Modeling the solid-liquid phase transition in saturated triglycerides

David A. Pink,1,2,a) Charles B. Hanna,2,3 Christophe Sandi,2,4 Adam J. MacDonald,1,2 Ronald MacEachern,1,2,5 Robert Corkery,3 and Dérick Rousseau1,2

1Department of Physics, St. Francis Xavier University, Antigonish, Nova Scotia B2G 2W5, Canada
2Advanced Foods and Materials Network of Centres of Excellence (AFMNet-NCE), Canada
3Department of Physics, Boise State University, Boise, Idaho 83725-1570, USA
4Department of Chemistry, St. Francis Xavier University, Antigonish, Nova Scotia B2G 2W5, Canada
5Institute for Surface Chemistry (YKI), Box 5607, Stockholm SE-114 86, Sweden
6Department of Chemistry and Biology, Ryerson University, Toronto, Ontario M5B 2K3, Canada

(Received 3 May 2009; accepted 16 November 2009; published online 2 February 2010)

We investigated theoretically two competing published scenarios for the melting transition of the triglyceride trilaurin (TL): those of (1) Corkery et al. [Langmuir 23, 7241 (2007)], in which the average state of each TL molecule in the liquid phase is a discotic “Y” conformer whose three chains are dynamically twisted, with an average angle of ~120° between them, and those of (2) Cebula et al. [J. Am. Oil Chem. Soc. 69, 130 (1992)], in which the liquid-state conformation of the TL molecule in the liquid phase is a nematic h−conformer whose three chains are in a modified “chair” conformation. We developed two competing models for the two scenarios, in which TL molecules are in a nematic compact-chair (or “h”) conformation, with extended, possibly all-trans, chains at low-temperatures, and in either a Y conformation or an h− conformation in the liquid state at temperatures higher than the phase-transition temperature, T∗ = 319 K. We defined an h−Y model as a realization of the proposal of Corkery et al. [Langmuir 23, 7241 (2007)], and explored its predictions by mapping it onto an Ising model in a temperature-dependent field, performing a mean-field approximation, and calculating the transition enthalpy ΔH. We found that the most plausible realization of the h−Y model, as applied to the solid-liquid phase transition in TL, and likely to all saturated triglycerides, gave a value of ΔH in reasonable agreement with the experiment. We then defined an alternative h-h∗ model as a realization of the proposal of Cebula et al. [J. Am. Oil Chem. Soc. 69, 130 (1992)], in which the liquid phase exhibits an average symmetry breaking similar to an h conformation, but with twisted chains, to see whether it could describe the TL phase transition. The h-h∗ model gave a value of ΔH that was too small by a factor of ~3−4. We also predicted the temperature dependence of the 1132 cm−1 Raman band for both models, and performed measurements of the ratios of three TL Raman bands in the temperature range of ~20 °C ≤ T ≤ 90 °C. The experimental results were in accord with the predictions of the h−Y model and support the proposal of Corkery et al. [Langmuir 23, 7241 (2007)] that the liquid state is made up of molecules that are each, on average, in a Y conformation. Finally, we carried out computer simulations of minimal-model TLs in the liquid phase, and concluded that although the individual TL molecules are, on average, Y conformers, long-range discotic order is unlikely to exist.


I. INTRODUCTION

Corkery et al.1 proposed that triglyceride (TG) molecules have played disordered chains in the liquid state, so that they approximate “Y” shapes [Y conformers, Fig. 1(c)], in which the three aliphatic chains are oriented with an average angle of approximately 120° between them. Recent molecular dynamics simulation results5 support this proposal. Corkery et al.1 also proposed that such Y conformers are loosely bound within disks, which stack into flexible, relatively short cylindrical rods of colloidal dimensions that in turn assemble into rod packings with short-range order, akin to disordered versions of thermotropic discotic liquid-crystalline phases in other lipidic systems.3 This is in contrast to the low-temperature solid phase,4 in which it is generally agreed that each molecule adopts a compact chair (“h”) conformation [Fig. 1(a)] that collectively forms a three-dimensional structure. Corkery et al.1 argued that both models of the TG liquid phase currently in the literature—the lamellar model first proposed by Larsson,4 and the nematic model of Cebula et al.5 [Fig. 1(b), in which there might be some gauche twists on the chains, as shown in Fig. 2]—warranted revisiting. These models were never specified in detail beyond a statement that the liquid phase exhibits an average symmetry breaking similar to an h conformation, but with (possibly) twisted chains, and no calculation was ever carried out to show whether they would undergo a phase transition that yielded thermodynamic quantities in accord with observations. Molecular dynamics simulation work by Sum et al.6 reported the existence of layered structures in liquid-state TGs, although such structures were not reported

a)Electronic mail: scorpiocarla@gmail.com.
by Hall et al.\textsuperscript{2} In this paper, we have considered the solid-liquid phase transition of TGs, using trilaurin (TL) as a model system, as well as TL structures in the high-temperature liquid phase. Our intent was to investigate the solid-liquid phase transition of TL, in order to establish whether it can be viewed as an “h-Y” transition, or whether instead it is better viewed as a transition from a low-temperature crystalline state of TGs in h conformations\textsuperscript{4} to a liquid phase of excited h structures which we call h*, thus supporting the models of Larsson\textsuperscript{4} and Cebula et al.\textsuperscript{5} for describing the liquid phase. Examples of these conformations are shown in Fig. 1.

TL exhibits a solid-liquid phase transition between $T=318$ K and $T=320$ K,\textsuperscript{7} so we took the midpoint $T'=319$ K as the phase-transition temperature. We modeled two scenarios: the h-Y transition of Corkery et al.\textsuperscript{1} and the h-h* nematic transition of Cebula et al.\textsuperscript{3} and showed how they predict different thermodynamic behaviors. We first describe a minimal model to carry out analytical studies of an h transition. We then define and study a reduced-order nematic-phase model, the h-h* model, relevant to Cebula et al.\textsuperscript{5} We used these models to calculate the transition enthalpy and to predict the temperature dependence of a Raman band centered at $T$=319 K as the phase-transition temperature. Our intent was to investigate the solid-liquid phase transition of TL, in order to establish whether it can be viewed as an “h-Y” transition, or whether instead it is better viewed as a transition from a low-temperature crystalline state of TGs in h conformations\textsuperscript{4} to a liquid phase of excited h structures which we call h*, thus supporting the models of Larsson\textsuperscript{4} and Cebula et al.\textsuperscript{5} for describing the liquid phase. Examples of these conformations are shown in Fig. 1.

TL exhibits a solid-liquid phase transition between $T=318$ K and $T=320$ K,\textsuperscript{7} so we took the midpoint $T'=319$ K as the phase-transition temperature. We modeled two scenarios: the h-Y transition of Corkery et al.\textsuperscript{1} and the h-h* nematic transition of Cebula et al.\textsuperscript{3} and showed how they predict different thermodynamic behaviors. We first describe a minimal model to carry out analytical studies of an h transition. We then define and study a reduced-order nematic-phase model, the h-h* model, relevant to Cebula et al.\textsuperscript{5} We used these models to calculate the transition enthalpy and to predict the temperature dependence of a Raman band centered at $T$=319 K as the phase-transition temperature. Our intent was to investigate the solid-liquid phase transition of TL, in order to establish whether it can be viewed as an “h-Y” transition, or whether instead it is better viewed as a transition from a low-temperature crystalline state of TGs in h conformations\textsuperscript{4} to a liquid phase of excited h structures which we call h*, thus supporting the models of Larsson\textsuperscript{4} and Cebula et al.\textsuperscript{5} for describing the liquid phase. Examples of these conformations are shown in Fig. 1.

In Sec. II, we outline our model of the h-Y transition, simplify it, and then change it to represent the h-h* transition. The penultimate section presents results: calculations of the transition enthalpies and comparison with experiment, and predictions and measurements of the temperature dependences of the 1132 cm\textsuperscript{-1} Raman-band intensities. It should be emphasized that we have searched, not for subtle effects, but for major differences between the h-Y and h-h* models, and for larger-scale effects that discriminate between discotic structures and other characteristics of the fluid phase.

II. THEORY

A. An analytical minimal model

The self-interactions involving a hydrocarbon chain give rise to a trans-gauche energy difference $E_g$ in rotations about a CH\textsubscript{2}--CH\textsubscript{2} axis.\textsuperscript{14} Such a rotation about the bond connecting two CH\textsubscript{2} groups exhibits one low-energy minimum (all-trans state at 0°) and two higher-energy minima (excited states at $\pm 120°$).\textsuperscript{14–17} Recent simulation results\textsuperscript{18} gave a value of $E_g=0.37 \times 10^{-20}$ J (0.54 kcal/mol), while the results of fitting calculated Raman spectra to experimental data\textsuperscript{19} yielded $E_g=0.56 \times 10^{-20}$ J (0.800 kcal/mol). Early experiments\textsuperscript{20,21} showed that the value of $E_g$ is approximately 0.35 to 0.42 $10^{-20}$ J, with a preference for the latter.\textsuperscript{21} In accord with the two more recent values, we chose the average $E_g=0.45 \times 10^{-20}$ J for our model. High temperature is thus defined as $k_BT> E_g$, where $k_B$ is Boltzmann’s constant.

We ignored the “pentane effect,”\textsuperscript{22} $E_{gg}>2E_g$, as well as the results of computer simulations that showed $E_{gg}<2E_g$. Their inclusion would likely make g*g* conformers more probable and g* g* conformers less likely.

As described in Sec. III, we assumed that the excited, high-temperature states of a single hydrocarbon chain encompassed all twisted chain conformations except those that (a) cause self-intersection, or (b) might result in intersections with other chains, oriented with an average angle of 120° between them, on the same molecule. We call this model, in which the phase transition of TL involves melting from an ordered low-temperature state in which all molecules are h conformers, to a high-temperature phase in which essentially all molecules appear as Y conformers, the h-Y model.

We also modeled the case in which the molecules that are in an excited, high-temperature state do not adopt a Y conformation, but instead possess an h-like geometry, but with some degree of trans-gauche isomerization\textsuperscript{4} disorder. This “excited h conformer” h* would possess a symmetry-breaking axis, the long axis of the disordered-h state. This h-h* model assumes that the h* conformer is the dominant state in the melt. Accordingly, the melting transition in the h-h* model would be driven by partial chain disorder and hindered molecular rotation. These conformations are shown in Fig. 1.

The Hamiltonian operator H for the system of N chains, attached in triplets to the CH group in the glycerol core of a TL molecule, is

$$H = \sum_{i,j} J_{nm}(i,j)P_{in}P_{jm} + \sum_i \sum_n e_n P_{in}. \quad (1)$$

Here $J_{nm}(i,j)$ is the interaction energy between two chains labeled $i$ and $j$, when they are in conformational states $n$ and $m$, respectively. The interaction energies encompass all van der Waals, electrostatic, hydrogen bonding, and other Coulomb interactions. In particular, they also include longer-range lattice-distortion energies. However, we do not explicitly include the Angstrom-scale repulsions between atomic moieties, since this level of detail is unnecessary for the questions we address in this work. The sum is over all pairs of chains and all conformational states. The energy $e_n$ is the internal energy of a single chain in conformational state $n$, which takes into account trans-gauche and other energies of a single chain. $P_{in}$ is a projection operator that is equal to one when chain $i$ is in conformation $n$, and equal to zero otherwise.
The system described by Eq. (1) is unnecessarily detailed for our purposes, so we simplified it by assuming that, on sufficiently long time scales, the system samples all the important twisted states of a hydrocarbon chain,23 so that there are only two important classes of states: a group $g$ with the $h$ conformation of the ground state (low-temperature solid phase) and a group $e$ of excited states, which according to recent simulation results are, on the average, Y conformers (high-temperature liquid phase).2 We further assume that we can estimate the enthalpy of the melting transition by constructing a two-state model in which the low-energy $h$ conformers are mapped onto a single effective ground state $g$ of energy $e_g$ and degeneracy $D_g$, and the excited-state conformers are mapped onto a single effective excited state $e$ of energy $e_e$ and degeneracy $D_e$. Under these assumptions, $H$ becomes

$$H \rightarrow 1/2 \sum_{i<j} \sum_{n=m} J_{nm}(i,j)P_{in}P_{jm} + \sum_{i} e_i P_i^m.$$  (2)

The indices $n,m$ now range over the states $g,e$, while the labels $i,j$ range over all chains. The reduction of a multistate polymer model of this kind to a two-state model was used by Doniach, by Pink et al., and by Caillé et al. to model the “main” phase transition in lipid bilayer membranes.13

In order to recast the model into a more transparent form, we transform to (pseudo)spin operators $\{\sigma_i\}$, where $\sigma_i=+1$ when chain $i$ has a low-energy $g$ conformation ($h$ conformer), and $\sigma_i=-1$ when chain $i$ has a high-energy $e$ conformation ($Y$ conformer),

$$\sigma_i = P_{ig} - P_{ie}, \quad I = P_{ig} + P_{ie},$$  (3)

where $I$ is the unit operator. We obtain an Ising-like effective Hamiltonian,

$$H = E_0 - \frac{1}{2} \sum_{i,j} J_{ij} \sigma_i \sigma_j - B_0 \sum_i \sigma_i,$$  (4)

where

$$J_{ij} = \frac{1}{2} [J_{gg}(i,j) - J_{ge}(i,j) + J_{ee}(i,j)],$$  (5a)

$$B_0 = \frac{1}{2} [2(e_e - e_g) - J_{gg}(0) + J_{ee}(0)],$$  (5b)

$$J_{nm}(0) = \sum_j J_{nm}(i,j),$$

$$E_0 = \frac{N}{8} [J_{gg}(0) + 2J_{ge}(0) + J_{ee}(0) + 4(e_e + e_g)],$$  (5c)

and $N$ is the total number of hydrocarbon chains. The effective Hamiltonian in Eq. (4) is similar to that of the Ising model13,24 in an external magnetic field $B_0$, with the difference that the states with $\sigma=+1$ and $\sigma=-1$ possess degeneracies $D_g$ and $D_e$, respectively. These degeneracies can be treated most transparently by adding to the Hamiltonian operator, as it appears in the Boltzmann exponential factor of the partition function, the entropic term

$$- \frac{1}{\beta} \sum_i \left[ \epsilon_i(D_g)P_{ig} + \epsilon_e(D_e)P_{ie} \right] = - \frac{N}{2\beta} \epsilon_n(D_g) + \frac{1}{2\beta} \epsilon_n(D_e) \sum_i \sigma_i,$$  (6)

where $\beta=1/k_BT$. The field $B_0$ in Eq. (4) is then replaced by $B$, where

$$B = \frac{1}{4} \left[ 2(e_e - e_g) - J_{gg}(0) + J_{ee}(0) - 2k_BT \epsilon_n \left( \frac{D_g}{D_e} \right) \right].$$  (7)

Because, at low temperatures, the ordered-chain conformation (close-packed $h$ phase) is known to be the thermodynamically stable phase,3 we take $J_{gg}(0)<0$. If the system of TL molecules in this phase begins to melt into a liquid phase made up of TL molecules in their $Y$ conformations, then the expansion of the lattice, together with the creation of lattice defects, will occur if $J_{gg}(0)<J_{ee}(0)$. In the liquid phase, where the molecules are more disordered than in the close-packed $h$ phase, it is likely that $J_{gg}(0)<J_{ee}(0)$. This means that when $T$ is sufficiently small, then $B>0$, and that as $T$ becomes sufficiently large, then $B<0$. At some temperature $T^*$, $B(T^*)=0$, corresponding to the TL molecules adopting the average conformation of the liquid state.

It is useful to consider the properties of the model when we ignore $B$, i.e., when we set $B=0$. Note that a model with $B=0$ does not necessarily represent any real TG system, since there is no parameter that we can vary to achieve this. We utilize this limit in order to make clearer what follows. When $B=0$, i.e., when $B$ is absent from Eq. (7), the phase transition is continuous at $T=T_c$. Comparing these two limits (with and without $B$), we note that if $T>T_c$, then the system will exhibit a continuous phase change at $T=T^*$, whereas if $T<T_c$, then the system will exhibit a discontinuous phase transition at $T=T^*$.

From our considerations of the interaction strengths $J_{nm}$ (above), we approximate $J_{gg}(0) = 0$ and $J_{ee}(0) \approx 0$, to obtain

$$J_{ij} = -J_{gg}(i,j) / 4,$$  (8a)

$$B = \frac{1}{4} \left[ 2(e_e - e_g) - J_{gg}(0) - 2k_BT \epsilon_n \left( \frac{D_g}{D_e} \right) \right].$$  (8b)

### B. Parameters of a single hydrocarbon chain

Let us first consider a single chain. We took the effective ground state $g$ to be the all-trans conformation with $e_g=0$ and $D_g=1$. Introducing a single trans-gauche twist to an otherwise all-trans saturated hydrocarbon chain costs the trans-gauche energy $E_g$. In accord with the discussion above, we chose $E_g=0.45 \times 10^{-20}$. Note that, in this model, a hydrocarbon chain with $n$ trans-gauche twists has an energy of $nE_g$. We grouped states with one or more trans-gauche twists into an effective excited state $e$. We took $e$ to be either Y-like (for the h-Y model) or h-like (for the h-h" model). Although simulations indicated that the average state of a TL molecule in the liquid phase is a Y conformer, we compared the predictions of the h-Y model with those of an h-h" model.
Accordingly, we also considered the parameters of an $h^*$ conformation. Once the hydrocarbon chain states belonging to the excited state $e$ (either Y or $h^*$) were identified, their enumeration determined the degeneracies $\{D_n\}$ and intensities $\{I_n\}$ that were used to calculate enthalpies and Raman intensities, respectively.

The molecular conformational states (Y or $h^*$) that we described in this section refer to the twists of an individual hydrocarbon chain, plus the molecular segment connecting the hydrocarbon chain to the CH group of each molecule. In both the h-Y and the h-$h^*$ models, we also allowed for motion of each TL molecule as a whole in the liquid state. Such motion contributes up to $k_BT/2$ per degree of freedom (translational and rotational) to the energy gained by the system as it is heated through the phase transition.

1. Y conformer

In the Y conformation, the only states omitted are those in which the twisted chain would attempt to intersect itself or occupy the space of the (C=O)$_2$O$_2$(CH$_2$)$_3$CH glycerol core. Figure 2(A)–(H) is a schematic diagram of eight examples of hydrocarbon chain states with trans-gauche twists, possessing energies from 0 to $7E_g$.

Making use of the observation$^{23}$ that the time to carry out conformational changes in short hydrocarbon chains is not greater than $10^{-1}$ s, we define the excited-state parameters using a thermal average over all such states,

$$D_e f_e = \frac{\sum_{n=1}^{n\rightarrow \infty} D_n e^{-n \beta E_g}}{Z_e}, \quad \varepsilon_e = \frac{\sum_{n=1}^{n\rightarrow \infty} nE_n D_n e^{-n \beta E_g}}{Z_e},$$

(9)

where we have included a factor $f_e$ in the degeneracy of the excited state. We shall use $f_e$ as a free variable, reflecting the possibility that we have missed the available states.

We shall also calculate the temperature dependence of the Raman-band intensity at 1132 cm$^{-1}$, which arises from a skeletal optical mode of a saturated hydrocarbon chain.$^{8–12,25}$ We calculated the average Raman intensities of the $e$ state using a thermal average as in Eq. (9),

$$I_e = \frac{\sum_{n=1}^{n\rightarrow \infty} I_n D_n e^{-n \beta E_g}}{Z_e},$$

(10)

where $I_n$ is the average Raman intensity from a hydrocarbon chain possessing $n$ trans-gauche twists.$^{9,13,25}$

2. $h^*$-conformer

Here, we are concerned with modeling a proposed$^5$ TL transition from an ordered close-packed solid h phase identified by Larsson$^1$ to the spatially disordered state of Cebula et al.$^5$ possessing “nematic domains.” In this case, when $T > T'$, disorder is brought about via a combination of reduced chain ordering, which nonetheless maintains a molecular axis (i.e., an h-like shape), and restricted orientational disorder of these molecular axes. The hydrocarbon chains of each molecule must be sufficiently extended for a molecular axis to be defined.$^{26}$ Restricted orientational disorder means that, while some degree of hindered molecular rotation takes place, free molecular rotation does not occur. We denote by $h^*$ the h-like molecular state with generally extended hydrocarbon chains with some conformational disorder [Fig. 1(b)]. Since the fully conformationally disordered Y conformer includes all twisted-chain states that neither self-intersect nor intersect other chains, an $h^*$-conformer will contain a subset of these states. The transition is seen as coming about via the appearance of some twisted-chain conformers on each TL molecule, combined with hindered rotation of each molecule.

We consider the set of generally extended states to be all conformational states that exhibit trans-gauche isomerization near the CH$_3$ groups, or which possess multiple “kinks,”$^{13,27}$ so that the chains are generally extended. Some of these are shown schematically in Fig. 2.(A)–(H). We omit states that double back. This set defines the excited state $h^*$. None of the states shown in Fig. 2(A)–(H) appears in the admissible set defining the $h^*$ conformation. It is clear that there is some ambiguity in defining the excited state $h^*$, since it was not specified in Ref. 5. The only condition that a molecule in its $h^*$ state must satisfy is that it should maintain a molecular axis, rather than the threefold, effectively dislikle symmetry of a fully disordered Y conformer. Based on this condition, we have attempted to present a plausible h-$h^*$ model of the proposal of Cebula et al.$^5$ The calculation for single-chain parameters of the $h^*$ excited state follows from Eqs. (9) and (10), where the sum over states is restricted to those described above.
C. Mean-field approximation

Because the effective molecular interactions (e.g., lattice distortions) are long-range, we use the standard mean-field approximation\textsuperscript{28} $H \rightarrow H_0$ to obtain

$$H_0 = E_0 - J(\sigma) \sum_i \sigma_i - B \sum_i \sigma_i,$$

(11)

$$J = - \frac{J_{se}(0)}{4},$$

(12a)

$$B = J + \frac{1}{2}(e_x - e_y) = \frac{1}{2} k_B T_c \ln \left( \frac{D_x}{D_y} \right).$$

(12b)

The solution for $\langle \sigma \rangle$ is the solution to the usual mean-field equation,\textsuperscript{28}

$$\langle \sigma \rangle = \tanh \beta(J(\sigma) + B),$$

(13)

and the average Raman 1132 cm$^{-1}$ band intensity is given by

$$I_{1132}(T) = \frac{(1 + T_c) + (1 - T_c)(\sigma)}{2}.$$  

(14)

If we had omitted $B$ from $H_0$ in Eq. (11), then the solution for the thermal average $\langle \sigma \rangle_0$ of $\sigma$ would have been

$$\langle \sigma \rangle_0 = \tanh \beta(J(\sigma)_0).$$

(15)

This function $\langle \sigma \rangle_0$ exhibits a continuous phase transition at the temperature $T_c = J/k_B$. Now, $\langle \sigma \rangle_0$ was obtained by setting $B = 0$ in the Hamiltonian of Eq. (11) and, therefore, does not necessarily describe a model of any TL chain. However, as we showed above, the position of the phase-transition temperature $T^*$, relative to the critical temperature $T_c$ of the function $\langle \sigma \rangle_0$ defined in Eq. (15), is useful for characterizing the phase transition or phase change at $T^*$. 

D. Interaction parameters of the models

In the case where the molecular excited state was assumed to be a Y conformer, we considered three choices for the degeneracy parameter, $f_e$. $f_e = 9, f_e = 1,$ and $f_e = 0.2$. These span the range of physical behaviors produced by the model. The choice $f_e = 9$ allows for rotations about two bonds per chain in the (C=O)$_3$O$_3$(CH$_2$)$_3$CH glycerol core. This is, a priori, the most realistic model in which chain rotations can take place around all bonds. The choices $f_e = 1$ and $f_e = 0.2$ represent cases where such rotations are restricted. The choice $f_e = 1$ assumes that no rotations take place around these two bonds. The choice $f_e = 0.2$ reflects the possibility that we have overcounted the hydrocarbon chain states because, for example, we may not have adequately accounted for molecular steric constraints in highly twisted hydrocarbon chains. The effect of changing the degeneracy parameter $f_e$ is to change the critical temperature $T_c$. The temperature $T^*$, defined to be the temperature at which $B = 0$, is the melting temperature (recall that experimentally, $T^* = 319$ K), and is thus constant by requirement. If, for example, $f_e$ is decreased, then by Eq. (12b), the interaction $J$ must also be decreased in order to keep $T^*$ constant. This implies that if $T_c > T^*$ for a given choice of $f_e$, then, as $f_e$ is reduced, $T_c$ decreases and eventually falls below $T^*$; hence, the transition changes from a discontinuous transition at $T = T_c$ to a continuous phase change.

Requiring that $B = 0$ at the experimentally observed phase-transition temperature $T^* = 319$ K, and using the results of Eq. (12b) at that temperature, we obtain

$J = 1.351 \times 10^{-20}$ J ($f_e = 9, T_c = 979$ K), $J = 0.868 \times 10^{-20}$ J ($f_e = 1, T_c = 628$ K), and $J = 0.513 \times 10^{-20}$ J ($f_e = 0.2, T_c = 372$ K). The purpose of the critical temperature $T_c$ defined by setting $B = 0$, is as a conceptual aid for understanding whether the phase transition at $T = T^*$ is discontinuous, by comparing $T_c$ to $T^*$. As pointed out above, the critical point at $T_c$ is not necessarily related to the physical properties of a TG model.

For the h-h$^*$ model, the value of the hydrocarbon chain degeneracy factor $f_e$ is defined by the extent of hindered rotation undergone by a molecule in the liquid phase, compared with that in the solid phase. The degeneracy defined in Eq. (9) describes that of a single chain. The maximum value of hindered rotation in the h-h$^*$ model is $\sim \pi/4$, with no molecule possessing relative angle $\geq \pi/2$; this constraint is chosen in order to retain a semblance of local nematic order. The length of an all-trans hydrocarbon chain comprising 12 C—C bonds is $\sim 1.6$ nm, and its cross-sectional area perpendicular to its axis is $\sim 0.2$ nm$^2$. If we consider such a chain, tethered by one end to the origin of a sphere of radius 1.6 nm, with its other end moving over an area defined by the angular ranges $0 \leq \theta \leq \pi/4$ and $0 \leq \phi \leq \pi$, then we obtain an area of $\sim 4.71$ nm$^2$. If we assume that the phase space available to a molecule in its h (h$^*$) state is proportional to the areas identified here, viz., $0.2$ nm$^2$ (1.68 nm$^2$), then we obtain a ratio of $\sim 23.6$. Bearing in mind what the degeneracy factor $f_e$ is for each chain, we obtain $f_e = 2.9$. Here we compare the choices $f_e = 1$ and $f_e = 3$. Requiring again that $B = 0$ at $T = 319$ K, we find that

$J = 0.285 \times 10^{-20}$ J ($f_e = 1, T_c = 207$ K) and $J = 0.527 \times 10^{-20}$ J ($f_e = 3, T_c = 381$ K). In the first case, there is a continuous change in phase; in the second case, there is a discontinuous phase transition. We compare the results of our model calculations of the transition entropy with the experimental measurements in Sec. IV below.

III. MATERIALS AND EXPERIMENTAL METHODS

We now describe our experimental measurements of the Raman spectrum of TL, which were carried out in order to test the theoretical calculations of the Raman intensity described in Sec. II. TL (Sigma-Aldrich Canada, Oakville, Canada) (>99% purity) was deposited directly onto the heating/cooling element of a PE120 stage (Linkam, Tadworth, U.K.). Raman spectra were recorded between 700 and 1800 cm$^{-1}$ with a Renishaw InVia microspectrometer (Renishaw, Wotton under Edge, U.K.) equipped with a 25 mW, 514.5 nm laser, an 1800 l/mm grating, a CCD, and a 20× objective. TL spectra were taken between 253 and 363 K with a 5-min equilibration time at each temperature step, which ranged from 1° (near the phase-transition temperature $T^* = 319$ K) to 10° (far from $T^*$). Three acquisitions...
of 1 min each were recorded in nonconfocal mode at each temperature. Spectra were baseline corrected and the area under the peaks at 1063, 1086, and 1132 cm\(^{-1}\) was computed by using a curve-fitting procedure in WIRE 2 software (Renishaw, Wotton under Edge, U.K.). The peak-area ratios were calculated in EXCEL 2002 (Microsoft, Mississauga, Canada).

**IV. MEAN-FIELD MODEL AND RAMAN SPECTROSCOPY: RESULTS AND DISCUSSION**

**A. The h-Y transition**

Figure 3 shows the results for the Raman-band intensity \(I_{1132}\) and the enthalpy \(H\) of a single hydrocarbon chain of the h-Y model for the three values of \(f_g = 0.2\), 1.0, and 9.0 (rows, top to bottom). The transition enthalpy per chain is given by the discontinuity \(\Delta H\) in the enthalpy \(H\) at the transition temperature, shown by the dashed lines in Fig. 2 (B, D, and F).

The transition enthalpies are, in units of \(10^{-20}\) J, 1.60 \((f_g = 0.2)\), 3.26 \((f_g = 1)\), and 4.35 \((f_g = 9)\). Bearing in mind that there are three such chains per molecule, the transition enthalpies \(\Delta H\) of these three cases are 6.89 \((f_g = 0.2)\), 14.1 \((f_g = 1)\), and 18.8 \((f_g = 9)\), in units of kcal/mole. The value of \(\Delta H\) for the case \(f_g = 0.2\) can be increased slightly by taking the transition region to be \(T^\ast \pm 5\) K, but this does not alter our conclusions. To these quantities can be added the energies of rotation and translation of \(3k_BT/2\) each, with values of 0.95 kcal/mole. Accordingly, the maximum value of the transition enthalpy would be \(\Delta H = 8.79\) \((f_g = 0.2)\), 16.0 \((f_g = 1)\), and 20.7 \((f_g = 9)\) in kcal/mol. The last number, for \(f_g = 9\), the most realistic model in which chain rotations can take place around all bonds, most closely represents what has been experimentally observed.

**B. The h-h’ transition**

Figures 4(a)–4(d) show the results for the h-h’ model, which we introduced to model the melting scenario of Cebula et al.\(^5\) for \(f_g = 1\) and \(f_g = 3\), respectively. The case of \(f_g = 1\) exhibits no phase transition, so that \(\Delta H = 0\). Even if one takes the transition to occur in a region \(T^\ast \pm 10\) K, the change in \(\Delta H\) remains far smaller than the observed values. The transition enthalpy per molecule for \(f_g = 3\), omitting the rotational and translational contributions, is \(\Delta H = 6.52\) kcal/mol. It would be inconsistent to include all of...
the $3k_BT/2$ contributions to the rotational and translational energies, since the h-h* model assumes that there is at least some degree of nematic ordering of the individual molecules. Accordingly, it seems clear that the h-h* model is unable to reproduce the observed values of $\Delta H$. This suggests that the total melting transition from the low-temperature solid phase to the high-temperature liquid phase is not described by the model of Cebula et al.\textsuperscript{5}

For $f_e=3$ ($T_e=381$ K), the h-h* model predicts a less abrupt transition than that of the h-Y with $f_e=9$, and this is reflected in the temperature dependence of the 1132 cm\textsuperscript{-1} Raman-band intensity. At $T=T^*$, the Raman intensity of the h-h* model decreases from $-0.85$ of the maximum low-temperature value $I_b$ to $-0.5I_b$. This result is easily distinguished from the prediction of the h-Y model with $f_e=9$.

Is there any aspect of the solid-liquid phase transition that might be described by the h-h* model that was motivated by the proposal of Cebula et al.\textsuperscript{5} The state h* is a combination of states with a few gauche bonds on the chains that leave the molecule in a generally h-like geometry. Accordingly, the model of Cebula et al.\textsuperscript{5} might describe an early stage in the phase transition that takes place as the system is heated for some range of temperatures around the phase-transition temperature, $T^*=319$ K. This does not necessarily imply that the h* state, or others similar to it, defines an intermediate stable phase, although we cannot rule out this possibility. Accordingly, if the model of Cebula et al.\textsuperscript{5} plays a role in the solid-liquid phase transition, it is possibly an intermediate phase that is stable over a small temperature range near $T^*=319$ K.

C. Raman measurements and comparison to the h-Y model

Figure 5 shows the results of measurements of the area under three Raman bands at 1132, 1086, and 1063 cm\textsuperscript{-1}. The areas under the bands were calculated as described above, and the ratios of the areas are shown in Fig. 5.

The band at 1132 cm\textsuperscript{-1} has been associated with collective transverse vibrations of a saturated hydrocarbon chain\textsuperscript{8–12} a crystalline C—C asymmetric stretch, or $k=0$ phonon mode\textsuperscript{30–32} that exhibits a maximum intensity when the chain is in an all-trans conformation, and which has been used to characterize phospholipid bilayers.\textsuperscript{10–13} The band at 1063 cm\textsuperscript{-1} has also been identified as due to hydrocarbon chains in their generally extended chain conformation.\textsuperscript{30–32}

The band at 1086 cm\textsuperscript{-1} has been associated with chains in conformations characteristic of “melted” states with many gauche bonds, an amorphous C—C stretch, arising in a fluid phase of lipid bilayers.\textsuperscript{8–12,30–32} Because of signal drift or other considerations, it is usual to compare the ratios of two bands measured simultaneously; the experimental results for the three ratios are shown in Fig. 5. It can be seen that (a) the ratio $I_{1132}/I_{1086}$ and $I_{1063}/I_{1086}$ follow similar curves, with the latter lying slightly below the former for $T<T^*$, and (b) the ratio $I_{1132}/I_{1063}$ is $\approx 1$.

Figure 6 shows a comparison of the theoretical temperature dependence (a) of the 1132 cm\textsuperscript{-1} band calculated here (Fig. 3E) for the only model (the h-Y model) that satisfies the transition enthalpy requirement (Fig. 3F), and the data (b) for the ratio $I_{1132}/I_{1086}$ shown in Fig. 5 as data set (a). It can be seen that (i) the system exhibits a hard (see above) discontinuity at $T^*$ almost as large as what is predicted by the model. Hard and “soft” also mean that the metastable region of one phase extends many degrees (hard), or not (soft), into the other phase. It is clear that the experimental data are not fit by the much “softer” transition predicted by the h-h* model, shown in Fig. 4. In addition, the experimental data suggest the possibility of a “pretransition” for $T<T^*$ identified by the arrow.

The discontinuous phase transition at $T=T^*$ takes place within a temperature range of $\leq 1$ °C, the temperature step that was used in the neighborhood of the phase transition. This narrow temperature range for the phase transition is in accord with the h-Y model, but not the h-h* model. If the arrow does indeed mark a pretransition, one must ask about its origin. The temperature of the position of the arrow is 273 K, which suggests that, if this is indeed a phase change, it is potentially associated with impurities or the ice-liquid phase transition of water. We are currently examining the possible role of water and contaminants on the solid-liquid transition.

V. SEARCH FOR DISCOTIC STRUCTURES IN THE FLUID PHASE

We used a minimal dissipative particle dynamics (DPD, see Refs. 33 and 34) model with united atom moieties mod-
eled as spheres, chemical bonds modeled as springs, and the forces used by Ter-Oganessian et al., with the addition of an attractive force between glycerol groups (below), to explore whether, in a fluid phase of a TL melt, Y conformers are loosely bound within disks and stack into flexible, relatively short cylindrical rods (discotic ordering). Each united atom (CH, CH₂, CH₃, C═O, and O) was represented by a soft sphere that interacted with its surroundings via soft-core repulsive interactions. Soft-core repulsions were used in order that the systems equilibrate rapidly. Although such a model might be inadequate for studying, for example, the compressibility and shearing properties of the system, it was successfully used to correctly predict exponents connected with dynamic phenomena and does permit rapid equilibration at the densities characteristic of a TL melt. Since we are interested only in the large-scale equilibrium structure, we considered this model adequate for our purposes.

We initialized the molecules into cylindrical stacks with an attractive interaction between the atoms of the glycerol core. Taking the range of the soft-core repulsion to represent the size of the TL atoms, the density was set to approximately 0.9. We then allowed the hydrocarbon chains to relax, while keeping the glycerol groups fixed so that the cylindrical stacks of TL molecules were maintained. Finally, we permitted the total system to equilibrate and compared the equilibrium structures thus obtained with the initial partially equilibrated cylindrical stacks. In this way, we studied the stability of such stacks and could posit that, if the stacks persist when the system has come to equilibrium, then it would be possible that cylindrical stacks existed in a fluid phase. If, however, no such persistence were observed, then such stacks would be unlikely to exist in a fluid phase.

We calculated the structure functions, defined as

\[ S_α(q) = \langle S_α(\tilde{q}) \rangle_{\tilde{q}=q}, \]

where the average is taken over all \( \tilde{q} \) vectors of magnitude \( q \).

The structure function

\[ S_α(\tilde{q}) = \int d^3 \tilde{r} b_α(\tilde{r}) \exp(i\tilde{q} \cdot \tilde{r}) \]

is related to scattering amplitudes \( b_α(\tilde{r}) \): (i) the set \( b_α(\tilde{r})=1 \) only if the atom at position \( \tilde{r} \) is one of the core glycerol atoms, and otherwise \( b_α(\tilde{r})=0 \); and (ii) the set in which \( b_α(\tilde{r}) \) is the neutron scattering length of the atom at position \( \tilde{r} \).

In addition to the soft-core repulsive conservative force \( f_{sc} \), between atoms, we introduced a short-range attractive conservative force \( f_a \) between any pair of glycerol atoms belonging to two different molecules. This is due to the C═O dipoles, and is the only force that involves only the glycerol core regions and which might, therefore, hold together the proposed discotic structures. The total conservative force \( f = f_a + f_{sc} \) acting between any pair of atoms with centers at \( R_1 \) and \( R_2 \) (see Fig. 7) was constructed using

![FIG. 7. Total conservative force (black) acting between any pair of glycerol core atoms belonging to two different molecules, as described in the text. Positive (negative) values represent repulsion (attraction).](image)

\[ f_a(s) = f(0) - 2s \quad 0 \leq s \leq 2 = 0 \quad s > 2, \]

\[ f_a(s) = -F \quad 0 \leq s \leq 2. \]

\[ f_a(s) = -F[1 - s/3.75] \quad 2 < s \leq 3.75, \]

\[ f_a(s) = 0 \quad s > 3.75, \]

where \( s \) is a distance related to the scale of the system in units of \( R_0 \). Here, \( R_0 \) is the sum of the radii \( R_1 \) and \( R_2 \), \( R_0 = R_1 + R_2 \), of the two interacting atoms. The units chosen here were such that one \( s \) unit = 2 Å. Accordingly, the wave vectors \( \tilde{q} \) used here are related to the wave vectors \( q \) that are usually employed by \( \tilde{q} = q/2 \). Hence the lengths \( d \), in angstrom, are obtained from \( \tilde{q} \) by \( d = 4\pi/\tilde{q} \).

VI. DISCOTIC STRUCTURES: RESULTS AND DISCUSSION

In order to obtain an estimate of the magnitude of the glycerol-core forces to be modeled, we need an estimate of the value of \( F \) of Fig. 7 and Eq. (18). We estimate this by considering a pair of idealized C═O dipoles represented by a system of four point charges, each equal in magnitude to an electronic charge, occupying the corners of a rectangle, with sides 4.5 and 1.5 Å, and alternating as one transverses the sides of the rectangle. This arrangement approximates two antiparallel atomic dipoles, a distance 4.5 Å apart, and possesses an energy of \( 5.27 \times 10^{-20} \) J. This should be compared with the thermal energy \( k_BT = 0.446 \times 10^{-20} \) J at 70°C. The pair of dipoles attract each other with a force of \( 3.33 \times 10^{-20} \) J/Å. Accordingly, we chose the attractive force \( F \) to range from 0 to 8 in units of \( 10^{-20} \) J/Å.

We found that after equilibration, the cluster distribution indicated the predominance of small clusters, quite unlike the discotic distribution. Instantaneous configurations were in accord with those shown by Hall et al. The simulation data were unambiguous in not supporting a proposal that the fluid is composed of cylinders of TL molecules.

We also calculated, but have not shown, the structure function which included all atoms; this approximates the x-ray structure function since, for all such atoms, the number of electrons is approximately the same. This is in contrast to the neutron scattering lengths, which vary between ~4.7 and +12.3. Because all atom moieties scatter essentially identically, x-ray scattering might not be a useful way to study fluid-phase TG structures.
VII. CONCLUSIONS

We have considered two two-state models, the h-Y and h-h¹ models, to describe the melting transition of TGs, specifically TL, between a low-temperature crystalline ordered solid phase and a high-temperature liquid melt. These models assumed that two types of states of individual molecules are sufficient to describe this melting transition: a nondegenerate ground state g, in which a TL molecule is an h conformation with maximally extended hydrocarbon chains in their all-trans states, and an excited degenerate state e. Both models possessed the same h-conformer ground state. In the h-Y model, we assumed that the chains in the e state make average angles of ~120° with each other (a Y conformer), with a number of trans-gauche isomers excited. In the h-h¹ model, which is intended to represent the proposals of Cebula et al., the excited state e was an h conformer, h¹, possessing only a limited set of gauche excitations on the hydrocarbon chains. There is no specification by Cebula et al. regarding the details of their excited state(s) and we created what appeared to be a reasonable model that preserved the h-like molecular shape while permitting a number of gauche bonds. In both models, we enforced self-avoidance by requiring that no chain intersects any part of its own molecule. We mapped the resulting models onto an Ising model in a temperature-dependent external field, and justified carrying out a mean-field approximation by arguing that the effective interactions are long-range. The h-Y and h-h¹ models possessed two free parameters: an effective interaction J between different molecules and a single-molecule degeneracy term fₑ that described either rotations near the glycerol core (in the h-Y model) or molecular rotational degrees of freedom (in the h-h¹ model).

We showed that (i) only one of these models, the h-Y model with fₑ=9—a priori the most realistic model in which chain rotations can take place around all bonds—yielded a transition enthalpy within the range of those reported experimentally, ΔH ~ 20.7 kcal/mol. However, the range of experimental values reported is large (19.4, 25.9, 27.9, and 29.4 kcal/mol) and, while our calculated value of 20.7 kcal/mol is on the low side of this extensive experimental spread, it is not out of place. We have included interaction energies (evaluated by requiring a phase transition at T⁰) without specifying their source; in this sense, we have not omitted van der Waals interactions. It is possible that our value of ΔH is low because of the simplified model in which all excited states are represented by one average state, as described in Eq. (9). Against this, however, is the good agreement between the predicted temperature dependence of the 1132 cm⁻¹ Raman band and its subsequent measurement. The model parameter (fₑ=9) is the most reasonable one from physical arguments, since it permits rotations about all bonds. The other two values considered, fₑ=1 and fₑ=0.2, describe restricted rotations in the glycerol core for which there is no obvious justification. We feel that, until an experimental value of ΔH can be specified more precisely, it is premature to seek for sources of error in our calculation—which might be absent. Our result of ~21 kcal/mol should be taken as a prediction. The phase transition described by

We calculated the structure function for the glycerol cores, S₈(q̃), which is shown in Fig. 8. The peak at d=5 Å (arrows) is seen in the discotic structure and for F≥0.5, but not in the F=0 case. This peak is due to the nearest neighbor glycerol cores, either in the discotics or in the small clusters. From the positions of this peak, the glycerol core atom-atom distances for core atoms on different molecules are d=5.0 Å (discotic), d=5.25 Å (F=2), d=5.0 Å (F=4), and d=4.48 Å (F=8). Although such numbers should be accepted with caution, given the approximate model used, the results, which show d decreasing as F increases, suggest that the dipole forces are sufficiently large to give rise to small clusters in the fluid melt.

Figure 9 shows the computed neutron structure function, and it is immediately seen that it should distinguish between discotics (a), random [F=0 (b)], and clusters [F=0.5 (c)–(f)]. The peak between 0<log(q̃)<5 for the discotics is very broad, perhaps representing overlapping peaks because of the longer-range order present in (a) but absent in (c)–(f). The positions and shift in the d=5 Å peak mimic the results of Fig. 8.

![Fig. 8. Computed structure function S₈(q̃) for glycerol cores only. (a) Initial discotic, (b) F=0, (c) F=0.5, (d) F=2, (e) F=4, and (f) F=8. Vertical bars indicate approximate standard deviations. In (a), peaks at log(q̃)<0 correspond to distances between nearest and next nearest neighbor cylinders of TL molecules. The peak at log(q̃)=0.4 (arrow) corresponds to distances between adjacent cores in the same cluster. Note that this is absent in the case of F=0.](image)

![Fig. 9. Computed neutron structure function S₈(q̃). (a) Initial discotic, (b) F=0, (c) F=0.5, (d) F=2, (e) F=4, and (f) F=8. Vertical bars indicate approximate standard deviations. In (a), peaks at log(q̃)<0 correspond to distances between nearest and next nearest neighbor cylinders of TL molecules. The peak at log(q̃)=0.4 appears and corresponds to distances between adjacent cores in the same cluster. Note that this is absent in the case of F=0.](image)
the h-h" model, intended to model the proposal of Cebula et al.,\textsuperscript{5} yielded a transition enthalpy that was only \~25\% of that measured experimentally, with no obvious mechanism to account for the shortfall. We also studied h-h" models with different sets of excitations on the hydrocarbon chains—with the constraint that the molecule exhibits an h-like structure—and found similar results.

We carried out experimental measurements of the Raman spectra of TL samples as functions of temperature for the bands at 1132, 1086, and 1063 cm\textsuperscript{-1}. These are associated with hydrocarbon chain modes characteristic of extended (1132, 1063 cm\textsuperscript{-1}) or twisted (1086 cm\textsuperscript{-1}) hydrocarbon-chain conformational states. We found that (ii) the data for the temperature dependence of the ratio \(I_{1132}/I_{1086}\) displayed a discontinuous phase transition at \(T^*\) that was in good agreement with the predictions of the h-Y model with \(f_d=9\), but not with those of the h-h" model.

We also noted (iii) what might be a pretransition at \(T=273\) K, but we were unable to say whether this is a transition intrinsic to TGs or whether it is driven by impurities or the ice-water phase transition of water inside the TL sample.

We used a DPD model of a TL molecule to carry out computer simulations to see whether an interaction between pairs of glycerol core atoms on different TLs, justified by calculations using finite-size nearest neighbor classical dipoles. We found that (iv) discotics were unstable against breakup at 70 C for any value of the force studied, and that (v) the broad \(d=4.6\) Å line observed in x-ray and neutron scattering is due to the core-core spacing on adjacent atoms, and appears in both a discotic system and in a fluid-phase melt in which the TL molecules form clusters via the attractive force \(F\) that models the interactions between the C==O dipoles of the glycerol cores in our computer simulation model (Fig. 7). It is, therefore, not an indicator of a discotic phase. We also found that (vi) because all atomic moieties in a TL melt essentially scatter x-rays identically, the x-ray structure factor does not easily distinguish between a discotic structure and a melt in which random transient clusters form.

We conclude the following.

(a) In symmetric TGs, the high-energy melted state is one in which the molecules are in Y conformations, with many trans-gauche twists on each hydrocarbon chain. This supports the proposal of Corkery et al.,\textsuperscript{1} where evidence was given that the high-energy state of TL is a Y conformer.

(b) Our most physically plausible two-state h-Y model with \(f_d=9\) predicted that the intensity of the 1132 cm\textsuperscript{-1} Raman band is essentially constant for all temperatures below the melting temperature, \(T^*=319\) K. At the melting transition, this intensity should decrease via a discontinuous phase transition from the near-maximum value \(\sim I_0\) to \(\sim0.18I_0\). Our subsequent measurements of the temperature dependence of the ratio \(I_{1132}/I_{1086}\) supported this prediction.

(c) The h-Y model predicted that the discontinuous phase transition should be hard: i.e., that it should possess a broad metastable region.

(d) The nematic model of Cebula et al.,\textsuperscript{5} cannot account for either the magnitude of the measured transition enthalpy, or the large discontinuity in the 1132 cm\textsuperscript{-1} Raman band at \(T=T^*\). We suggested\textsuperscript{4} that the model of Cebula et al.,\textsuperscript{5} might possibly describe some of the intermediate states that we have referred to here. Whether it is an intermediate stable thermodynamic phase rather than simply a set of states that is manifested in the region of a few degrees around \(T^*=319\) K is a question we have not addressed.

(e) The liquid phase exhibits the formation of clusters for nonzero attractive glycerol-glycerol forces, and these (probably transient) clusters give rise to the observed peak in the scattering function at \(d=4.6\) Å.

(f) Because of the characteristics of x-ray scattering from the atomic moieties in this system, neutron scattering might be a better technique to use to study liquid-phase structures of TGs.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor Truis Smith-Palmer of the Chemistry Department, St. Francis Xavier University, for the use of the confocal Raman microscope on which the Raman measurements were carried out, and the Atlantic Innovation Fund for providing this equipment. D.A.P. and D.R. are grateful to the Natural Sciences and Engineering Research Council of Canada, who supported this work via Discovery Grants. C.B.H. was supported by U.S. NSF Grant No. DMR-0605652, and thanks St. Francis Xavier University for his appointment to the James Chair during the period 2005–2006. We also thank the Advanced Foods and Materials Network of Centres of Excellence (AFMNet-NCE), and the Atlantic Innovation Fund for their support of HQPs. We thank two referees for bringing to our attention the extensive work that has been done in recent years on the equilibrium thermodynamics of TGs.


\textsuperscript{4}K. Larsson, \textit{Fette, Seifen, Anstrichm.} \textbf{74}, 136 (1972).


The characteristic times of trans-gauche isomerization have been measured and simulated and found to range from $10^{-9} - 5 \times 10^{-11}$ s (Refs. 14–16). If there are $10^4 - 10^5$ twisted-chain states to average over (below), then “sufficiently long” sampling time scales are longer than $10^{-8}$ s.