Distribution of Gauche Bonds in Crystalline *n*-$C_{21}H_{44}$ in Phase II

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Significant conformational disorder has been shown[1,2] to exist in crystalline *n*-alkanes in phase II, the "hexagonal" or "rotator" phase as it is sometimes called. This disorder, which is manifest as a low concentration of gauche bonds in otherwise trans-planar chains, makes phase II *n*-alkanes a particularly suitable model system for the study of more complex assemblies of hydrocarbon chains such as lipid bilayers.[3] The distribution of defects along the chain still remains in question. In this communication we report the results of an infrared study in which the concentration of gauche bonds located at four sites in the *n*-alkane *n*-C_{21} in phase II was determined directly. In summary we have found that conformational disorder may occur anywhere along the chain although it tends to be greatest nearest the chain ends.

Gauche-bond concentrations in *n*-C_{21} were measured by a method described by Snyder and Poore[4] in which deuterium substitution is used to create conformationally sensitive infrared bands. In particular, if one methylene group is doubly deuterated, its rocking mode vibration becomes nearly uncoupled from those of the other (undeuterated) methylenes, and its frequency depends on the conformation of the pair of CC bonds that adjoin this group: 622 cm^{-1} for a trans-trans (tt) pair and 650 cm^{-1} for a trans-gauche or gauche-trans (tg ≡ gt) pair. The CD_2 rocking mode can be easily observed in the infrared spectrum, and the intensities of the 622- and 650-cm^{-1} bands measure the relative numbers of tt and tg pairs unless the CD_2 group is at the 2-carbon position. In that case, band intensities measure the t and g concentrations of the bond between carbons 2 and 3.

Using a method of synthesis described elsewhere,[5] we prepared four *n*-C_{21} compounds labeled with CD_2 groups in the 2-, 4-, 6-, and 11-carbon positions. Purity with respect to chain length was >99% for compounds labeled in the 2-, 4-, and 6-positions and approximately 95% for the 11-position compound.

Infrared spectra in the CD_2 rocking mode region are shown in Figure 1 for *n*-C_{21} with a CD_2 in the 4-position. These spectra, which are representative of the other labeled compounds, display tt and tg bands near 622 and 650 cm^{-1}. The tg band was not observed in the spectrum of any sample in phase I (the orthorhombic form), in keeping with our earlier conclusion that the defect concentrations in this low-temperature phase represent only a small fraction of that in phase II.[2] We note that spectra of samples in the liquid state enable us to calibrate our measurement of concentration since the relative numbers of tt and tg pairs can be computed on the basis of the rotational isomeric state model.[6] The intrinsic intensities of the tt and tg vibrations were found to be equal to within about 5% so that the observed intensities of the 622- and 650-cm^{-1} bands are a direct measure of the relative concentrations of tt and tg pairs.

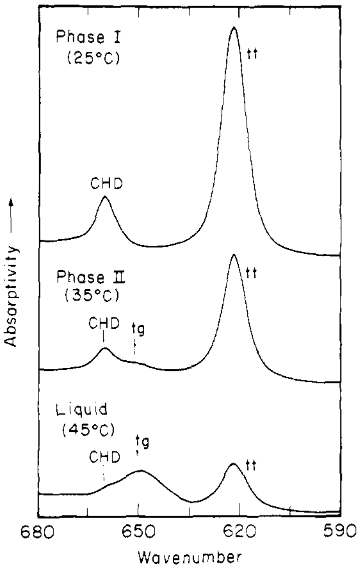

Figure 1. Infrared spectra of *n*-$C_{21}H_{42}D_2$ with the two deuteriums on the fourth carbon. Spectra are of phase I (orthorhombic), phase II (hexagonal-rotor), and the liquid. Bands are labeled to indicate tt and tg bond pairs and the CHD impurity. (These spectra were measured with a Nicolet Fourier transform infrared spectrometer at 1.0-cm^{-1} resolution. See ref 2 for details.)

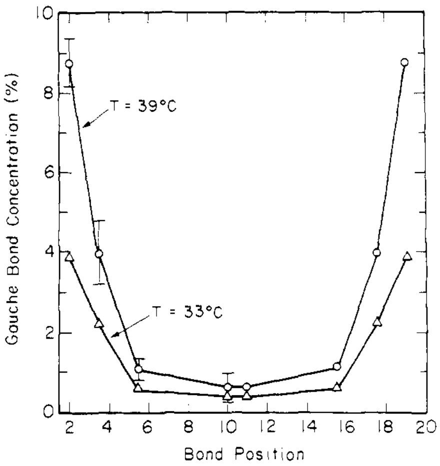

Figure 2. Gauche concentrations at various positions along the *n*-C_{21} chain for phase II at two temperatures. (For pure *n*-$C_{21}H_{44}$, the melting and solid-solid phase-transition (I → II) temperatures are 40.2 and 32.5 °C, respectively.[7]) A fractional bond position $n + {}^1/_2$ is used when the bond pair (tg) is located at bond positions n and $n + 1$. Estimated uncertainties in gauche concentrations are approximately the same for both the 33 and 39 °C plots although uncertainties are indicated only for the latter temperature.

Our principal findings are summarized in Figure 2, where gauche-bond concentration is plotted as a function of bond position. The data shown are for *n*-C_{21} in phase II at a temperature about 1 °C above the I → II transition temperature (32.5 °C) and also at a temperature about 1 °C below the melting point (40.2 °C).[2,7] The distribution curve is remarkable for its shape and temperature dependence.

Considering first the temperature dependence, we note that in going from 33 to 39 °C within phase II the concentration of gauche bonds at each of the four sites appears to increase by a factor of about 2. This change, which is continuous at intermediate temperatures,[8] parallels changes in the unit cell dimensions[9] and

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intermolecular vibrational coupling.[10] However, in spite of the large temperature dependence of gauche concentration, the overall shape of the distribution curve is maintained.

The concentration of gauche bonds increases substantially toward the ends of the chain. This finding is at odds with the assumption of a more or less uniform distribution used in the interpretation of X-ray diffraction measurements on phase II.[11] In progressing away from the chain ends the number of gauche bonds decreases, reaching a minimum in the center that is about one-tenth the number at the ends. However, a substantial concentration of gauche bonds is observed in the middle of the chain so that our results conflict with those recently reported from an infrared study of n-C_{19} in phase II in which it was concluded that defects occur *only* at or near the ends.[12] We note that analogous gradients in conformational disorder have been previously inferred from NMR measurements on lipid bilayers in the liquid crystalline state,[3] and a variety of statistical models have been proposed to account for them.[13]

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cis-Azoalkanes. Mechanisms of Scission and Isomerization[1,2]

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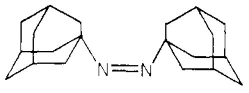
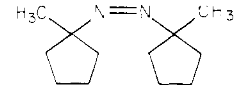
We propose, on the basis of pressure effects and solvent effects, that thermal decomposition of the symmetric *cis*-azoalkanes **1** and **2** proceeds via intermediate diazenyl radicals (Scheme I). This



1
(*cis*-azo-1-adamantane)



2
(*cis*-azo-1-methylcyclopentane)

scheme has been proposed by Porter for asymmetric arylalkyldiazenes,[3] but it has been generally accepted that **1** and other symmetric *cis*-azoalkanes isomerize (k_i) via inversion at nitrogen without radical formation[4],[5a] and that symmetric azo compounds lose nitrogen (k_{N_2}) via simultaneous two-bond scission.[5]

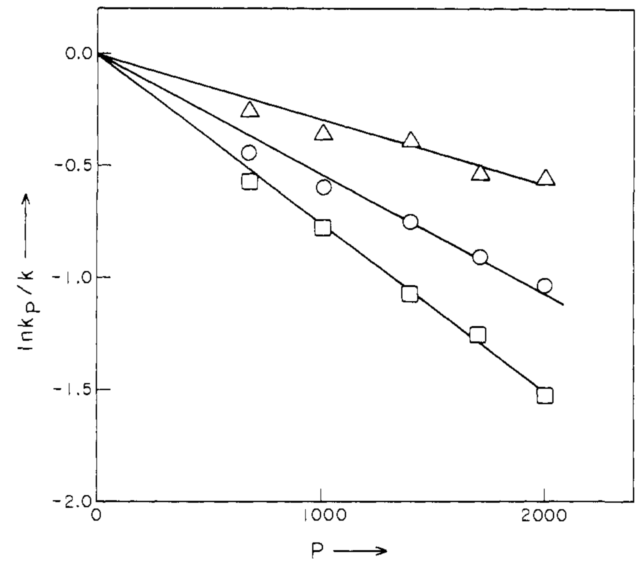


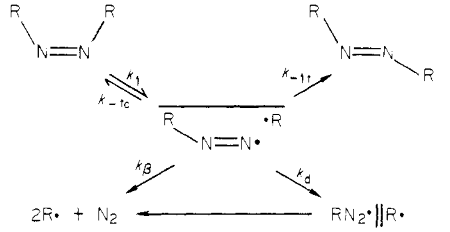
Figure 1. Pressure dependence of ln k_{N_2} (□), ln k_i (△), and ln k_0 (○) for decomposition of **1** in hexane (21.0 °C, 0.24 M *tert*-butylamine, degassed); k_0 is the observed decomposition rate constant for **1** and is equal to k_{N_2} + k_i (P in atm).

Table I. Activation Volumes for Deazatization and Isomerization of 1 and **2**[a]

compd	solvent	T, °C	ΔV_0^*, cm^3/mol	$\Delta V_{N_2}^*$, cm^3/mol	ΔV_i^*, cm^3/mol
1	hexane	21.0	+12	+18	+7
	EtOH	35.7	+7	(+28)[b]	+6
2	EtOH	9.0	+15	+17	(+9)[b]

[a] Calculated from the data by using the equation $\Delta V = -RT(\Delta \ln k/\Delta P)$.[7,9] [b] Unreliable because the particular reaction contributes little to the overall decomposition of the *cis*-azoalkane.

Scheme I



We have previously shown[6] that "one-bond scission" initiators have *large* positive decomposition activation volumes[7] (ΔV_0^*: phenylazotriphenylmethane,[8a,b] +18 to +20 cm^3/mol; *tert*-butylperbenzoate,[8c] + 12 cm^3/mol) while "two-bond scission" initiators have *small* positive decomposition activation volumes[7] (ΔV_0^*: azocumene,[6e] +5 cm^3/mol; di-*tert*-butylhyponitrite,[8d] +5 cm^3/mol; *tert*-butylphenylperacetate,[8c] +2 cm^3/mol). The activation volumes for deazatization ($\Delta V^*_{N_2}$) of **1** and **2** are consistent with one-bond scission (Figure 1, Table I).[9] Since these large positive values of $\Delta V^*_{N_2}$ show that recombination (k_{-1c}) of $RN_2 \cdot R \cdot$ to give **1** or **2** competes with separative diffusion and β

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(9) For **1** and **2**, $\Delta V^*_{N_2}$ and ΔV_i^* are the apparent activation volumes for deazatization (k_{N_2}) and isomerization (k_i), respectively; $k_0 = k_{N_2} + k_i$.

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