the nonrigid part of the spectrum while the urea molecules which form the channel walls yield a full width rigid lattice spectrum. However, it would require quite large quantities of urea included within the channels to produce the observed effects in the line shape, and the numerous previous studies of urea inclusion compounds provide no evidence of this. It might also be argued that the mobile part of the spectrum derives from included solvent molecules. While it is possible that small amounts of solvent are included, the use of 2-propanol rather than methanol for the recrystallization should ensure that the quantity of included solvent is negligible.

**Orientation of the Quadrupole Coupling Tensor.** Because  $\eta$  is nonzero for urea deuterons, we expect the mobile part of the UIC powder pattern to depend not only on the orientation of the  $Z$  components of the quadrupole tensors relative to the flipping axis

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(C=O bond) but also on the orientations of the  $X$  and  $Y$  components. For clarity it is helpful to define the quadrupole interaction for a deuteron in a molecule fixed axis system as illustrated in Figure 4a. The molecular axes are chosen such that  $Z_M$  lies along the C=O bond and  $X_M$  is in the plane of the molecule. The components of the quadrupole interaction tensor in the molecular frame can be written as

$$T_2^M q = \sum_p D_q^{2*}(\alpha, \beta, \gamma) T_2^P p \quad (1)$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  are the Euler angles, defined using the Rose conventions,<sup>38</sup> which rotate the molecular axes (M) into the principal axes (P) of the quadrupole interaction tensor. The principal components, in Hz, are

$$T_2^P 0 = (3/2)^{1/2} e^2 q Q / h \quad T_2^P \pm 1 = 0$$

$$T_2^P \pm 2 = (\eta/4) e^2 q Q / h \quad (2)$$

and the asymmetry parameter is defined by  $\eta = (q_{xx} - q_{yy}) / q_{zz}$  with  $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$  so that  $0 \leq \eta \leq 1$ . The frequencies,  $\pm \nu_q$ , of lines corresponding to a particular deuteron are then

$$\pm \nu_q = \pm (3/2)^{1/2} T_2^L 0 = \pm (3/2)^{1/2} \sum_p D_0^{2*}(\theta, \phi) T_2^M p \quad (3)$$

where  $\theta$ ,  $\theta$ , and  $\phi$  are the Euler angles describing the orientation of the molecular axes in a laboratory frame (see Figure 4b) and  $T_2^L 0$  is the zeroth component of the quadrupole interaction tensor expressed in this frame.

Ignoring minor distortions due to crystal packing forces, the symmetry of the urea molecule dictates that the angle,  $\gamma$ , be either  $0^\circ$  or  $90^\circ$ . Alternatively, one can assume that  $\gamma$  is  $0^\circ$  and allow  $\eta$  to be positive or negative, changing the sign of  $\eta$  being equivalent to a  $90^\circ$  rotation of the principal axes. By adopting the convention that  $\eta$  be positive, we allow  $\gamma$  to be  $0^\circ$  or  $90^\circ$ . Note that it is not possible using NMR to differentiate between  $\gamma = 0^\circ$  and  $\gamma = 180^\circ$  or between  $\gamma = 90^\circ$  and  $\gamma = 270^\circ$ . The angle  $\alpha$  can be fixed at  $0^\circ$  and  $180^\circ$  for two exchanging deuterons while  $\beta$  is  $\sim 60^\circ$  for the D' sites and  $\sim 180^\circ$  for the D sites. Figure 3, b and c, shows simulated line shapes for urea deuterons undergoing  $180^\circ$  jumps about the C=O bond at a rate,  $k = 2.0 \times 10^6 \text{ s}^{-1}$ . The spectrum in Figure 3b was calculated with  $\gamma = 0^\circ$  and that in Figure 3c with  $\gamma = 90^\circ$ . For both simulations the angles  $\beta$  and  $\beta'$  were taken to be  $180^\circ$  and  $60^\circ$ , respectively, and  $e^2 q Q / h = 212 \text{ kHz}$  and  $\eta = 0.145$  (the values determined for pure urea) were used for both D and D'. As we should expect, the two cases yield very different spectra. It is immediately apparent that the  $\gamma = 0^\circ$  simulation most closely matches the experimental spectrum of UIC. We are unable to determine  $\gamma$  for the D sites from the line shapes since these deuterons, with  $\beta = 180^\circ$ , give rise to a virtually rigid lattice spectrum which provides information only on the magnitudes of  $e^2 q Q / h$  and  $\eta$ . However, since the deuterons have similar electronic environments, it is reasonable to assume the  $\gamma = 0^\circ$  so that  $q_{xx}$  lies in the plane of the urea molecule for D as well as D' deuterons.

Although the  $\gamma = 0^\circ$  simulation reproduces all the major features of the UIC spectrum (Figure 3a), the calculated splitting and the frequencies of the central peaks are both slightly too large. These discrepancies may result from an inaccurate choice of values for  $e^2 q Q / h$  and  $\eta$ ,  $\beta$ , and  $\beta'$ . In addition, the rigid and mobile deuterons may have intrinsically different  $e^2 q Q / h$  and  $\eta$ , but any such differences are likely to be small and are henceforth ignored. The exchange rate also has a profound effect on the spectrum. However, it affects only the relative intensities of different parts of the spectrum and not the frequencies of the singularities. By fitting the line shape at a single temperature we are, in principle, able to determine a range of possible values for  $e^2 q Q / h$ ,  $\eta$ ,  $\beta$ , and  $\beta'$ . However, since  $\beta$  and  $\beta'$  can be varied independently, and because small changes in these angles may be compensated to some extent by variations in  $e^2 q Q / h$  and  $\eta$ , the error limits in the fitting procedure are large. It should be noted that fast librational motion

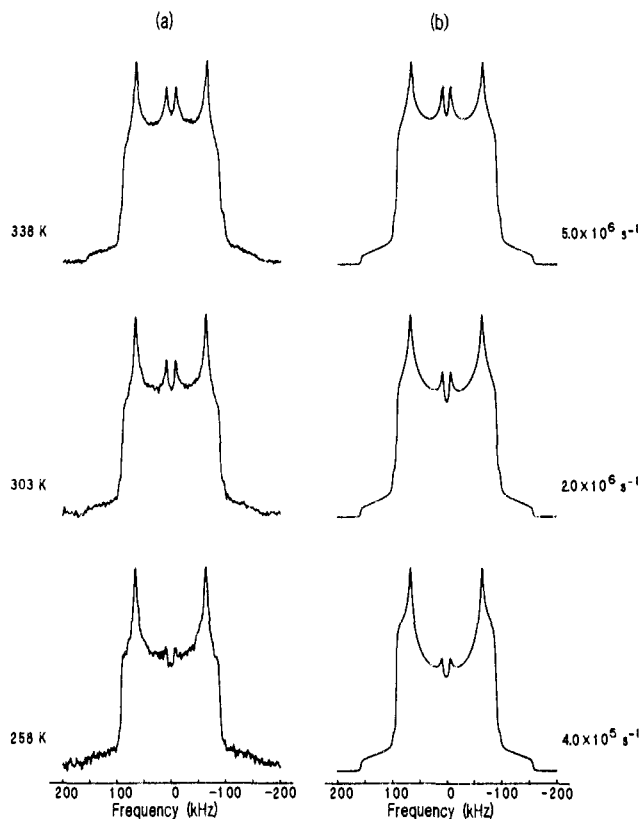
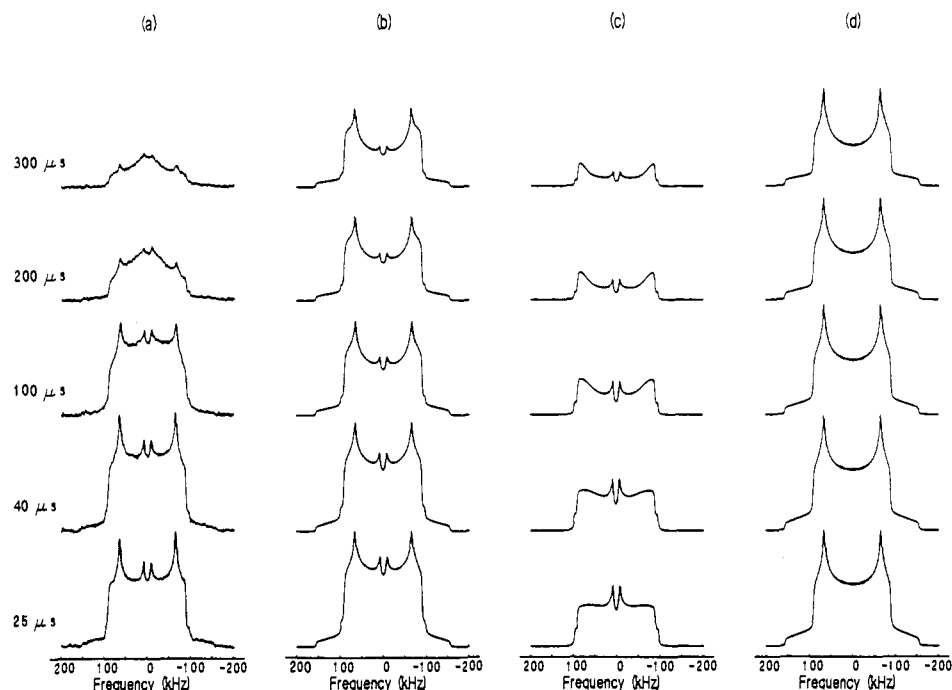


Figure 5. (a) Deuterium quadrupole echo spectra of urea- $d_4$ /C<sub>19</sub>H<sub>40</sub> obtained with a pulse spacing of  $40 \mu\text{s}$  at three temperatures. (b) Simulations calculated for urea deuterons with  $e^2 q Q / h = 208 \text{ kHz}$  and  $\eta = 0.155$  undergoing  $180^\circ$  jumps at  $4.0 \times 10^5$ ,  $2.0 \times 10^6$ , and  $5.0 \times 10^6 \text{ s}^{-1}$ . The angles,  $\beta$  and  $\beta'$  (i.e., the angles which the principal components of the quadrupole coupling tensors,  $q_{zz}$ , for the D and D' deuterons make with the C=O bond) were fixed at  $177^\circ$  and  $59^\circ$ , respectively.

of the N-D bonds, uncorrelated with the  $180^\circ$  jump motion, will result in an averaging of the deuterium quadrupole tensor components. Consequently, the  $e^2 q Q / h$  determined from fitting powder or single crystal line shapes is, in general, less than a "static"  $e^2 q Q / h$  value. Although our knowledge of the molecular geometry restricts  $\beta$  and  $\beta'$  to be close to  $180^\circ$  and  $60^\circ$ , respectively, deviations of several degrees from these angles are possible, in particular, since the principal Z axis of the deuterium quadrupole tensor need not lie along the N-D bonds. A better approach is to fit the experimental line shapes over a range of temperatures. Spectra have been recorded at several temperatures between 258 and 338 K. Three typical spectra obtained with a pulse spacing of  $40 \mu\text{s}$  are shown in Figure 5 together with a set of simulations calculated using  $e^2 q Q / h = 208 \pm 3 \text{ kHz}$ ,  $\eta = 0.155 \pm 0.005$ ,  $\beta = 177 \pm 3^\circ$ , and  $\beta' = 59.0 \pm 0.5^\circ$  and exchange rates as indicated. As for the case of pure urea, the  $e^2 q Q / h$  and  $\eta$  values obtained for the powder may be subject to additional errors since, again, no account has been taken to any possible  $^{14}\text{N}$ -D dipolar coupling. However, preliminary results from single crystal studies of UIC<sup>33</sup> agree with those derived here from the powder line-shape analysis.

Although the angles  $\beta$  and  $\beta'$  can be determined unequivocally, within the specified error limits, there remains some ambiguity in the angle  $\alpha$ . With our choice of molecular axes,  $\alpha$  is defined to be  $0^\circ$  and  $180^\circ$  for the two exchanging sites. However, in the case of the D deuterons, we do not know which of the two possible sites correspond to  $\alpha = 0^\circ$ . If it is assumed that the principal axes of the quadrupole interaction tensors are coincident with the N-D bonds, then, in terms of molecular geometry, this ambiguity implies that we are unable to determine whether the D-D internuclear distance is greater or shorter than the N-N distance. The same ambiguity also exists for the D' sites, but in this case there is only one physically reasonable possibility, the alternative situation requiring that the N-D' bonds be coincident with the C-N bonds. To our knowledge there has been no precise determination of the

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**Figure 6.** (a) Urea- $d_4$ / $C_{19}H_{40}$  quadrupole echo spectra recorded at 303 K as a function of pulse spacing. (b) Simulated line shapes for urea deuterons ( $e^2qQ/h = 208$  kHz,  $\eta = 0.155$ ,  $\beta = 177^\circ$ , and  $\beta' = 59^\circ$ ) undergoing  $180^\circ$  jumps about the carbonyl bond at a rate,  $k$ , of  $2.0 \times 10^6$  s $^{-1}$ , calculated using different pulse spacings. The experimental spectra and simulated line shapes are normalized by factors given by their total integrated intensities divided by those for the 25- $\mu$ s experimental spectrum or simulation, respectively. The experimental and simulated 25- $\mu$ s spectra are normalized such that they have the same maximum intensity. (c) Contribution to simulated line shapes from D' deuterons and (d) D deuterons, calculated as a function of pulse spacings. The spectra were calculated using the same parameters as those in (b). Normalization factors for the spectra in (c) and (d) are equal to their total integrated intensities divided by that for the 25- $\mu$ s simulation for the D deuterons.

urea hydrogen atom positions in inclusion compounds. However, in a neutron diffraction study of pure urea, the H...H distance was found to be slightly shorter than the N...N distance<sup>34</sup> corresponding to the CNH and NCN angles both being less than  $120^\circ$ , and a value of  $176.5 \pm 1.0^\circ$  was obtained for the angle which the N-H vector makes with the C=O bond. Similarly, a value of  $61.5 \pm 1.0^\circ$  was obtained for the angle made by the N-H' vector with the C=O bond. When comparing these results with the values for  $\beta$  and  $\beta'$  obtained from the deuterium line-shape analysis, it must be remembered that bond angles derived from the neutron diffraction study pertain to pure urea rather than the inclusion compound. Furthermore, neutron diffraction is sensitive to nuclear positions while  $^2H$  NMR monitors the orientation of the electric field gradient. Nevertheless, the values for  $\beta$  and  $\beta'$  derived here agree satisfactorily with those obtained from neutron diffraction data.

The deuterium spectra in Figure 5 show that the simple  $180^\circ$  jump model provides a reasonable description of the urea motion over the range of temperatures studied. While agreement between experimental and simulated spectra is not perfect, most notably at the lower temperatures, all essential features including the temperature dependence are reproduced. By fitting the line shapes at five temperatures between 258 and 338 K, we obtain an activation energy of  $23 \pm 2$  kJ mol $^{-1}$  for the urea motion. Since four hydrogen bonds are broken during each  $180^\circ$  jump, this means that the energy barrier for breaking each individual hydrogen bond is about 6 kJ mol $^{-1}$ . This rather low value is consistent with the bond lengths (2.98 and 3.03 Å) which are slightly greater than usual<sup>39</sup> and probably reflects the inefficiency of the oxygen atoms in supporting four hydrogen bonds each.

**Effect of Unresolved Dipolar Couplings.** Thus far we have restricted our discussion to the interpretation of quadrupole echo spectra obtained at just one relatively short (40  $\mu$ s) pulse spacing. However, it is desirable to investigate the effects of pulse spacing as well as temperature on the line shapes. A particular model for the molecular motion is usually regarded as a reasonable

description of the true dynamics only if both of these effects can be reproduced. Figure 6 shows the effect of pulse spacing on experimental spectra (a) recorded at 303 K together with simulated line shapes (b) obtained with a jump rate of  $2.0 \times 10^6$  s $^{-1}$ . It is apparent from Figure 6a,b that the  $180^\circ$  jump model described above cannot account for the pulse spacing dependence of the line shape. The separate simulations for D' and D deuterons in Figure 6 parts c and d, respectively, illustrate more directly the source of the discrepancy. For the D deuterons the calculations predict a long  $T_2$ , since for all crystallite orientations the difference in the quadrupole coupling,  $\Delta\omega_q$ , for exchanging D deuterons is much smaller than the jump rate. For the D' deuterons,  $\Delta\omega_q/k$  is as high as 0.1 for certain orientations, so that the  $T_2$  for the D' sites is relatively short and anisotropic. Consequently, we expect the relative contribution to the line shape from the D' deuterons as shown in Figure 6c to decrease with increasing pulse spacing. The experimental line shapes in Figure 6a, on the other hand, show that the D deuterons also have a short  $T_2$ , and the outer wings of the spectra, which derive solely from these sites, disappear at long pulse spacings. It appears that the central part of the powder pattern survives most strongly as the pulse spacing is increased.

The observed pulse spacing dependence seems to suggest that the two-site jump model for the urea motion is inadequate. This striking failure of the model to explain the observed deuterium line shapes for long pulse spacings is quite unexpected in view of its success in reproducing the temperature dependence of the line shape for short pulse spacings. Small deviations from the observed line shape are to be expected since other very slow or low amplitude fast motions must make some contribution. However, these processes are not expected to have such a profound effect on the  $T_2$  anisotropy as that observed experimentally. Several simulations were performed using multi-axis models for the urea motion, but no model was found which was able to reproduce the experimental results. Consequently, one must conclude that the  $T_2$  process responsible for the loss of intensity of the D part of the line shape does not result from the usual dephasing which accompanies multisite exchange.

In the present case, we ascribe the loss of transverse magnetization observed in the deuterium spectra of UIC to dephasing

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caused by unresolved dipolar couplings. There are two distinct mechanisms by which dipolar couplings can affect the observed deuterium  $T_2$ . One<sup>40</sup> involves the dephasing of static dipolar interactions which are not refocused in the quadrupole echo experiment. Both D-D and  $^{14}\text{N}$ -D dipolar couplings are present in urea- $d_4$  and will contribute to the dephasing. A second source of dephasing can arise if the spin-lattice relaxation rate of one of the coupled nuclei is comparable with the dipolar coupling.<sup>41</sup> This will not be important for the D-D couplings since the deuterium spin-lattice relaxation rate is too slow ( $T_1 \sim 40$  ms at 303 K). However,  $^{14}\text{N}$  has a large quadrupole moment ( $e^2qQ/h = 3.5$  MHz in pure urea<sup>42</sup> and, consequently, the  $^{14}\text{N}$  relaxation rate could be of the right order of magnitude to affect the  $^{14}\text{N}$ -D dipolar interaction. This type of "self-decoupling" mechanism has previously been observed in proton spectra of single crystals of *trans*-diiodoethylene.<sup>43</sup>

In principle, one might hope to determine the relative contributions of the different mechanisms to the deuterium transverse relaxation rate by conducting a more detailed analysis of the pulse spacing dependence of the line shapes. However, a rigorous treatment of all the dipolar couplings in UIC would be extremely time-consuming computationally and is beyond the scope of this paper. A more practical approach involves comparing the pulse spacing dependence of the echo amplitude for UIC with that found for pure urea- $d_4$ . It is useful then to consider qualitatively how each of the possible dephasing mechanisms is expected to affect the pulse spacing dependences for UIC and pure urea- $d_4$ . In the event that the static D-D' dipolar interaction is the principal cause of dephasing, we should expect to observe a shorter  $T_2$  for pure urea- $d_4$  since the D-D' interactions in the pure compound are larger by a factor of about  $((3 \cos^2 30^\circ - 1)/2)^{-1} = 1.6$  than those in UIC where these interactions are averaged by the  $180^\circ$  jump motion. On the other hand, if the N-D static dipolar interaction is primarily responsible for the loss of magnetization, then we should expect to observe similar pulse spacing dependences for the "rigid" part of the UIC spectrum and pure urea- $d_4$  (at least for long pulse spacings when most of the UIC D' magnetization has already decayed) since this interaction is largely unaffected by the jump motion in UIC. Finally, if the dominant  $T_2$  process in UIC is the partial decoupling of the N-D and N-D' dipolar interactions caused by rapid transitions between the  $^{14}\text{N}$  spin states, then the UIC deuterons should have significantly shorter  $T_2$ 's than those in pure urea- $d_4$ .

Figure 7 shows the pulse spacing dependence of the echo amplitude measured for powder samples of urea- $d_4$  and UIC at 303 K. It is clear from Figure 7 that in both materials the transverse magnetization decays approximately exponentially at about the same rate ( $T_2 \sim 430$   $\mu\text{s}$ ). In the case of pure urea- $d_4$  there is an additional modulation in the decay curve which is consistent with static N-D dipolar dephasing.<sup>33</sup> The considerable reduction in amplitude of the modulation observed for UIC indicates that in this compound the N-D and N-D' interactions experience some degree of self-decoupling. Single-crystal studies of UIC have also been carried out and these provide more concrete evidence of this mechanism.<sup>33</sup> We note that a similar modulation in the echo amplitude is predicted for a system of isolated dipolar coupled D-D spin pairs.<sup>44</sup> However, in the case of urea- $d_4$ , the predicted modulation frequency resulting from the D-D' interaction is too low to be detectable over the range of pulse spacings used here. Nonetheless, dephasing of the D-D' coupling is expected to reduce the observed  $T_2$  for the deuterium powder echo.

Without performing detailed calculations accounting for all the possible interactions contributing to  $T_2$  in UIC, it is difficult to predict the deuterium powder line shapes for long pulse spacings.

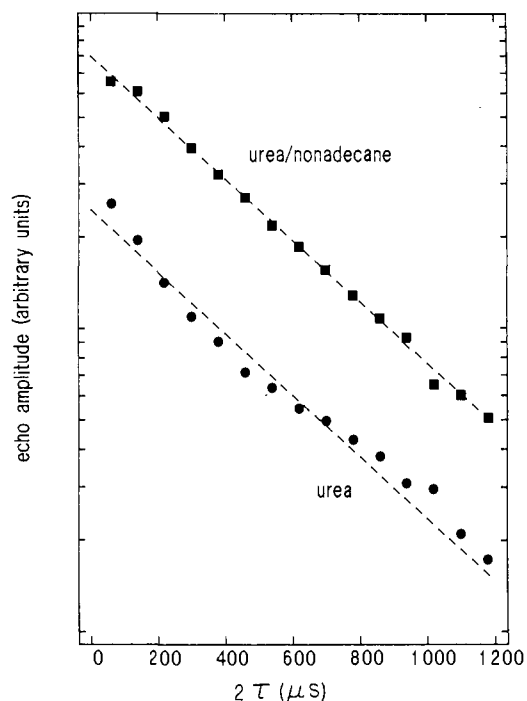


Figure 7. Echo amplitudes following a quadrupole echo sequence for urea- $d_4$  and  $\text{C}_{19}\text{H}_{40}/\text{urea-}d_4$  plotted as a function of  $2\tau$  where  $\tau$  is the pulse spacing. The dashed lines represent the purely exponential decays with a  $T_2$  of 430  $\mu\text{s}$ .

In the case of the static N-D interaction, this is expected to be most effective as a cause of dephasing in the wings of the spectrum where the coupling is greatest. However, if  $^{14}\text{N}$  spin-lattice relaxation also shortens the deuterium  $T_2$ , then this will depend on both the N-D dipolar interaction and the (anisotropic)  $^{14}\text{N}$  transition rates. The overall effect on the line shape will be rather complex. On the other hand, in the central part of the spectrum, where the N-D dipolar interaction is weak, the effects of both the static coupling and any N-D self-decoupling should be least important. The results in Figure 6a show that  $T_2$  for this part of the spectrum is indeed relatively long, suggesting that the N-D dipolar interaction plays an important role in the overall  $T_2$  process for UIC. Conversely, the D-D' dipolar interaction has an orientation dependence different from those of the quadrupole and N-D dipolar interactions (i.e., the D-D' internuclear vector is obviously not collinear with the N-D or N-D' bonds). Indeed, in the central region of the deuterium powder line shape ( $\omega_q \sim 0$ ), the D-D' interaction is relatively strong. Thus, if this interaction was principally responsible for the short  $T_2$  observed in UIC, we should expect the central part of the spectrum to decay relatively quickly. While it is certain that the D-D' interaction makes some contribution to the overall dephasing of magnetization, the experimental results for UIC are not consistent with this being the primary cause of the discrepancies between the experimental and simulated line shapes in Figure 6, parts a and b.

One surprising aspect of the results in Figure 7 is that the echo amplitudes for urea- $d_4$  and UIC decay exponentially. For systems of rigid deuterium nuclei containing dipole-dipole couplings the powder echo amplitude following a  $(\pi/2)_0 - \tau - (\pi/2)_{\pi/2} - \tau$  pulse sequence is generally found to be approximately Gaussian in  $\tau$ ,<sup>40</sup> although exact expressions for rigid systems of isolated D-D or N-D spin pairs predict more complicated functions for the  $\tau$  dependence of the echo.<sup>33,44</sup> Presumably, for urea- $d_4$  and UIC, several dephasing mechanisms combine to produce an effective process which coincidentally results in an approximate exponential decay of the transverse magnetization over the range of  $\tau$  values used in these experiments.

## Conclusions

By analysis of deuterium NMR powder line shapes we have shown that urea molecules in UIC undergo  $180^\circ$  jump motion

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about their carbonyl bonds. The motion occurs at a rate of  $\sim 2 \times 10^6 \text{ s}^{-1}$  at room temperature and has an activation energy of  $23 \pm 2 \text{ kJ mol}^{-1}$ . This value may be interpreted as the energy associated with the breaking of four hydrogen bonds. Thus, each individual hydrogen bond experiences a barrier of about  $6 \text{ kJ mol}^{-1}$ , a rather low value which probably reflects the inefficiency of the oxygen atoms in supporting four hydrogen bonds.

A quadrupole coupling constant,  $e^2qQ/h = 212 \pm 2 \text{ kHz}$  and asymmetry parameter,  $\eta = 0.145 \pm 0.005$  were determined for the deuterons in pure urea- $d_4$ , while the same parameters in UIC were found to be  $208 \pm 3 \text{ kHz}$  and  $0.155 \pm 0.005$ , respectively. In UIC, the  $180^\circ$  jump motion distinguishes those deuterons for which the N-D bond makes an angle of approximately  $60^\circ$  with the jump axis (i.e., the C=O bond) from those for which the N-D bond is virtually parallel with this axis. Values of  $59.0 \pm 0.5^\circ$  and  $177 \pm 3^\circ$ , respectively, were determined for the angles made by the principal components of the electric field gradient tensors of the two types of deuterons with the jump axis, in good agreement with values found by neutron diffraction for the angles which the N-D vectors make with C=O bond in pure urea. For the D' deuterons it was found that the X component (i.e., the component with the smallest absolute value assuming  $\eta = (V_{xx} - V_{yy})/V_{zz} \geq 0$ ) of the principal electric field gradient tensor lies in the urea plane.

While the  $180^\circ$  jump model for the urea motion is able to reproduce the deuterium line shape for short pulse spacings over a range of temperatures, it does not account for the pulse spacing dependence of the line shape. This inability to explain the spectra obtained with long pulse spacings results not from any major flaw in the model proposed for the urea motion, but instead arises from a significant anisotropic contribution to the deuterium transverse relaxation rate from unresolved D-D and especially N-D dipolar couplings. Such dipolar interactions will, in general, cause dephasing of the transverse magnetization in quadrupole echo experiments and may be expected to complicate the line shape analysis at long pulse spacings. In addition, comparison of the pulse spacing dependence of the echo amplitude for pure urea- $d_4$

with that for UIC indicates some degree of self-decoupling of the N-D interaction in UIC. This effect, due to transitions between the  $^{14}\text{N}$  spin states occurring at frequencies comparable to or higher than the N-D dipolar coupling, can be shown to provide an anisotropic contribution to the deuterium  $T_2$ . Although we have not attempted a detailed quantitative analysis of the pulse spacing dependence of the UIC deuterium line shapes, the expected contribution from these mechanisms is consistent with the observed discrepancies between experimental and simulated line shapes. Their relative importance is currently under evaluation in a relaxation study on single crystals of UIC.

Having identified the nature and rate of urea motion in the  $\text{C}_{19}\text{H}_{40}$  complex, it is natural to consider what implications this type of motion might have on the stability and other properties of the complex. In view of the dimensions of the channels, it is conceivable that there is some relationship between the urea motion and the character and dynamics of guest molecules. It is known that the correlation times for the  $\text{C}_{19}\text{H}_{40}$  motion are short, typically about  $10^{-12} \text{ s}$ ,<sup>17,45</sup> compared with the lifetime for the urea flipping process ( $\sim 10^{-6} \text{ s}$ ), suggesting that the guest and host dynamics are essentially independent. Nonetheless, there remains the possibility that there is some connection between the length of the guest molecules and the rate of urea motion. Accordingly, we are investigating the effect of the alkane by performing relaxation measurements on  $\text{C}_{36}\text{H}_{74}$  and  $\text{C}_8\text{H}_{18}$  urea adducts. It would be of interest to explore this possibility further by investigating the behavior of urea complexes with other types of guest such as fatty acids, for instance, which contain chemically more diverse groups and whose motion is considerably slower<sup>15</sup> than that of the alkanes.

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## Anisotropy of the $^1\text{H}$ and $^{13}\text{C}$ Chemical Shifts and of the $^{13}\text{C}$ - $^{14}\text{N}$ Spin-Spin Couplings of Methyl Isocyanide As Determined by NMR in Nematic Mesogens

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**Abstract:** Proton and carbon-13 chemical shift anisotropies have been determined for methyl isocyanide by applying the NMR method which utilizes a proper mixture of nematic liquid crystals with opposite diamagnetic anisotropies. The resulting anisotropies,  $\Delta\sigma$ , are the following:  $4.26 \pm 0.01 \text{ ppm}$  for proton,  $52.4 \pm 0.3 \text{ ppm}$  for the  $\text{CH}_3$  carbon, and  $359 \pm 5 \text{ ppm}$  for the NC carbon. The agreement between the experimental and recently published theoretical anisotropies for carbon-13 nuclei is very good. The anisotropies of the indirect  $^{13}\text{C}$ - $^{14}\text{N}$  spin-spin coupling tensors,  $\Delta J$ , were determined by applying a new approach which takes into consideration the deformational contributions both in the direct dipolar couplings and in the corresponding anisotropic indirect couplings. The analysis yielded the values of  $8.7 \pm 1.7$  and  $42.8 \pm 2.8 \text{ Hz}$  for the couplings over the single and triple CN bonds, respectively.

### I. Introduction

The NMR spectroscopy of molecules partially oriented in liquid crystals (LCNMR) has been applied to the determination of chemical shift as well as spin-spin coupling anisotropies almost since the invention of the technique in 1963.<sup>1</sup> The early experiments were, however, in most cases carried out in only one

liquid crystal solvent, which prevented researchers from becoming aware of the remarkable solvent dependence of these quantities. Furthermore, chemical shift anisotropies were derived by methods which today are known to lead to large errors. The various techniques proposed and applied until recently are described in the review of Lounila and Jokisaari.<sup>2</sup>

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