second trypanocidal antibody against *T. lewisi*.

Humans and rodents may show similar rheumatoid factor responses during lactation. Rheumatoid factor occurs more commonly in women than men (*16*), and an increase in rheumatoid factor activity in humans during pregnancy or postpartum has been reported (*17*). This suggests that the ability of rheumatoid factor to enhance resistance to *T. cruzi* in rodents should be investigated and that the production of rheumatoid factor during human pregnancy and lactation should be reexamined. These results also suggest that it might be possible to treat Chagas' disease by temporarily inducing the production of rheumatoid factor. At present there are no drugs for the treatment of chronic Chagas' disease, and drugs for the acute stage are inadequate and highly toxic (*11*).

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Phase Transitions and Nonplanar Conformers in Crystalline *n*-Alkanes

Abstract. *Crystals of* n-*alkanes show a remarkable series of solid-solid phase transitions. In the odd* n-*alkanes C_{25}, C_{27}, and C_{29} a previously unknown transition is found by both calorimetry and infrared spectroscopy. The ubiquitous presence of nonplanar conformations of the chains is shown by infrared spectroscopy. The nonplanar conformers constitute approximately half the molecules in the highest temperature solid phase of C_{29}.*

The structure and phase behavior of hydrocarbon chain systems are of interest in areas as diverse as the thermal processing of synthetic polymers and the biological activity of lipid biomembranes. The high-pressure solid-solid transition of polyethylene (*1, 2*), for example, has provided a basis for understanding why cooling the polymer under high pressure leads to an unusual nonlamellar morphology (*2*). Model biomembrane systems are known to undergo two (*3, 4*) and possibly three (*5*) phase transitions in which the hydrocarbon chains play an important role. These transitions have been studied to determine their nature and biological significance (*6*).

Crystalline *n*-alkanes also undergo solid-solid phase transitions (*7, 8*) and therefore are attractive model systems. In the lowest temperature phase, the carbon skeleton of the *n*-alkane molecule is planar zigzag (all *trans*). This structural simplicity has made it possible to analyze the vibrational spectra of these molecules in great detail (*9, 10*) and to extend this analysis to include nonplanar forms (*11*). These analyses have provided the basis for interpreting the changes in the infrared spectra that we have found to accompany the solid-solid phase transitions.

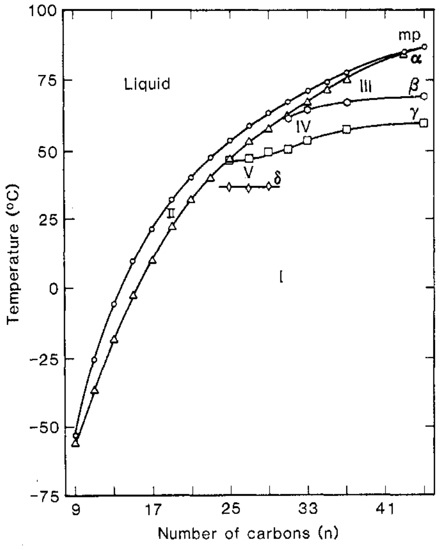

Fig. 1. Transition temperatures of odd *n*-alkanes C_n. Like transitions are connected as in a phase diagram. The solid-solid transition curves α, β, γ, and δ separate crystalline phases I, II, III, IV, and V. Transition temperatures corresponding to α, β, and γ are from (*8*), (*15*), and (*16*) and that of δ is from the present study (*17*).

We report here our observations that certain kinds of nonplanar molecules exist in crystals of *n*-alkanes and that there is a discontinuous jump in the concentration of such nonplanar molecules at each solid-solid phase transition as temperature is increased. These results were derived from infrared measurements on highly purified odd (*12*) *n*-alkanes (C_{17} through C_{29}) (*13*).

The ubiquity of nonplanar conformers is notable in that the role of conformational disorder in the high-temperature phases has not been generally recognized. Solid-solid phase transitions of *n*-alkanes have been discussed in many theoretical treatments in terms of intermolecular motion, especially rotation, of rigid planar molecules (*7, 14*). However, Strobl and co-workers (*8*) recently reported evidence for conformational defects involving *gauche* bonds in the highest temperature phase of C_{33}.

That many crystalline *n*-alkanes undergo a solid-solid phase transition a few degrees below their melting point has been known since 1932, when Müller (*7*) reported the high-temperature "hexagonal" or "rotator" phase of these systems. However, the solid phase behavior of the crystalline *n*-alkanes is complex. The situation up to about 1962 was summarized by Broadhurst (*15*) in a critical review in which the transition temperatures for the hexagonal form were tabulated. Since then, other solid-solid transitions have been reported by Strobl and co-workers (*8*) for C_{33} and by Oyama *et al.* (*16*) for C_{31}, C_{37}, and C_{45}.

Figure 1 shows transition temperatures for the odd *n*-alkanes with $n = 11$ to 45. This plot was constructed from the data cited above together with our own data from differential scanning calorimeter (DSC) measurements on C_{25}, C_{27}, and C_{29} (*17*). Our measurements revealed a new, weak transition near 37°C, which is designated δ in Fig. 1. The phases are designated I, II, and so on. Phase I is the lowest temperature phase.

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The unit cell is orthorhombic and the structure has been worked out in detail for C_{23} (*18*). Phase II is the so-called hexagonal or rotator phase.

The existence of nonplanar rotamers in the high-temperature phases is clearly indicated in the infrared spectra (*19*). Figure 2 shows a region of the infrared spectra of the low- and high-temperature phases of C_{27}. These spectra are representative of odd *n*-alkanes C_{17} through C_{29} in phases I and II. Except for slightly broader bands, the low-temperature (20°C) spectrum is nearly identical to that reported for C_{27} near liquid nitrogen temperature, and virtually all the bands can be assigned to vibrations of the planar form of the molecule (*9*). The doubling of some bands in the spectrum of phase I is the result of intermolecular interaction between molecules in the orthorhombic unit cell (*20*). There are bands in the spectrum of phase II that are not present in phase I. These belong to nonplanar *n*-alkane molecules.

The presence of specific kinds of nonplanar conformations can be inferred from the frequencies and intensities of the bands that appear only in the high-temperature infrared spectra. Identification rests primarily on a comparison of observed frequencies with those calculated for specific nonplanar conformers (*11*) and, to a lesser extent, on a comparison of observed and calculated infrared intensities (*21*).

It is useful to classify the bands observed only in the high-temperature phases as constant-frequency bands or variable-frequency bands according to whether or not their frequencies are independent of chain length. Constant-frequency bands are associated with localized conformational structure and variable-frequency bands with molecules that have a high degree of conformational order.

Table 1. Observed and calculated frequencies (ν_{obs} and ν_{calc}) and descriptions of constant-frequency modes associated with nonplanar conformation of the *n*-alkanes. The estimated value of m represents the minimum number of *trans* bonds needed so that, if the $m + 1$ bond is *gauche*, the frequency of the localized mode will be within about 5 cm^{-1} of the limiting frequency for large m. The end of the chain is indicated by $m = 0$.

ν_{obs} (cm^{-1})	ν_{calc} (cm^{-1})	Description of mode	Conformation	
1354	1354	CH_2 wag	$. . .t_m g g t_{m'} . . .$	$(m,m' \geq 0)$
1342	1345	CH_2 wag	$g t_m . . .$	$(m \geq 1)$
1305	1312	CH_2 wag	$. . .t_m g t g^* t_{m'} . . .^*$	$(m,m' \geq 0)$
1164	1167	CH_2 rock, CH_3 rock	$g t_m . . .$	$(m > 1)$
1078	1079	CH_2 wag, C–C stretch	$g t_m . . .$	$(m > 1)$
956	960	CH_3 rock, C–C stretch	$g t_m . . .$	$(m > 8)$
874	878	CH_3 rock, C–C stretch	$g t_m . . .$	$(m > 5)$

*An alternative but less likely conformation is $t_m g t g t_{m'}$.

Most constant-frequency bands that are observed in the high-temperature phases are associated with molecules having an "end-*gauche*" conformation; that is, the end of the molecule has a conformation that may be designated $g t_m . . .$. In this case, the penultimate bond is *gauche* (*g*) and is adjacent to m consecutive *trans* (*t*) bonds.

The spectroscopic evidence indicating the existence of the end-*gauche* conformation in the cystalline *n*-alkanes is compelling: the observed frequencies of the constant-frequency bands are within a few wave numbers of the frequencies calculated for this conformation (Table 1); conversely, virtually all the calculated modes that are characterized by their normal coordinates as end-*gauche* vibrations of appreciable intensity were observed (*22*). The end-*gauche* conformation is most often associated with molecules that are otherwise planar. This can be inferred from the presence of certain variable-frequency bands in the region 1050 to 700 cm^{-1} (Fig. 2B). These bands are associated with methylene rocking and twisting modes. In brief, our frequency and intensity calculations show that these bands are unique to molecules that have *trans* bonds except at one or possibly both ends (*22*).

Nonplanar conformers other than end-*gauche* are indicated by the broad band near 1305 cm^{-1} (not shown) whose temperature behavior is different from that of bands associated with end-*gauche* rotamers. The 1305 cm^{-1} band has been assigned (*11*) to the conformational sequences (Table 1) $t_m g t g t_{m'}$, and $t_m g t g^* t_{m'}$ where g and g^* are *gauche*

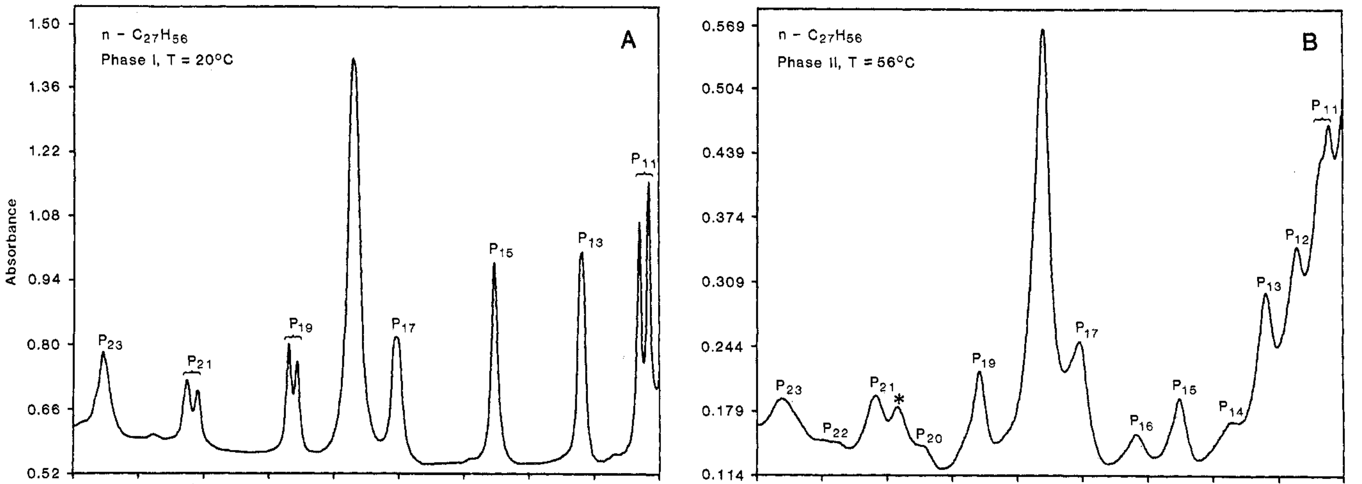

Fig. 2. Infrared spectra of crystalline *n*-$C_{27}H_{56}$ in (A) phase I at 20°C and (B) phase II at 56°C, which is about 3°C below the melting point. The absorptivity scales for the two spectra are different, reflecting in part the lower background scattering of phase II. The assignment (k) of each band belonging to the series of methylene rocking and twisting modes is from (*9*) and is indicated by P_k. Only odd k is allowed for the planar molecule. The variable-frequency even-k bands of phase II are from the end-*gauche*, otherwise fully extended conformer. The constant-frequency band (*) at 956 cm^{-1} is from an end-*gauche* conformation. Note that in phase II some of the bands belonging to nonplanar forms have intensities comparable to those of the planar form. The signal-to-noise ratio in these measurements is such that nonplanar forms can be observed at concentration levels about 1/50 of that shown here for phase II.

bonds whose rotational angles have opposite signs. The $t_m g t g^* t_{m'}$ conformation connects parallel but laterally displaced planar segments; it has been postulated to exist in biomembranes (*23*) and crystalline polyethylene (*24*) and has been invoked to explain certain dielectric relaxation phenomena in polyethylene (*25*). Although the presence of the 1305 cm^{-1} band does not unambiguously prove the existence of either of these conformational sequences, it does indicate *gauche* disruptions in the interior regions of some chains.

All the solid-solid phase transitions lead to similar changes in the infrared spectrum. The change in band intensities at each transition is approximately proportional to the change in enthalpy. Of the bands associated with nonplanar forms, those most easily detected belong to the end-*gauche* conformation. Consequently, only these bands could be clearly observed to increase in intensity at the weak δ transition.

It is significant that a band near 1352 cm^{-1}, known to be characteristic of pairs of adjacent *gauche* bonds (Table 1) (*11*), was not observed except at temperatures near the melting point. This band is prominent in the infrared spectra of liquid *n*-alkanes and is found in the spectrum of highly crystalline polyethylene (*11*). Its absence in the high-temperature phases of the crystalline *n*-alkanes, where nonplanar chains are known to be present, indicates that only very limited kinds of nonplanar conformations are allowed in the crystal. The appearance of a band at 1352 cm^{-1} when the temperature of the *n*-alkane approaches the melting point may signal the onset of a new conformational regime, although more measurements are needed to settle this point.

Plots of integrated band intensities against temperature (not shown) led to the following observations. (i) As the *n*-alkane is warmed, abrupt changes in the concentration of nonplanar conformers occur at temperatures that correspond, within the estimated experimental error (< 1 K), to the transition temperatures determined from the DSC measurements. (ii) Nonplanar conformers are observed in phase I at temperatures at least 20 K below the first (lowest temperature) transition. As the sample is warmed, their concentration gradually increases; a discontinuous jump occurs at each transition. (iii) The concentration of nonplanar conformers in the highest temperature phase is significantly greater for longer *n*-alkanes. In C_{29} in phase II, roughly half the molecules are nonplanar. (iv) The temperature dependence of nonplanar forms varies in the temperature regions between transitions depending on the *n*-alkane. (v) The T_α transitions occur over a temperature interval of about 0.5 K or less. The other solid-solid transitions are somewhat broader. (vi) In cases where there are multiple transitions, if two transition temperatures are sufficiently close the transitions, especially the lower, are broadened. (vii) Where there are multiple transitions, there is a qualitative correspondence between the relative values of ΔH determined from the DSC measurements and the change in concentration of nonplanar conformation at the transition. Thus for C_{27}, $\Delta H_\delta \ll \Delta H_\gamma < \Delta H_\alpha$, and these inequalities are reflected in the relative magnitude of changes in band intensities at the transitions. The sensitivity of the infrared method is indicated by the fact that the entropy change associated with the δ transition is about 0.1 entropy unit.

We have demonstrated the existence of a variety of nonplanar conformers in the solid phases of the *n*-alkanes and have found a new phase transition. The concentrations of these conformers increase with temperature. The existence of these nonplanar molecules must be linked with the existence of the many different solid phases of hydrocarbon chain systems.

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Steady-State Relationship of Calcium-45 Between Bone and Blood: Differences in Growing Dogs, Chicks, and Rats

Abstract. *In young animals that had received multiple doses of calcium-45, a constant ratio of calcium-45 specific activity in blood to that in bone was found in growing dogs and chicks but not in rats. This steady-state relationship of calcium-45 between bone and blood suggests that during growth in dogs and chicks most of the skeletal calcium is in an active state of turnover. In growing rats, after the first 2 weeks of life, the blood/bone ratio of calcium-45 decreases due to a decrease in bone resorption.*

The stability of the serum calcium concentration under various clinical and experimental conditions has led to the concept of a strong homeostatic mechanism for the regulation of calcium (*1*). The rapidity with which the skeleton responds and maintains normal levels of serum calcium after multiple calcium-