*J. Am. Chem. Soc.* **1984**, *106*, 2267–2270

Coriolis interaction were off by 25–307 MHz for the measured transitions of $J > 30$. Further least-squares refinement using the Nielson/Halonen program led to the fit which is shown in Table III. The agreement can be improved using sextic C.D. constants. The final rotational constants, quartic C.D. constants, and Coriolis parameters for parent malonaldehyde are included in Table I. Thus this experiment unambiguously shows the two-level coupled Hamiltonian model to be much more accurate than the separate effective Hamiltonian,[3] and the value of 21.583 cm$^{-1}$ for $\Delta E_{01}$ from the microwave spectra should be quite reliable. This gives a period $\tau$ in which the H atom oscillates between the two wells of 0.8 ps, where $\tau = h/2\Delta E_{01}$. This result was used in paper 3 to help determine the barrier.

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**Registry No.** Malonaldehyde, 542-78-9.

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# Molecular Motions in the Solid Phases of *n*-Heneicosane: A $^{2}$H NMR Study

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**Abstract:** The nature and rate of the molecular motions undergone by heneicosane in the orthorhombic (phase I) and rotator (phase II) phases were investigated. Individual samples of heneicosane, specifically deuterated at positions 2, 4, 6, and 11, were studied at various temperatures by $^{2}$H NMR. The spectra of phase I indicate that the central portion of the chain is immobile on the $^{2}$H NMR time scale (10$^{5}$ s$^{-1}$). At low temperatures this is also the case at the ends of the chains. However, as the temperature approaches that of the transition to phase II ($T_{\mathrm{I}\rightarrow\mathrm{II}}$), a torsional motion is introduced near the ends of the chain. In phase II the data provide evidence for the chains undergoing hindered rotation. They also support the existence of a gauche population concentrated near the chain ends.

The long-chain *n*-alkanes, containing an odd number of carbon atoms, are known to undergo a solid–solid phase transition some 2–15 °C prior to melting.[1-3] The low-temperature phase (phase I) has chains which are all-trans and packed parallel to each other in an orthorhombic unit cell. The higher-temperature phase, phase II (also called the rotator or hexagonal phase), is characterized by an expansion of the unit cell dimensions[4] and the onset of hindered rotation about the chain long axis.[5-8] Andrew has suggested that in phase II there is a cooperative molecular motion around the long axis of the chain, much as in the manner of a set of meshed gears.[5] A $^{1}$H NMR relaxation study of the C$_{19}$ *n*-alkane in phase II showed that the relaxation of the methylene protons has contributions from two mechanisms.[6] These are proposed to be a fast rotational reorientation of the entire alkane as a rigid rotator and a slow diffusion of the alkane. The fast reorientation has a mean jump time much less than 10$^{-9}$ s. This corresponds to inelastic neutron scattering results which indicate that the alkane chains exist in an all-trans configuration and reorientation has a mean jump time of approximately $3.5 \times 10^{-12}$ s.[7]

In a recent $^{2}$H NMR study[8] of deuterated nonadecanes, phase II was modeled with an acyl chain undergoing fast (>10$^{7}$ s$^{-1}$), 82° jumps between equivalent sites. However, the $^{2}$H NMR results also indicated that the chains do not reorient as a rigid rotator. Rather, the ends of the chain undergo higher amplitude torsional motions than the center.

Phase II is also characterized by the appearance of gauche rotamers.[2,3,9,10] Infrared studies have shown that populations are greatest at the ends of the chains and that the gauche population increases as the temperature is increased within phase II.[9] In the case of heneicosane ($n$-C$_{21}$H$_{44}$) as many as 8% of the chains contain a gauche rotamer at the 2 positions, just prior to the phase II melt.

In this paper we report on a study of the temperature dependence of the $^{2}$H NMR spectra of several specifically deuterated heneicosanes. In phase I the data provide evidence for torsional motions near the chain ends at temperatures near that of the transition from phase I to phase II. In phase II there is evidence for hindered rotation and a positional-dependent gauche population.

## Experimental Section

The synthesis of the heneicosanes deuterated at positions 2 (C$_{21}$-*2,2*-*d*$_2$), 4 (C$_{21}$-*4,4*-*d*$_2$), 6 (C$_{21}$-*6,6*-*d*$_2$), and 11 (C$_{21}$-*11,11*-*d*$_2$) has been reported elsewhere.[11] Gas chromatography showed the C$_{21}$-*11,11*-*d*$_2$ to be approximately 95% pure, while all other compounds were better than 99% pure. Mass spectroscopy showed that less than 3.5% of the methylenes were CH$^{2}$H.[11]

The $^{2}$H NMR spectra were acquired on a Bruker CXP-300 spectrometer operating at 46.063 MHz. The quadrupole echo technique[12] with full phase cycling of the radio-frequency pulses was used with a pulse spacing of 50 $\mu$s between $\pi/2$ pulses of 6 $\mu$s. For phase I spectra

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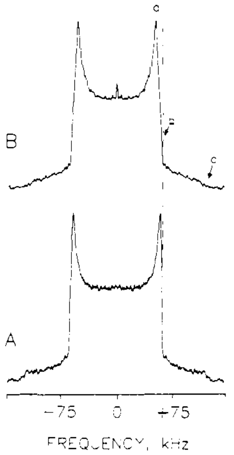

**Figure 1.** $^2H$ NMR spectra of $C_{21}$-*2,2-d*$_2$ at (A) −30 °C and (C) 25 °C. The broken line is at the rigid limit quadrupole splitting of 122 kHz. $V_{XX}{}^J$, $V_{YY}{}^J$, and $V_{ZZ}{}^J$ are labeled as a, b, and c, respectively.

the pulses were 3 μs (45°) in order to achieve more complete excitation across the pattern.[13] Recycle times were 60 s (for phase I spectra) and 3 s (for phase II spectra) with a 1-MHz spectral width. Between 200 and 2000 scans were collected, and the spectra were acquired on resonance and folded, thereby increasing signal to noise by $2^{1/2}$. Spectra were checked prior to folding in order to ensure that no distortion was introduced.

Samples were run in 10-mm tubes which had been sealed on a vacuum line. The sample temperature was controlled by passing heated air into an insulated glass dewar which enclosed the sample and coil. Samples were allowed to equilibrate for 15 to 30 min at a given temperature prior to acquisition. Since the spectra acquired just below the melt show both phase II spectra and a narrow line, it would suggest a slight temperature gradient across the sample cavity.

## Results

**(i) Phase I.** Figure 1, A and B, shows the $^2H$ NMR spectra of $C_{21}$-*2,2-d*$_2$ at −30 °C and 25 °C, respectively, with the broken line indicating the rigid limit quadrupole splitting. The −30 °C spectrum is a typical rigid limit spectrum[14] and was observed for all heneicosanes at this temperature. This is characteristic of $C^2H_2$ groups which are static on the $^2H$ NMR time scale; that is, they are not subject to large amplitude motions at a rate greater than $10^5$ s$^{-1}$. At 25 °C (7.5 °C below $T_{I \to II}$) the spectral width is reduced from the rigid limit, indicating the presence of rapid motions of small, but finite amplitude, in the $C_{21}$-*2,2-d*$_2$ crystal.

A close examination of the spectrum of $C_{21}$-*2,2-d*$_2$ at 25 °C reveals a non-zero asymmetry parameter ($\eta$), defined as[14]

$$\eta = (V_{XX} - V_{YY})/V_{ZZ} \qquad (1)$$

where $V_{XX}$, $V_{YY}$, and $V_{ZZ}$ are the principal components of the electric field gradient tensor.[15] Since the quadrupolar splitting tensor usually has axial symmetry in $sp^3$ hybridized systems, this asymmetry most likely arises from asymmetric motions, similar to those found earlier in nonadecane.[8]

At 25 °C the spectrum of $C_{21}$-*2,2-d*$_2$ yields an asymmetry parameter of 0.06 while for $C_{21}$-*4,4-d*$_2$ at the same temperature $\eta = 0.03$. For labels at position 6 and 11 the asymmetry parameter is zero, and a rigid limit $^2H$ NMR spectrum is obtained. This indicates that the segment $C_6$–$C_{16}$ is immobile on the $^2H$ time scale. However, there are motions, which are fast on the $^2H$ time scale, localized at the ends of the chains.

Figure 2 shows the temperature dependence of the asymmetry parameter of $C_{21}$-*2,2-d*$_2$ in phase I. As the temperature is reduced, so is $\eta$; however, non-zero values of $\eta$ persist until at least −10 °C below $T_{I \to II}$. A similar trend is evident in the spectrum of $C_{21}$-*4,4-d*$_2$, with the rigid limit spectrum being observed at 0 °C.

**(ii) Phase II.** The $^2H$ NMR spectra of $C_{21}$-*11,11-d*$_2$ and $C_{21}$-*2,2-d*$_2$ at 33 °C (0.5 °C above $T_{I \to II}$) and 39 °C (1.5 °C below $T_{melt}$) are shown in Figure 3. As with nonadecane,[8] the phase II spectra are substantially narrower than those of phase I. The spectra are also highly asymmetric, and the degree of asymmetry varies substantially with temperature and position.

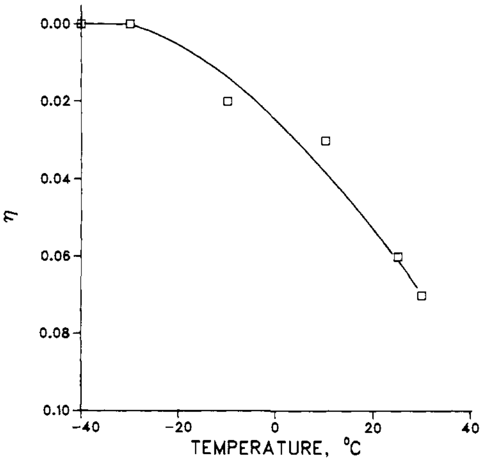

**Figure 2.** Variation of the asymmetry parameter, η, with temperature for $C_{21}$-*2,2-d*$_2$ in phase I.

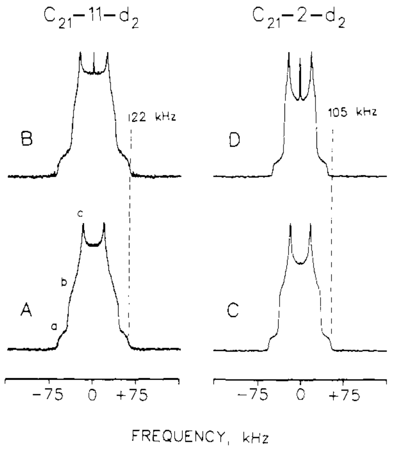

**Figure 3.** $^2H$ NMR phase II spectra of $C_{21}$-*11,11-d*$_2$ at (A) 33 °C and (B) 39 °C and $C_{21}$-*2,2-d*$_2$ at (C) 33 °C and (D) 39 °C. The broken lines indicate $V_{YY}{}^J$, and a, b, and c represent the $V_{YY}{}^J$, $V_{ZZ}{}^J$, and $V_{XX}{}^J$ components, respectively.

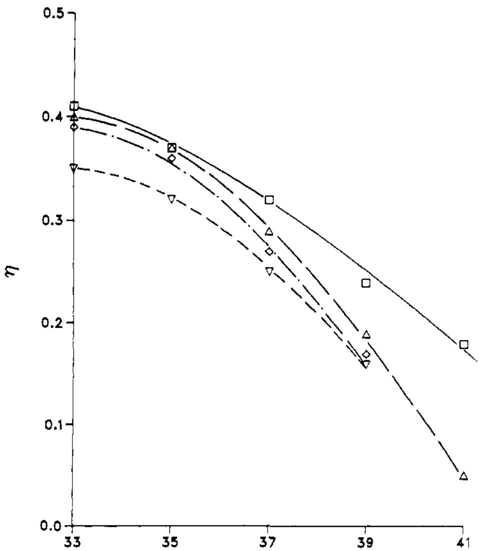

**Figure 4.** The variation of the asymmetry parameter, η, with temperature for the four labeled positions: $C_{12}$-*11,11-d*$_2$ (—), $C_{21}$-*6,6-d*$_2$ (– – –), $C_{21}$-*4,4-d*$_2$ (-·-), and $C_{21}$-*2,2-d*$_2$ (-·-).

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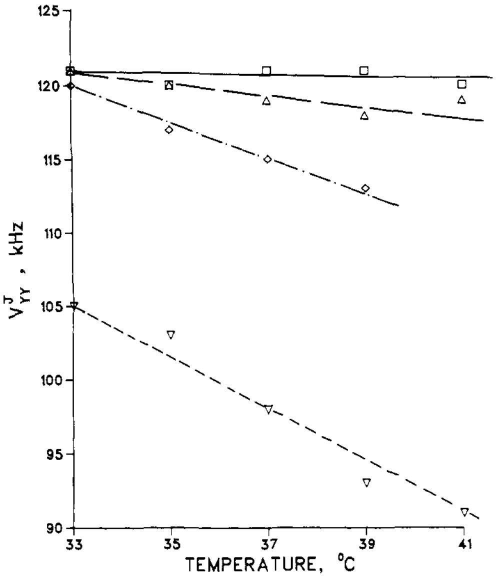

**Figure 5.** The variation of the $V_{YY}{}^J$ component of the jumping frame tensor with temperature for the four labled positions: $C_{21}$-*11,11-d*$_2$ (—), $C_{21}$-*6,6-d*$_2$ (– – –), $C_{21}$-*4,4-d*$_2$ (·–·), $C_{21}$-*2,2-d*$_2$ (– · –).

Figure 4 shows the phase II temperature and positional dependence of the asymmetry parameter, $\eta$. It encompasses a range of 0.41 ($C_{21}$-*11,11-d*$_2$ at 33 °C) to 0.02 ($C_{21}$-*2,2-d*$_2$ at 41 °C). At a given temperature, the closer the $C^2H_2$ group is to the end of the chain, the lower the value of $\eta$, and at a given chain position, the higher the temperature, the lower the value of $\eta$.

A comparison of the spectra in Figure 3 also shows that the spectral feature with the largest frequency separation (the shoulders, marked with a broken line) is constant at 122 kHz in the spectra of $C_{21}$-*11,11-d*$_2$ at all temperatures in phase II. This feature corresponds to the component of the electric field gradient tensor along the chain long axis ($V_{YY}{}^J$). However, $V_{YY}{}^J$ is less for $C_{21}$-*2,2-d*$_2$ in phase II and decreases as the temperature is raised. Figure 5 shows the temperature and positional dependence of this spectral feature in phase II. At 33 °C, only the spectrum of $C_{21}$-*2,2-d*$_2$ has shoulders significantly less than 122 kHz, indicating substantial off-axis motion of the chain.[14] As the temperature is raised, all positions, except the center of the chain, show evidence of the introduction of such motions, with the motions being greatest at the ends of the chain.

## Discussion

In the presentation of the results, two parameters have been emphasized: the asymmetry parameter ($\eta$) and the component of the electric field gradient tensor which lies along the long axis of the acyl chain. In order to rationalize the variation of these two parameters, we must consider the effect of both the onset of rapid restricted jumps and the appearance of gauche rotamers.

The asymmetry of the spectra can be modeled by allowing the chains to undergo rapid jumps between two equivalent sites, in a plane perpendicular to the long axis of the acyl chain. The components of the electric field gradient tensor ($V_{XX}$, $V_{YY}$, $V_{ZZ}$) in the two static orientations, before and after a jump of angle $\theta$, can be transformed and averaged into a jumping frame tensor ($V^J$).[8] The resulting components of $V^J$ are

$$V_{XX}{}^J = V_{XX}\cos^2\frac{\theta}{2} + V_{ZZ}\sin^2\frac{\theta}{2} \qquad (2)$$

$$V_{YY}{}^J = V_{YY} \qquad (3)$$

$$V_{ZZ}{}^J = V_{XX}\sin^2\frac{\theta}{2} + V_{ZZ}\cos^2\frac{\theta}{2} \qquad (4)$$

It is clear from the above equations that a reorientation of the acyl chain will cause an averaging of the $V_{XX}$ and $V_{ZZ}$ components of the static tensor (to give $V_{XX}{}^J$ and $V_{ZZ}{}^J$), while leaving the tensor component along the chain long axis ($V_{YY}$ or $V_{YY}{}^J$) unchanged.[16]

Table I. Phase II Gauche Concentrations (%) of Heneicosanes on the Basis of Infrared[9] and $^2$H NMR[19] Data

| | infrared; $T$, °C | | $^2$H NMR;[a] $T$, °C | |
|---|---|---|---|---|
| position | 33 | 39 | 33 | 39 |
| 2 | 4.0 ± 0.5 | 8.7 ± 0.5 | 7 | 10 |
| 4 | 2.0 ± 0.8 | 4.0 ± 0.5 | 1 | 4 |
| 6 | 0.5 ± 0.3 | 1.1 ± 0.3 | 0 | 1 |
| 11 | 0.4 ± 0.4 | 0.7 ± 0.3 | 0 | 0 |

[a] The concentrations determined by $^2$H NMR are all ±1%.

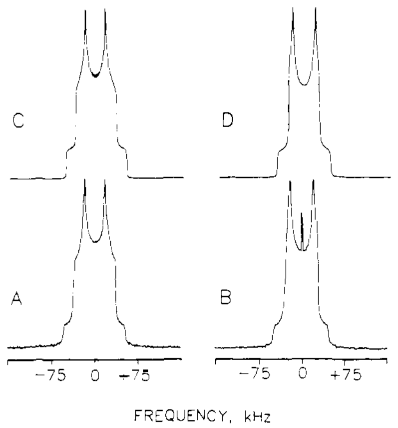

**Figure 6.** $^2$H NMR spectra of $C_{21}$-*2,2-d*$_2$ at (A) 33 °C and (B) 39 °C. Simulations are of the 33 °C spectrum (C) [$V_{YY}{}^J$ = 105 kHz, $\theta$ = 83°, line width = 500 Hz] and the 39 °C spectrum (D) [$V_{YY}{}^J$ = 92.8 kHz, $\theta$ = 85°, line width = 750 Hz].

This model was employed in our previous study of nonadecane.[8] Since then it has been shown that small concentrations of gauche rotamers can contribute substantially to a reduction in the $V_{YY}{}^J$ tensor component, if those rotamers experience rapid trans-gauche isomerization.[17] Recent infrared data on these heneicosanes[9] provide quantitative estimates of the gauche populations in the different phases, and this should allow a separation of the effects of chain jumps and gauche rotamers.

In phase I, the only evidence for gauche rotamers is for an extremely low (<1% of all C–C–C bonds) population immediately below $T_{\mathrm{I}\to\mathrm{II}}$.[9,18] There is no evidence for gauche rotamers persisting beyond a point 2–3 °C below $T_{I\to\mathrm{II}}$. Therefore, the non-zero $\eta$ values indicate the occurrence of rapid ($>10^5$ s$^{-1}$), small-angle jumps at the ends of the chains with, possibly, some slight off-axis motion. In other words, torsional oscillations occur in the regions $C_1$–$C_5$ and $C_{17}$–$C_{21}$. When this model is used, phase I spectral simulations employing eq 2–4 indicate a jump angle of 22° for $C_{21}$-*2,2-d*$_2$ and 10° for $C_{21}$-*4,4-d*$_2$ at 25 °C. As the temperature

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(15) For the deuterated alkanes in phase I, $V_{YY}$ lies along the chain long axis, $V_{ZZ}$ lies along the C–$^2H_2$ bond, and $V_{XX}$ is perpendicular to $V_{ZZ}$ and $V_{YY}$. (See ref 8 and 14 for more complete details.)

(16) For a rigid limit spectrum the static tensor has $V_{XX} = V_{YY} = \pm 122$ kHz while $V_{ZZ} = \pm 244$ kHz (the sign cannot be determined). For an acyl chain executing jumps of less than 70° about the chain long axis, the averaging of the $V_{XX}$ and $V_{ZZ}$ components will still leave $V_{ZZ}{}^J > V_{YY}{}^J > V_{XX}{}^J$. This is seen in the spectrum of $C_{21}$-*2,2-d*$_2$ in phase I (Figure 1B) where the spectral features $V_{XX}{}^J$, $V_{YY}{}^J$, and $V_{ZZ}{}^J$ are labeled as a, b, and c, respectively. For jumps of greater than 70°, as occur in phase II, the averaging of the tensor leaves the $V_{YY}$ component with the largest absolute magnitude. Convention (see ref 14) requires that the largest component of the tensor be labeled as the $Z$ component so it is necessary to relabel the tensor components (see ref 8 for complete details). For the purpose of this work, however, it is sufficient to note that the largest spectral feature, calculated by using eq 2–4, is $V_{YY}{}^J$ (labeled as a in Figure 3A). $V_{XX}{}^J$ and $V_{ZZ}{}^J$ are labeled as c and b, respectively. Values of $\eta$ are simply

$$\eta = (b - c)/a$$

where $a$, $b$, and $c$ are the measured frequencies in kHz.

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Table II. Jump Angles vs. Position in Phase II of Heneicosane

| position | 33 °C | 39 °C | 41 °C |
|---|---|---|---|
| 2 | 83.0 | 85.0 | 89.5 |
| 4 | 81.8 | 84.7 | |
| 6 | 82.0 | 84.7 | 87.4 |
| 11 | 82.2 | 83.5 | 86.4 |

is reduced the torsion is frozen out, and it is absent at position 4 at 0 °C and position 2 at −20 °C.

In phase II infrared spectroscopy has demonstrated the existence of a positional- and temperature-dependent population of gauche rotamers. Table I lists these populations, together with those which would be estimated on the basis of the reduction in the $V_{YY}{}^J$ spectral features shown in Figure 5.[19] There is quite good agreement, and it is apparent that substantial off-axis motion occurs in phase II and that it can be largely attributed to the introduction of gauche rotamers.

However, even with gauche rotamers taken into account, the spectra are still typical of $C{-}^2H_2$ groups undergoing hindered rotation.[8] This is particularly well demonstrated for the $C_{21}$-*11,11-*$d_2$ spectra, where $\eta$ is large, and decreases with increasing temperature, while the average gauche population is very low and varies from 0.4% to 0.8%. The phase II spectra were thus simulated by using the restricted jump model, having first assumed that trans-gauche isomerization had modulated the electric field gradient tensor. The results of the simulations of $C_{21}$-*2,2-*$d_2$ spectra are shown in Figure 6, while Table II lists the jump angles required as a function of temperature and position. Near $T_{I\rightarrow II}$ the jump angle is virtually constant in positions 4–18, but larger at positions 2 and 20. As the temperature is increased to 41 °C the jump angle at position 2 and 20 increases by 6.5° compared to 4.2° at position 11. These data indicate that the predominant motions in phase II are hindered rotation and fast trans-gauche isomerization.

We should emphasize that the two site jump model employed here is only one of several possible choices.[17,23] For example, jumps of fixed angle between states of variable population could yield similar spectra. As yet there appears to be no means to distinguish unequivocally between these models. The derived $\theta$ values must therefore be considered as empirical parameters useful for comparison of behavior at different positions and temperatures. However, our analysis in terms of two types of motion, rapid gauche-trans interconversion, and limited torsional oscillation is unequivocal.

Recent X-ray studies of *n*-alkanes[4] have demonstrated that, within phase II, the cross-sectional area of the unit cell increases as the temperature is raised, permitting more mobility about the long axis. The rate of change of the ratio $a/b$, where $a$ and $b$ are the unit cell dimensions, is nonlinear and correlates with the nonlinear rate of change of $\eta$ (Figure 4). We have also found that in phase II the rate of introduction of gauche rotamers into the 2 position of 2,2-dideuteriononadecane is nonliner, increasing with increasing temperature.[20] This suggests that all three effects are interrelated, but the causative factor remains unexplained, particularly as recent studies have demonstrated further weak transitions within phase II.[21,22]

## Conclusion

When considered in conjunction with the evidence for a negligible phase I gauche population, the $^2H$ NMR spectra of the selectivity deuterated heneicosanes indicate that in this phase the $C_6$–$C_{16}$ segment of the chain is rigidly packed and immobile on a time scale of $10^5$ s$^{-1}$. However, there is present a torsional motion in the $C_5$–$C_1$ and $C_{17}$–$C_{21}$ segments, with an amplitude of 10–20° at temperatures just below $T_{I\rightarrow II}$. As the temperature is reduced the amplitude of the torsion decreases, and it is not present below −30 °C.

Recent studies have shown that the phase II structure and dynamics are complex, and temperature dependent. These data indicate that temperature-dependent, hindered rotation and fast trans-gauche isomerization are the principle disordering mechanisms in phase II.

**Registry No.** $CH_3CD_2(CH_2)_{18}CH_3$, 86369-65-5; $CH_3(CH_2)_2CD_2(CH_2)_{16}CH_3$, 84010-39-9; $CH_3(CH_2)_4CD_2(CH_2)_{14}CH_3$, 86369-66-6; $CH_3(CH_2)_9CD_2(CH_2)_9CH_3$, 86369-67-7.

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(19) The gauche populations were estimated by comparing our measured $V_{YY}{}^J$ components with the quadrupole splittings determined in simulations of specifically deuterated phosphatidylethanolamine (PE) acyl chains in their gel state (see ref 17). These simulations had PE undergoing 120° rotational jumps about the long axis, with fast trans-gauche isomerization superimposed. Rapid 120° jumps will not affect $V_{YY}$ (or $V_{YY}{}^J$) and will leave it as the largest spectral feature in the spectrum of gel-state PE. However, rapid jumps between a trans orientation ($C{-}^2H$ at 90° to the long axis) and a gauche orientation ($C{-}^2H$ at 35.3° to the long axis) will modulate $V_{YY}{}^J$. Gauche populations of approximately 7% were sufficient to reduce $V_{YY}{}^J$ by 21 kHz from the rigid limit spectrum of PE.

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# The Distribution of Carbon in Boron Carbide: A $^{13}C$ Nuclear Magnetic Resonance Study

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*Contribution from AT&T Bell Laboratories, Murray Hill, New Jersey 07974.*

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**Abstract:** The symmetry and local bonding of carbon in boron carbide ($B_{12}C_3$) are studied with $^{13}C$ nuclear magnetic resonance (NMR) spectroscopy. The $^{13}C{-}^{11}B$ heteronuclear dipolar couplings determined from the results of spin–echo experiments indicate that carbon is present only as $C_3$ chains. That is, there is no evidence of boron substituting for the middle carbon atom in the chain. The chemical shift powder patterns resolved from the experimental spectra indicate environments consistent with the assignments based on dipolar couplings. From the spectral assignments made in this study it is proposed that the distribution of carbon in samples of boron carbide can be determined from the isotropic shifts resolved by magic-angle spinning. In addition, this study demonstrates the applicability of a spin-diffusion model to analyze heteronuclear couplings and presents a formalism to separate overlapping spectra.

The crystal structure of boron carbide, $B_{12}C_3$, as proposed originally from X-ray diffraction studies,[1,2] is a rhombohedral arrangement of two structural units: icosahedra of boron atoms and linear chains of three carbon atoms. The boron atoms are