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Size and Asymmetry of Spatial Distributions for Unperturbed Triglycerides

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Abstract: A triglyceride in the interior of a chylomicron or very low density lipoprotein is essentially unperturbed by long-range interactions. Configuration-dependent properties for unperturbed triglycerides are obtained from a representative sample generated by Monte Carlo methods. Necessary a priori and conditional probabilities were obtained from a rotational isomeric state treatment which incorporates first- and second-order interaction. Triglycerides studied have 1–22 carbon atoms in each acyl group. Unperturbed radii of gyration, $\langle s^2 \rangle_0^{1/2}$, are in the range 8–10 Å for those triglycerides which occur most frequently in human chylomicrons and very low density lipoproteins. Asymmetry of the spatial distribution was assessed by examination of averaged principal moments ($\langle L_1^2 \rangle_0 \geq \langle L_2^2 \rangle_0 \geq \langle L_3^2 \rangle_0$) of the moment of inertia tensor. An increase in asymmetry occurs upon progressing from triformin to tricapylin, due almost entirely to a decrease in $\langle L_2^2 \rangle_0 / \langle L_1^2 \rangle_0$. The higher triglycerides examined all have essentially identical asymmetries, $\langle L_2^2 \rangle_0 / \langle L_1^2 \rangle_0 \approx 1/3$ and $\langle L_3^2 \rangle_0 / \langle L_1^2 \rangle_0 \approx 1/12$. Thus the increase in average dimensions as the acyl group goes from C8 to C22 is achieved with no alteration in the asymmetry of the spatial distribution. Introduction of unsaturation, as it occurs in oleic and linoleic acids, brings about a reduction in $\langle s^2 \rangle_0^{1/2}$, but does not significantly alter the asymmetry.

Triglycerides are transported in blood primarily by chylomicrons and very low density lipoproteins. These large lipid-protein complexes have molecular weights of about 0.5×10^9 and $8-31 \times 10^6$, respectively.¹ Triglycerides account for $5/6$ of the dry weight of chylomicrons² and half the dry weight of very low density lipoproteins.³ According to these results, each chylomicron contains about 500 000 molecules of triglyceride, while roughly 10 000 triglyceride molecules occur in each very low density lipoprotein molecule.¹ Neutron⁴ and X-ray⁵⁻¹³ scattering from dilute aqueous solutions of high- and low-density lipoproteins reveals that neutral lipid occurs preferentially at the core. This arrangement apparently also occurs in chylomicrons and in very low density lipoproteins.¹ Mobility of fatty acid chain nuclei in very low density lipoproteins is that of lipids in a liquid-like state, although segmental and rotational motion is not as free as for lipids in organic solvents.¹⁴

The foregoing considerations of composition, segregation, and mobility suggest that triglyceride at the core of a chylomicron or very low density lipoprotein approaches the bulk amorphous state, in which it would be unperturbed by long-range interactions. Size and asymmetry (more precisely, mean square radius of gyration and average principal moments of the moment of inertia tensor) for unperturbed triglycerides can be obtained from a successful rotational isomeric state treatment.¹⁵⁻¹⁹ These terms assume importance in determining transport properties for triglycerides within a chylomicron or very low density lipoprotein.

The present work has as its foundation a recent rotational isomeric state treatment of triacetin which successfully accounts for experimentally determined dipole moments, optical anisotropies, and molar Kerr constants.²⁰ Confidence can therefore be placed in the accuracy of the representation of conformational preferences within the glycerol moiety. Most additional bonds in saturated carboxylic acid moieties will experience the well-characterized short-range interactions which occur in polymethylene.²¹ The few remaining bonds are readily treated by customary methods.

Computational Methods

Structure. Carbon and oxygen atoms in a representative triglyceride are depicted in Figure 1. The molecule is comprised of three branches. Each atom is indexed by a presubscript which denotes the branch and by a postsuffix which denotes sequential position within a branch. Branch *j* contains n_j bonds in its main chain. Atoms in the carbonyl group are denoted by primes, and a single subscript *j* is used for each carbonyl oxygen atom. Ester groups are maintained in the planar trans configuration.

Bond lengths and bond angles are collected in Table I. Geometry for triacetin, as well as $\angle CCC'$, corresponds to the average of the relevant parameter in crystalline β -tricaprin.²² Structural parameters required for longer saturated carboxylic acid chains are those appropriate for polymethylene.²¹ Geometry for the *cis* carbon-carbon double bond is that used for poly(*cis*-1,4-butadiene).²³

Statistical Weight Matrices and Rotational States. The statistical weight matrix for bond *i* in branch *j* is denoted by ${}_j\mathbf{U}_i$. Matrices for bonds in the glycerol moiety have been described by Mattice and Saiz.²⁰ They may be written as shown in eq 1–5.

$${}_1\mathbf{U}_{n_1} = \begin{bmatrix} t(20^\circ) & g^+(102.7^\circ) \\ 1 & 1 \end{bmatrix} \quad (1)$$

$${}_2\mathbf{U}_1 = \begin{matrix} t(-5^\circ) & g^+(126.4^\circ) & g^-(-117.3^\circ) \\ t \left[\begin{matrix} \sigma_1 & \sigma_2 & 1 \\ \sigma_1 & \sigma_2 & \omega_1 \end{matrix} \right] \end{matrix} \quad (2)$$

$${}_2\mathbf{U}_2 = \begin{matrix} t(0^\circ) & g^+(102.7^\circ) & g^-(-102.7^\circ) \\ t \left[\begin{matrix} 1 & \sigma_3 & \sigma_3\omega_4 \\ 1 & \sigma_3\omega_4 & \sigma_3\omega_4 \\ g^- & 1 & \sigma_3 \end{matrix} \right] \end{matrix} \quad (3)$$

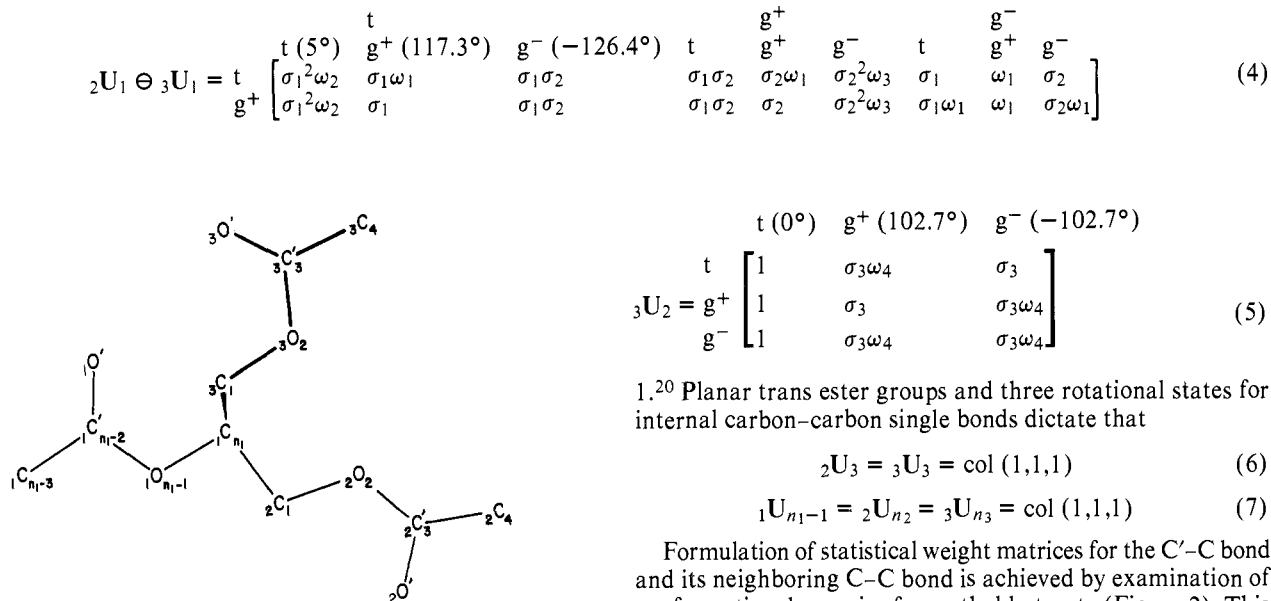
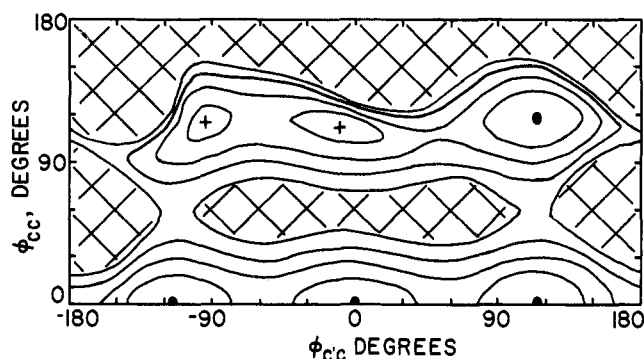


Figure 1. Carbon and oxygen atoms in triacetin.


 Figure 2. Conformational energy for methyl butyrate as a function of dihedral angle at the $C'C$ bond ($\phi_{C'C}$) and neighboring $C-C$ bond (ϕ_{CC}). Essentially identical energies are obtained at four minima denoted by ●, while an energy higher by 0.5 kcal/mol is attained at minima denoted by +. Contour lines are drawn at energies of 1, 2, 3, and 4 kcal/mol above the minimum. Cross-hatched areas have energies exceeding 4 kcal/mol.

Rows are determined by the state of the preceding bond, while columns define the state of bond i in branch j . Columns for ${}_2U_1 \ominus {}_3U_1$ define the states for the first bond in branches 2 and 3.¹⁷ The first three columns have a trans state for the first bond in branch 2 and the three possible states for the first bond in branch 3. Dihedral angles for various rotational states are given in column headings. Statistical weights at 25 °C are $\sigma_1 = 2.3$, $\sigma_2 = 0.16$, $\sigma_3 = 0.71$, $\omega_1 = \omega_3 = \omega_4 = 0.034$, and $\omega_2 =$

Table I. Structural Parameters

bond length, Å		bond angle, deg	
C-C'	1.50	$\angle CC'O'$	126.3
C-O	1.44	$\angle OC'O'$	122.3
C'-O	1.35	$\angle COC'$	116.7
C'-O'	1.20	$\angle OCC'$	106.4
C=C	1.34	$\angle CCC'$	113.7
C-C (glycerol)	1.51	$\angle CC=C$	125.0
C-C (acyl)	1.53	$\angle CCC$ (glycerol)	114.7
		$\angle CCC$ (acyl)	112.0

$${}_3U_2 = \begin{matrix} t & g^+ & g^- \\ t (0^\circ) & g^+ (102.7^\circ) & g^- (-102.7^\circ) \\ g^+ \begin{bmatrix} 1 & \sigma_3 \omega_4 & \sigma_3 \\ 1 & \sigma_3 & \sigma_3 \omega_4 \\ 1 & \sigma_3 \omega_4 & \sigma_3 \omega_4 \end{bmatrix} & & \end{matrix} \quad (5)$$

1.²⁰ Planar trans ester groups and three rotational states for internal carbon-carbon single bonds dictate that

$${}_2U_3 = {}_3U_3 = \text{col}(1,1,1) \quad (6)$$

$${}_1U_{n-1} = {}_2U_{n-2} = {}_3U_{n-3} = \text{col}(1,1,1) \quad (7)$$

Formulation of statistical weight matrices for the $C'-C$ bond and its neighboring $C-C$ bond is achieved by examination of conformational energies for methyl butyrate (Figure 2). This energy surface incorporates torsional potentials for the $C'-C^{24}$ and $C-C^{21}$ bonds, as well as pairwise 6-12 potentials.²⁴ Symmetry dictates that equal energies be obtained at $\phi_{C'C}$, ϕ_{CC} , and $-\phi_{C'C}$, $-\phi_{CC}$. Calculated energies differ by only 0.13 kcal/mol for minima corresponding to $\phi_{C'C}$, ϕ_{CC} being tt , $g^\pm t$, and $g^\pm g^\pm$. These slight differences in energy will be ignored. Energies for the remaining minima in Figure 2 are elevated by 0.54 ± 0.09 kcal/mol owing to a repulsive second-order interaction between the methyl group and carbonyl oxygen atom. The statistical weight for this interaction will be ω_a . Its value at 25 °C is 0.43. These considerations lead to

$${}_1U_{n-3} = \begin{matrix} t & g^+ & g^- \\ t (0^\circ) & g^+ (115^\circ) & g^- (-115^\circ) \\ g^+ \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & \omega \\ 1 & \omega & 1 \end{bmatrix} & & \end{matrix} \quad (8)$$

$${}_1U_{n-2} = \begin{matrix} t & g^+ & g^- \\ t (0^\circ) & g^+ (115^\circ) & g^- (-115^\circ) \\ g^+ \begin{bmatrix} 1 & 1 & 1 \\ \omega_a & 1 & \omega_a \\ \omega_a & \omega_a & 1 \end{bmatrix} & & \end{matrix} \quad (9)$$

$${}_2U_4 = {}_3U_4 = \begin{matrix} t & g^+ & g^- \\ t (0^\circ) & g^+ (115^\circ) & g^- (-115^\circ) \\ [1 & 1 & 1] \end{matrix} \quad (10)$$

$${}_2U_5 = {}_3U_5 = \begin{matrix} t & g^+ & g^- \\ t (0^\circ) & g^+ (115^\circ) & g^- (-115^\circ) \\ g^+ \begin{bmatrix} 1 & \omega_a & \omega_a \\ 1 & 1 & \omega_a \\ 1 & \omega_a & 1 \end{bmatrix} & & \end{matrix} \quad (11)$$

All remaining internal carbon-carbon single bonds in triglycerides obtained from saturated carboxylic acids have the statistical weight matrix which applies to internal carbon-carbon bonds in polymethylene.²¹

$$\begin{matrix} t & g^+ & g^- \\ t (0^\circ) & g^+ (115^\circ) & g^- (-115^\circ) \\ g^+ \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \omega \\ 1 & \sigma \omega & \sigma \end{bmatrix} & & \end{matrix} \quad (12)$$

Values for σ and ω at 25 °C are 0.43 and 0.034, respectively. The second-order interaction whose statistical weight is ω also occurs in eq 8.

Additional statistical weight matrices are required to describe interactions which occur near the cis carbon-carbon

double bond in oleic acid. If the i th bond in branch j is a cis carbon-carbon double bond, interactions described in Mark's²³ study of poly(*cis*-1,4-butadiene) can be taken into account using the following matrices.²⁵

$${}_j\mathbf{U}_{i-2} = \begin{matrix} & t(0^\circ) & g^+(115^\circ) & g^-(-115^\circ) \\ \begin{matrix} t \\ g^+ \\ g^- \end{matrix} & \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \sigma' & \sigma'\omega \\ 1 & \sigma'\omega & \sigma' \end{bmatrix} \end{matrix} \quad (13)$$

$${}_j\mathbf{U}_{i-1} = \begin{matrix} & t(0^\circ) & g^+(60^\circ) & g^-(-60^\circ) \\ \begin{matrix} t \\ g^+ \\ g^- \end{matrix} & \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \end{matrix} \quad (14)$$

$${}_j\mathbf{U}_i = \begin{matrix} & t \text{ cis}(180^\circ) & g^+ \text{ cis}(180^\circ) & g^- \text{ cis}(180^\circ) \\ \begin{matrix} t \\ g^+ \\ g^- \end{matrix} & \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{matrix} \quad (15)$$

$${}_j\mathbf{U}_{i+1} = \begin{matrix} & t(0^\circ) & g^+(60^\circ) & g^-(-60^\circ) \\ \begin{matrix} t \text{ cis} \\ g^+ \text{ cis} \\ g^- \text{ cis} \end{matrix} & \begin{bmatrix} 0 & \zeta & \zeta \\ \zeta & 1 & 1 \\ \zeta & 1 & 1 \end{bmatrix} \end{matrix} \quad (16)$$

$${}_j\mathbf{U}_{i+2} = \begin{matrix} & t(0^\circ) & g^+(115^\circ) & g^-(-115^\circ) \\ \begin{matrix} t \\ g^+ \\ g^- \end{matrix} & \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \sigma' & \sigma' \\ 1 & \sigma' & \sigma' \end{bmatrix} \end{matrix} \quad (17)$$

Appropriate values for ζ and σ' are 0.1 and 1.4, respectively.²⁵

Configuration-Dependent Properties for Specified Configurations. Specification of rotational states for all internal bonds in a triglyceride defines the location of each carbon and oxygen atom in an internal coordinate system. The moment of inertia tensor for this configuration is¹⁶

$$\mathbf{S}_{\times 2} = N^{-1} \sum_{i=0}^N \mathbf{r}_{0i} \times 2 - \mathbf{g} \times 2 \quad (18)$$

Here \mathbf{r}_{0i} denotes the vector from atom ${}_1\text{C}_0$ to the i th atom, N is the total number of carbon and oxygen atoms (including carbonyl oxygen atoms) in the triglyceride, \mathbf{g} is the center of mass vector, and $\times 2$ as a superscript denotes the self-direct product. We ignore the difference in mass of carbon and oxygen atoms.

$$\mathbf{g} = N^{-1} \sum_{i=0}^N \mathbf{r}_{0i} \quad (19)$$

The representation for $\mathbf{S}_{\times 2}$ is as a column comprised of the nine elements in reading order. The squared radius of gyration, s^2 , is the trace of $\mathbf{S}_{\times 2}$. Principal moments ($L_1^2 \geq L_2^2 \geq L_3^2$) for $\mathbf{S}_{\times 2}$ may be obtained via an appropriate similarity transform. Components of $\mathbf{S}_{\times 2}$, principal moments, and s^2 are conveniently expressed as a dimensionless ratio obtained through division by the sum of the squared length of all carbon-carbon and carbon-oxygen bonds in the triglyceride. This sum will be denoted by Σl^2 .

The squared distance between ${}_1\text{C}_0$ and either ${}_2\text{C}_{n2}$ or ${}_3\text{C}_{n3}$ is also obtained directly from atomic coordinates in the specified configuration. This squared distance will be denoted by r^2 . In general, subscripts should be appended to specify whether it is being measured from ${}_1\text{C}_0$ to ${}_2\text{C}_{n2}$ or ${}_3\text{C}_{n3}$. They will not be used because our interest will be in unperturbed statistical mechanical averages, $\langle r^2 \rangle_0$, under conditions where symmetry dictates identical results for both squared distances.

A dimensionless ratio is obtained from r^2 through division by the sum of squared lengths for all bonds in the chain connecting the two atoms. This sum will be denoted by Σl^2 , which is the same notation used for a different sum in the preceding paragraph. Confusion should not arise because the present sum will be used exclusively in conjunction with $\langle r^2 \rangle_0$, while the preceding sum will appear only with $\langle s^2 \rangle_0$ or $\langle L_i^2 \rangle_0$.

Monte Carlo Sampling of Configurations. Exact results for $\langle r^2 \rangle_0$ and $\langle s^2 \rangle_0$ could be obtained by appropriate combination of statistical weight matrices and generator matrices for specified configurations.^{17,18} Special attention must be given to the manner in which $\langle \mathbf{S}_{\times 2} \rangle_0$ is obtained from the various $\mathbf{S}_{\times 2}$. One procedure would be to transform each $\mathbf{S}_{\times 2}$ into its representation in an internal coordinate system defined by the position of two sequential bonds in the triglyceride. Corresponding elements of these tensors can now be averaged exactly using matrix generation schemes.¹⁹ This procedure, however, will suppress the asymmetry of individual configurations. If asymmetry of individual configurations is to be retained, it is necessary to obtain the L_i^2 from $\mathbf{S}_{\times 2}$ for each configuration. Corresponding moments are then averaged to obtain $\langle L_1^2 \rangle_0$, $\langle L_2^2 \rangle_0$, and $\langle L_3^2 \rangle_0$. A representative sample of configurations is required for this purpose. Since a Monte Carlo sample is used to obtain $\langle L_i^2 \rangle_0$, it shall also be used to evaluate $\langle s^2 \rangle_0$, $\langle r^2 \rangle_0$, and $\langle \mathbf{S}_{\times 2} \rangle_0$.

Monte Carlo sampling is achieved using a random number generator in conjunction with a priori and conditional probabilities obtained from the configuration partition function, Z .¹⁷

$$Z = {}_1\mathbf{U}_1^{(n_1)} ({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) [({}_2\mathbf{U}_2^{(n_2-1)}) \otimes ({}_3\mathbf{U}_2^{(n_3-1)})] \quad (20)$$

Here ${}_1\mathbf{U}_1^{(n_1)}$ denotes the product of n_1 successive statistical weight matrices commencing with ${}_1\mathbf{U}_1$. Necessary probabilities are obtained from Z by following exactly procedures described previously in detail for a molecule which contains a trifunctional branch point.¹⁷

Four sets of 100 configurations each were generated for triglycerides obtained from carboxylic acids containing eight or fewer carbon atoms. Five sets of $10(n+3)$ configurations each were generated for the larger triglycerides. Here n is the number of carbon atoms in one of the carboxylic acid molecules used to form the triglyceride. Reported standard deviations reflect the variation in the average for the four (or five) sets.

Results and Discussion

Radius of Gyration. Figure 3 depicts $\langle s^2 \rangle_0 / \Sigma l^2$ as a function of number of carbon atoms in a saturated carboxylic acid substituent. This ratio is essentially identical for triformin, triacetin, and tripropanoin. It increases with molecular weight for the remainder of the triglycerides for which results are depicted in Figure 3. The value of $\langle s^2 \rangle_0 / \Sigma l^2$ will approach unity as the number of carbon atoms in the carboxylic acid approaches infinity. This limiting behavior is defined by the unperturbed dimensions of linear polymethylene,²⁸ their temperature coefficient,^{28,29} and the effect of a single trifunctional branch point on the asymptotic behavior of $\langle s^2 \rangle_0 / \Sigma l^2$. It is clear from Figure 3 that the asymptotic limit is not attained for any triglycerides of biochemical interest.

A value of $2.50 \pm 0.04 \text{ \AA}$ is obtained as $\langle s^2 \rangle_0^{1/2}$ for the carbon and oxygen atoms in triformin. This result measures the size of the head group in a triglyceride. Those triglycerides of greatest physiological interest are derived from carboxylic acids which contain 16 or 18 carbon atoms. Tripalmitin and tristearin have $\langle s^2 \rangle_0^{1/2}$ of 8.58 ± 0.06 and $9.37 \pm 0.10 \text{ \AA}$, respectively. These results are comparable to the radii of gyration for small globular proteins. For example, the conformation adopted in the crystalline state by the rubredoxin from *Clostridium pasteurianum* has a radius of gyration of 11.3 \AA .³² Of

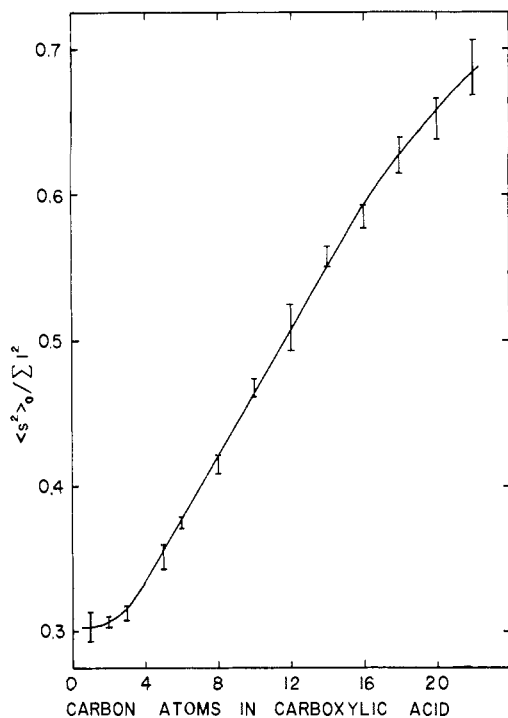


Figure 3. Dependence of $\langle s^2 \rangle_0 / \Sigma l^2$ for triglycerides on the number of carbon atoms in a carboxylic acid substituent.

course, the density of chain segments is much higher near the center of mass of a globular protein than is the case for an unperturbed triglyceride.

Asymmetry of the Spatial Distribution. Figure 4 depicts behavior of averaged principal moments of the moment of inertia tensor. Thus $\langle L_1^2 \rangle_0$ denotes the statistical mechanical average of the largest principal moment of the moment of inertia tensor for individual configurations. Each of the $\langle L_i^2 \rangle_0$ becomes larger with an increase in size of the carboxylic acid substituent. This increase is strong enough for $\langle L_1^2 \rangle_0$ so that $\langle L_1^2 \rangle_0 / \Sigma l^2$ rises continuously. In contrast, $\langle L_2^2 \rangle_0 / \Sigma l^2$ and $\langle L_3^2 \rangle_0 / \Sigma l^2$ experience a minimum as the molecular weight of the carboxylic acid substituents increases.

Ratios of principal moments are depicted in Figure 5. An increase in asymmetry occurs upon going from trifirmin to tricaprilyn, due primarily to a decrease in $\langle L_2^2 \rangle_0 / \langle L_1^2 \rangle_0$. Higher triglycerides of biological interest have $\langle L_2^2 \rangle_0 / \langle L_1^2 \rangle_0 \approx 1/3$ and $\langle L_3^2 \rangle_0 / \langle L_1^2 \rangle_0 \approx 1/12$. An unperturbed linear polymethylene of the same molecular weight has $\langle L_2^2 \rangle_0 / \langle L_1^2 \rangle_0 \approx 1/4$ and $\langle L_3^2 \rangle_0 / \langle L_1^2 \rangle_0 \approx 1/25$.²⁶ Individual configurations for triglycerides are, on the average, less asymmetric. They are, however, more asymmetric than native structures of typical globular proteins. Rubredoxin, for example, has $L_2^2 / L_1^2 \approx 1/2$ and $L_3^2 / L_1^2 \approx 1/3$.

Figure 5 demonstrates that the average instantaneous configuration of an unperturbed triglyceride cannot be accurately represented by a prolate or oblate ellipsoid. If one were forced to an ellipsoid model, an oblate ellipsoid would clearly be preferable for trifirmin and triacetin. For these two triglycerides $\langle L_2^2 \rangle_0$ differs from $\langle L_1^2 \rangle_0$ by less than a factor of 2, while $\langle L_3^2 \rangle_0$ and $\langle L_2^2 \rangle_0$ differ by a factor of 6. Prolate and oblate ellipsoids are equally bad models for the average configuration of unperturbed triglycerides of greatest biological interest.

The symbol $\langle S_{\times 2} \rangle_0$ denotes a tensor obtained from the $S_{\times 2}$ for individual configurations by averaging them when they are expressed in an internal coordinate system defined by the first two bonds in branch 1. Diagonalization of $\langle S_{\times 2} \rangle_0$ yields three virtually identical principal moments if the carboxylic acid

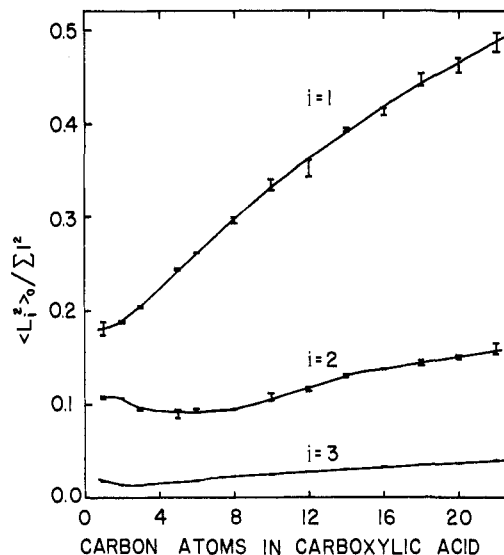


Figure 4. Dependence of $\langle L_i^2 \rangle_0 / \Sigma l^2$ for triglycerides on the number of carbon atoms in a carboxylic acid substituent.

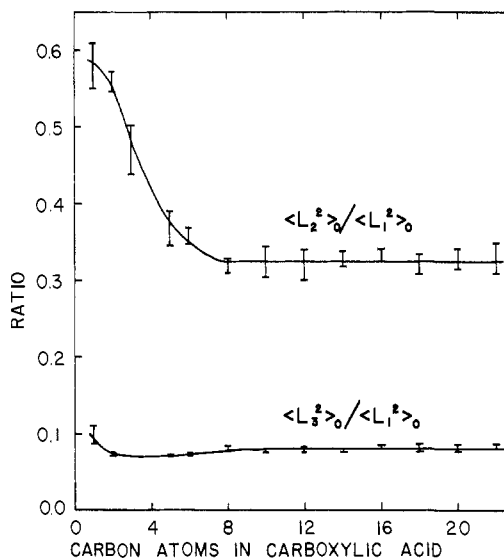


Figure 5. Ratios of the averaged principal moments for unperturbed triglycerides.

contains more than ten carbon atoms. Hence a symmetric spatial distribution is attained for the larger triglycerides in this internal coordinate system. This result illustrates the importance of a precise definition for the asymmetry which pertains to a particular property of an unperturbed triglyceride. Molecules such as tripalmitin and tristearin have a definitely asymmetric instantaneous spatial distribution, as shown by behavior of the $\langle L_i^2 \rangle_0$. Nevertheless, the spatial distribution sensed for these same molecules, when averaged in an internal coordinate system, may have no asymmetry.

End to End Distance. Figure 6 depicts behavior of $\langle r^2 \rangle_0 / \Sigma l^2$ where $\langle r^2 \rangle_0$ is the unperturbed mean square distance between ${}_1C_0$ and either ${}_2C_{n2}$ or ${}_3C_{n3}$. The dimensionless ratio increases with molecular weight for molecules depicted in this figure. Consideration of the unperturbed dimensions of polymethylene,²⁸ and their temperature dependence,^{28,29} yields an asymptotic limit of about 7.5 at infinite molecular weight. Comparison of Figures 3 and 6 demonstrates that the limiting value is attained more slowly by $\langle s^2 \rangle_0 / \Sigma l^2$ than by $\langle r^2 \rangle_0 / \Sigma l^2$. Values of $\langle r^2 \rangle_0^{1/2}$ for tripalmitin and tristearin are 22.91 ± 0.36 and 25.43 ± 0.55 Å, respectively.

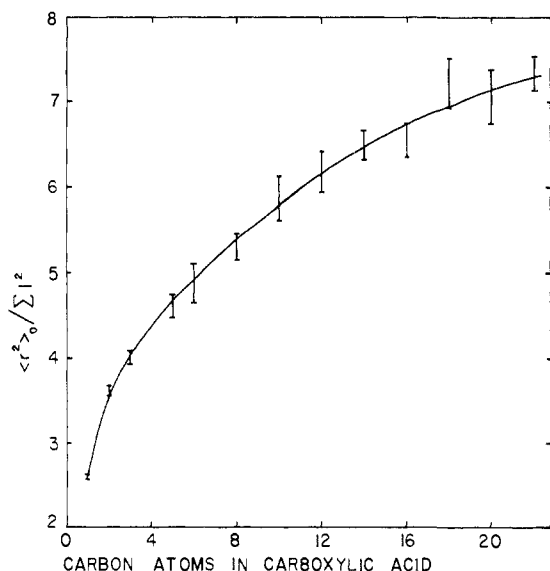


Figure 6. Dependence of $\langle r^2 \rangle_0 / \langle \Sigma l^2 \rangle$ for triglycerides on the number of carbon atoms in a carboxylic acid substituent.

Table II. Conformational Properties of Unperturbed Tripalmitin, Triolein, Trilinolein, and Tristearin^a

triglyceride	$\langle s^2 \rangle_0, \text{\AA}^2$	$\langle L_2^2 \rangle_0 / \langle L_1^2 \rangle_0$	$\langle L_3^2 \rangle_0 / \langle L_1^2 \rangle_0$
tripalmitin	73.56 (0.96)	0.333 (0.009)	0.081 (0.003)
triolein	75.30 (2.00)	0.317 (0.020)	0.086 (0.005)
trilinolein	78.24 (2.62)	0.321 (0.023)	0.079 (0.006)
tristearin	87.73 (1.78)	0.321 (0.013)	0.081 (0.005)

^a The figure in parentheses is the standard deviation of average results for five Monte Carlo sets of 210 (190 for tripalmitin) configurations each.

Configurational Consequences of Unsaturation. Comparison of tristearin and triolein permits an assessment of consequences of a cis double bond between the ninth and tenth carbon atoms in an 18-carbon carboxylic acid. Figure 7 depicts the a priori probabilities that a trans state will be occupied by bond i in a stearyl or oleyl group when it constitutes part of branch 1 in a triglyceride. The double bond in oleic acid produces a profound reduction in the probability of a trans placement for five successive bonds. The stearyl group has an average of 9.7 trans placements for the 16 internal C-C bonds, and 2.8 bonds is the average length of a sequence of consecutive trans placements. Corresponding bonds in an oleyl moiety have an average of 7.3 trans placements, with the average length of a sequence of consecutive trans placements being reduced to 1.9.

Results for $\langle s^2 \rangle_0$ and $\langle L_i^2 \rangle_0$ are summarized in Table II along with those for the C16 and C18 saturated triglycerides. Unsaturation is seen to produce a reduction in $\langle s^2 \rangle_0$, which is the result anticipated from its effect on the probability of trans placements. The reduction in $\langle s^2 \rangle_0$ is nearly equivalent to the result which would have been obtained by removal of two terminal carbon atoms from each carboxylic acid moiety (compare triolein and tripalmitin). Reduction in unperturbed dimensions is achieved along all three principal axes so that little change occurs in $\langle L_2^2 \rangle_0 / \langle L_1^2 \rangle_0$ and $\langle L_3^2 \rangle_0 / \langle L_1^2 \rangle_0$. Computed results for unperturbed trilinolein (C18 carboxylic acid with cis double bonds at C9-C10 and C12-C13) do not differ significantly from those obtained with triolein. We conclude that $\langle L_2^2 \rangle_0 / \langle L_1^2 \rangle_0 \approx 1/3$ and $\langle L_3^2 \rangle_0 / \langle L_1^2 \rangle_0 \approx 1/12$ for both saturated and unsaturated unperturbed triglycerides in which there are 10-22 carbon atoms per carboxylic acid moiety.

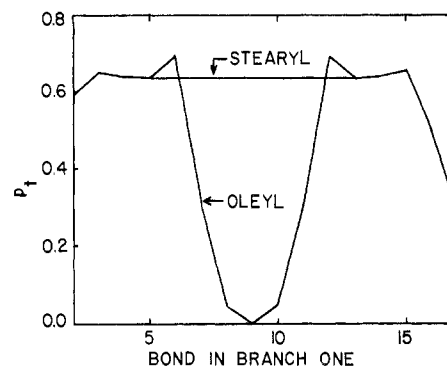


Figure 7. A priori probability for a trans placement at bond i in a stearyl or oleyl group in an unperturbed triglyceride. The stearyl or oleyl group in question occurs in branch 1 (see Figure 1).

The great majority of acyl groups found in the triglycerides of human chylomicrons³³ and very low density lipoproteins³⁴ are those of palmitic, stearic, oleic, and linoleic acid. Therefore the most abundant triglycerides in these lipid-protein complexes have $\langle s^2 \rangle_0^{1/2} = 9 \pm 1 \text{\AA}$, $\langle L_2^2 \rangle_0 / \langle L_1^2 \rangle_0 = 0.32 \pm 0.02$, and $\langle L_3^2 \rangle_0 / \langle L_1^2 \rangle_0 = 0.08 \pm 0.01$.

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References and Notes

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