Mean-Squared Optical Anisotropies for Alkanes Containing a Single Trifunctional or Tetrafunctional Branch Point[1]

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Abstract: Rotational isomeric state theory has been used to assess the effects of a single trifunctional or tetrafunctional branch point on the optical anisotropy exhibited by alkanes. The *n*-alkanes are treated in precisely the same fashion as that utilized by Patterson and Flory, with identical results. Branching reduces the optical anisotropy of alkanes of low to moderate molecular weight, the effect increasing with the functionality of the branch point. At high molecular weight the effect of the branch point on the optical anisotropy is eliminated. The optical anisotropy is more sensitive than the radius of gyration to the presence of a branch in small alkanes. Optical anisotropies calculated for small alkanes containing a trifunctional branch point are affected significantly by the distinction between the kinds of three-bond interactions which occur in butane and the C_s form of 2-methylbutane, and they are also sensitive to slight alterations in the dihedral angles assigned to the rotational states at the trifunctional branch point.

The mean-squared optical anisotropy, $\langle\gamma^2\rangle$, of linear molecules is an example of a configuration-dependent physical quantity which is susceptible to valuation via rotational isomeric state theory.[2-6] Agreement between experimental results and theory is attained for *n*-alkanes[5] through the use of chain geometry and statistical weights which are consistent with the parameters required to reproduce the unperturbed dimensions of linear polyethylene.[7] Recent extensions[8,9] of the rotational isomeric state theory permit its application to branched polymers. This theory has been applied to the mean-squared unperturbed radius of gyration, $\langle s^2\rangle_0$, of a molecule containing a trifunctional or tetrafunctional branch point. The molecule weight dependence of $\langle s^2\rangle_0$ for the branched molecule and of g, defined as the ratio of $\langle s^2\rangle_0$ for the branched and linear molecules containing the same number of bonds, depends on the nature of the short-range interactions present.[10] The current objective is to utilize rotational isomeric state theory in order to determine the effect of a single trifunctional or tetrafunctional branch point on $\langle\gamma^2\rangle_0$ for alkanes. Of particular interest will be those factors affecting $g_{\gamma 2}$, defined as the ratio of $\langle\gamma^2\rangle_0$ for the branched alkane and the *n*-alkane containing an identical number of carbon atoms.

Computations

Configuration Partition Function. The configuration partition function, Z, for an *n*-alkane consisting of $n + 1$ carbon atoms is shown in (1),[6] in which the symbolism $\mathbf{U}_1^{(n)}$ denotes

$$Z = \mathbf{U}_1^{(n)} \qquad (1)$$

the product of n statistical weight matrices, commencing with $\mathbf{U}_1$. Terminal matrices are defined in (2) and (3),[6] and all remaining statistical weight matrices are given by (4).[3,6,7] A gauche three-bond interaction has a statistical weight of σ, and

$$\mathbf{U}_1 = [1 \quad 0 \quad 0] \qquad (2)$$

$$\mathbf{U}_n = \mathrm{col}\ [1 \quad 1 \quad 1] \qquad (3)$$

$$\mathbf{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \qquad (4)$$

$$1 < i < n$$

ψ and ω represent the statistical weights for four-bond interactions generated by successive gauche placements of the same and opposite signs, respectively.

When a trifunctional branch point is present, the configuration partition function is written as (5).[8] The number of

$$Z = {}_1\mathbf{U}_1^{(n_1)}({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1)\{({}_2\mathbf{U}_1^{(n_2-1)}) \otimes {}_3\mathbf{U}_1^{(n_3-1)})\} \qquad (5)$$

carbon–carbon bonds in branch j is n_j, and ${}_j\mathbf{U}_i$ is the statistical weight matrix for bond i in branch j. The first bond in branch 1 is CH_3–CH_2, and the first bond in branches 2 and 3 is CH–CH_2. The expression in (2) is used for ${}_1\mathbf{U}_1$, while ${}_2\mathbf{U}_{n_2}$ and ${}_3\mathbf{U}_{n_3}$ are given by (3). All other statistical weight matrices, except those specified in eq 6–9, are given by (4). The terms

$${}_1\mathbf{U}_{n_1} = \begin{bmatrix} 1 & 1 & \tau \\ \omega & \psi & \tau\psi\omega \\ \psi & \omega & \tau\psi\omega \end{bmatrix} \qquad (6)$$

$${}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1 =$$
$$\begin{bmatrix} \omega & \omega & \tau\psi^2 & \tau\psi & \tau\omega & \tau^2\psi\omega & 1 & \omega & \tau\psi \\ \omega & 1 & \tau\psi & \tau\psi^2 & \tau\psi & \tau^2\psi\omega & \omega & \omega & \tau\omega \\ \omega & \psi & \tau\psi\omega & \tau\psi\omega & \tau\psi\omega & \tau^2\omega^3 & \psi & \psi^2 & \tau\psi\omega \end{bmatrix} \qquad (7)$$

$${}_2\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \qquad (8)$$

$${}_3\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\omega & \sigma\psi \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \end{bmatrix} \qquad (9)$$

σ and σ^2 have been factored out of (6) and (7), respectively. The statistical weight for two gauche three-bond interactions of the type which occur in the C_s form of 2-methylbutane is $\sigma\tau$.[3] Distinction between σ and τ has only a trivial effect on $\langle s^2\rangle_0$ for an alkane with a single trifunctional branch point, and consequently ${}_1\mathbf{U}_{n_1}$ and ${}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1$ were written with $\sigma = \tau$ in the investigation of the effect of short-range interactions on g.[10] The distinction between σ and τ has a considerable effect on $\langle\gamma^2\rangle_0$ for small alkanes containing a trifunctional branch point, prompting its utilization in (6) and (7).

The configuration partition function for the case where a tetrafunctional branch point is present is shown in (10).[8] Statistical weight matrices are formulated as for the case where the branch point is trifunctional, with the exceptions of eq 11–13. The three-bond interactions $\sigma\tau$ and $\sigma^3\tau^3$ have been

$$Z = {}_1\mathbf{U}_1^{(n_1)}\{({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \ominus {}_4\mathbf{U}_1\}\{({}_2\mathbf{U}_2^{(n_2-1)}) \otimes ({}_3\mathbf{U}_2^{(n_3-1)}) \otimes ({}_4\mathbf{U}_2^{(n_4-1)})\} \quad (10)$$

$${}_1\mathbf{U}_{n_1} = \begin{bmatrix} 1 & 1 & 1 \\ \psi\omega & \psi\omega & \psi\omega \\ \psi\omega & \psi\omega & \psi\omega \end{bmatrix} \quad (11)$$

$$\{({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1 \ominus {}_4\mathbf{U}_1\} = \begin{bmatrix} \omega^3 & \psi^2\omega & \psi\omega^2 & \psi\omega^2 & \psi^2\omega & \omega^3 & \psi^2\omega & \psi^4 & \psi^2\omega & \psi\omega & \psi^2 & \psi^2\omega & \psi\omega & \psi\omega & \omega^3 & \psi\omega & \psi^2\omega & \psi\omega^2 & \psi\omega & \psi\omega & \psi\omega & \psi^2\omega & \psi\omega^2 & \omega^3 & \psi^2 & \psi^2\omega & \psi\omega \\ \omega^3 & \psi\omega^2 & \psi^2\omega & \psi\omega & \psi\omega & \psi\omega & \psi\omega & \psi^2\omega & \psi^2 & \psi^2\omega & \psi^2\omega & \psi^4 & \psi^2 & \psi\omega & \psi^2\omega & \psi\omega & \psi\omega^2 & \psi^2\omega & \psi\omega^2 & \omega^3 & \psi^2\omega & \psi^2\omega & \omega^3 & \psi\omega^2 & \psi\omega & \omega^3 & \psi\omega \\ \omega^3 & \psi\omega & \psi\omega & \psi^2\omega & \psi^2 & \psi\omega & \psi\omega^2 & \psi^2\omega & \psi\omega & \psi\omega^2 & \psi\omega & \psi^2\omega & \psi^2\omega & \psi\omega & \psi\omega^2 & \omega^3 & \omega^3 & \omega^3 & \psi^2\omega & \psi\omega & \psi^2 & \psi^4 & \psi^2\omega & \psi^2\omega & \psi^2\omega & \psi\omega^2 & \psi\omega \end{bmatrix} \quad (12)$$

$${}_2\mathbf{U}_2 = {}_3\mathbf{U}_2 = {}_4\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\psi\omega & \sigma\psi\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \end{bmatrix} \quad (13)$$

factored out of ${}_1\mathbf{U}_{n_1}$ and $({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \ominus {}_4\mathbf{U}_1$, respectively.

Mean-Squared Optical Anisotropies. The mean-squared optical anisotropy of the *n*-alkanes was calculated as described by Flory.[4–6] Equation 14, appropriate for the case where a single trifunctional branch point is present, has been obtained previously.[9] The generator matrices, ${}_{ij}\boldsymbol{F}_k$, are defined in that work.[9] They differ from those appropriate for the linear molecule[6] only in the vicinity of the branch point. Following the procedure utilized for the case of a single trifunctional branch point,[9] we obtain (15) for the case where the alkane has a single tetrafunctional branch point, with all branches being of equal length. The first term evaluates the contribution from the six identical chains, and the second term corrects for two extra countings of each branch. The identity matrix of order 11 is $\mathbf{E}_{11}$.

$$\begin{aligned} \frac{Z\langle\gamma^2\rangle_0}{1.5} = {}& ({}_{1,2}\boldsymbol{F}_{[1})({}_{1,2}\boldsymbol{F}_2^{(n_1)})\{(({}_{1,2}\boldsymbol{F}_{n_1+2}^{(n_2-2)}) \times ({}_{1,2}\boldsymbol{F}_{n_1+n_2]})) \otimes_{s,1} ({}_{1,3}\mathbf{U}_{n_1+2}^{(n_3-1)})\} \\ & + ({}_{1,3}\boldsymbol{F}_{[1})({}_{1,3}\boldsymbol{F}_2^{(n_1)})\{({}_{1,2}\mathbf{U}_{n_1+2}^{(n_2-1)}) \otimes (({}_{1,3}\boldsymbol{F}_{n_1+2}^{(n_3-2)})({}_{1,3}\boldsymbol{F}_{n_1+n_3]}))\} \\ & + ({}_{2,3}\boldsymbol{F}_{[1})({}_{2,3}\boldsymbol{F}_2^{(n_2)})\{(({}_{2,3}\boldsymbol{F}_{n_2+2}^{(n_3-2)})({}_{2,3}\boldsymbol{F}_{n_2+n_3]})) \otimes_{s,1} ({}_{2,1}\mathbf{U}_{n_2+2}^{(n_1-1)})\} \\ & - ({}_{1,2}\boldsymbol{F}_{[1})({}_{1,2}\boldsymbol{F}_2^{(n_2)})({}_{1,2}\boldsymbol{F}_{n_1]})({}_{1,2}\mathbf{U}_{n_1+1} \ominus {}_{1,3}\mathbf{U}_{n_1+1})\{({}_{1,2}\mathbf{U}_{n_1+2}^{(n_2-1)}) \otimes ({}_{1,3}\mathbf{U}_{n_1+2}^{(n_3-1)})\} \\ & - ({}_{1,2}\mathbf{U}_1^{(n_1)})({}_{1,2}\boldsymbol{F}_{[n_1+1})\{(({}_{1,2}\boldsymbol{F}_{n_1+2}^{(n_2-2)})({}_{1,2}\boldsymbol{F}_{n_1+n_2]})) \otimes_{s,1} ({}_{1,3}\mathbf{U}_{n_1+2}^{(n_3-1)})\} \\ & - ({}_{1,3}\mathbf{U}_1^{(n_1)})({}_{1,3}\boldsymbol{F}_{[n_1+1})\{({}_{1,2}\mathbf{U}_{n_1+2}^{(n_2-1)}) \otimes (({}_{1,3}\boldsymbol{F}_{n_1+2}^{(n_3-2)})({}_{1,3}\boldsymbol{F}_{n_1+n_3]}))\} \end{aligned} \quad (14)$$

$$\begin{aligned} Z\langle\gamma^2\rangle_0 = {}& 9({}_{1,4}\boldsymbol{F}_{[1})({}_{1,4}\boldsymbol{F}_2^{(n_1-1)})\{\{({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \ominus {}_4\mathbf{U}_1\} \otimes \mathbf{E}_{11}\}\|{}_{1,4}\boldsymbol{F}_{n_1+1}\|\{({}_2\mathbf{U}_2^{(n_2-1)}) \otimes ({}_3\mathbf{U}_2^{(n_3-1)}) \otimes \\ & (({}_{1,4}\boldsymbol{F}_{n_1+2}^{(n_4-2)})({}_{1,4}\boldsymbol{F}_{n_1+n_4]}))\} - 12({}_{1,4}\boldsymbol{F}_{[1})({}_{1,4}\boldsymbol{F}_2^{(n_1-2)})({}_{1,4}\boldsymbol{F}_{n_1]}) \times \\ & \{({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \ominus {}_4\mathbf{U}_1\}\{({}_2\mathbf{U}_2^{(n_2-1)}) \otimes ({}_3\mathbf{U}_2^{(n_3-1)}) \otimes ({}_4\mathbf{U}_2^{(n_4-1)})\} \end{aligned} \quad (15)$$

Bond Angles. As in the case of the treatment of *n*-alkanes,[2,3,5] the geometry about methyl groups will be tetrahedral and methylene groups will have ∠CCC and ∠HCH of 112 and 109°, respectively. The geometry at trifunctional branch points will be that of isobutane,[11] i.e., ∠CCC = 111° and ∠CCH = 107.9°. Symmetry dictates that the geometry about the tetrafunctional branch point must be tetrahedral.

Rotational States. The dihedral angles for the trans and gauche states for bonds sufficiently remote from a trifunctional branch point are 0 and ±120°.[5] Bonds involving the atom at a trifunctional branch point have one rotational state assigned where ${}_1C_{n_1-2}$–${}_1C_{n_1-1}$–${}_1C_{n_1}$–H, ${}_2C_2$–${}_2C_1$–${}_1C_{n_1}$–H, or ${}_3C_2$–${}_3C_1$–${}_1C_{n_1}$–H is in the trans conformation. The other two rotational states are assigned at $\pm(120° + \Delta\phi)$ from the above angle. Values assigned to ϕ at a trifunctional branch point are summarized in Table I.

Table I. Rotational States at a Trifunctional Branch Point

Branch	Bond	State	Atoms which are planar trans	ϕ
1	n_1	t	None	$2° + \Delta\phi$
		g$^+$	None	$122° - \Delta\phi$
		g$^-$	${}_1C_{n_1-2}$–${}_1C_{n_1-1}$–${}_1C_{2_1}$–H	$-118°$
2	1	t	None	$-2° - \Delta\phi$
		g$^+$	${}_2C_2$–${}_2C_1$–${}_1C_{n_1}$–H	$118°$
		g$^-$	None	$-122° + \Delta\phi$
3	1	t	None	$2° + \Delta\phi$
		g$^+$	None	$122° - \Delta\phi$
		g$^-$	${}_3C_2$–${}_3C_1$–${}_1C_{n_1}$–H	$-118°$

Anisotropic Part of the Group Polarizability Tensor. The anisotropic part of the group tensors, $\hat{\alpha}$, was formulated as in the treatment of the *n*-alkanes,[5] with the exception of the following group tensors which are required by the presence of the branch points.

The atoms near a trifunctional branch point are shown in Figure 1. As in the case of the *n*-alkanes,[2,3,5] the anisotropic part of the group tensor associated with the ${}_1C_{n_1-1}$–${}_1C_{n_1}$ bond includes contributions from both ${}_1C_{n_1}$–${}_1$H bonds. In contrast, only one C–H bond can contribute to the anisotropic part of the group tensors associated with the ${}_1C_{n_1}$–${}_2C_1$ and ${}_1C_{n_1}$–${}_3C_1$ bonds. The contribution of the ${}_1C_{n_1}$–H bond will arbitrarily

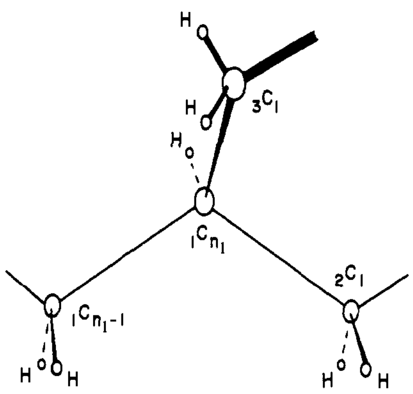

Figure 1. Atoms near a trifunctional branch point.

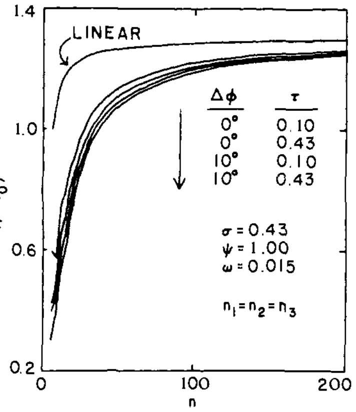

Figure 2. Optical anisotropies for n-alkanes and for alkanes which contain a single trifunctional branch point, the branches being of equal length. Results for the branched alkanes are presented for two values of τ (0.10 and 0.43) and two values of $\Delta\phi$ at the branch point (0 and 10°), starting with 3-ethylpentane.

be assigned to the group tensor associated with the ${}_1C_{n_1}$–${}_2C_1$ bond. Consequently the anisotropic part of the group tensor, ${}_3\hat{\alpha}_1$, associated with the ${}_1C_{n_1}$–${}_3C_1$ bond includes only the contribution from that bond. The polarizabilities parallel and perpendicular to the bond axis are $\alpha_\parallel$ and $\alpha_\perp$, respectively, and $\Delta\alpha = \alpha_\parallel - \alpha_\perp$.

$$ {}_3\alpha_1 = \begin{bmatrix} \tfrac{2}{3}\Delta\alpha_{CC} & 0 & 0 \\ 0 & -\tfrac{1}{3}\Delta\alpha_{CC} & 0 \\ 0 & 0 & -\tfrac{1}{3}\Delta\alpha_{CC} \end{bmatrix} \qquad (16) $$

Both the ${}_1C_{n_1}$–H and ${}_1C_{n_1}$–${}_2C_1$ bonds will contribute to ${}_2\hat{\alpha}_1$. The proper form for ${}_2\hat{\alpha}_1$ can be found by attaching a coordinate system to the ${}_1C_{n_1}$–H bond as follows: The origin lies at ${}_1C_{n_1}$, the ${}_1C_{n_1}$–H bond lies along the positive x axis, the y axis lies in the H–${}_1C_{n_1}$–${}_2C_1$ plane and has a positive projection on ${}_1C_{n_1}$–${}_2C_1$, and the z axis completes a right-handed coordinate system. The transformation from this coordinate system to the one attached to ${}_1C_{n_1}$–${}_2C_1$ is accomplished by a rotation of χ_1 about the z axis to align the x axes, followed by a rotation of χ_2 about the x axis. Addition of the contribution from the ${}_1C_{n_1}$–${}_2C_1$ bond produces (17), the column consisting of the elements of ${}_2\hat{\alpha}_1$ in "reading order". The geometry adopted dictates that $\chi_1 = 107.9°$ and $\chi_2 = -118°$.

Similar consideration for a tetrafunctional branch point requires that the ${}_j\hat{\alpha}_1$ ($j = 2, 3, 4$) contain only the contribution from the ${}_1C_{n_1}$–${}_jC_1$ bond. Consequently they are given by (16).

The numerical values used for $\Delta\alpha_{CC}$ and $\Delta\alpha_{CH}$ were 0.95 and 0.21 Å³, respectively, which conform to the requirement[5] that $\Gamma = 0.54 \pm 0.05$ Å³.

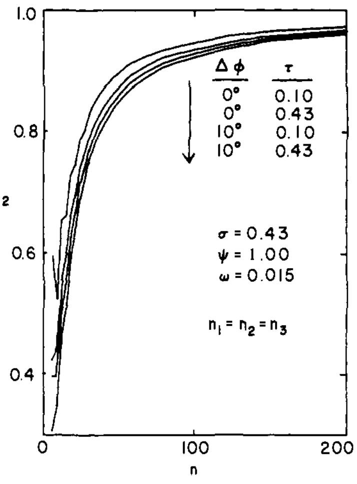

Figure 3. Molecular weight dependence of $g_{\gamma 2}$ for the molecules presented in Figure 2.

$$ {}_2\alpha_1{}^c = \begin{bmatrix} \tfrac{2}{3}\Delta\alpha_{CC} + (\cos^2\chi_1 - \tfrac{1}{3})\Delta\alpha_{CH} \\ -\cos\chi_1 \sin\chi_1 \cos\chi_2\, \Delta\alpha_{CH} \\ \cos\chi_1 \sin\chi_1 \sin\chi_2\, \Delta\alpha_{CH} \\ -\cos\chi_1 \sin\chi_1 \cos\chi_2 \Delta\alpha_{CH} \\ -\tfrac{1}{3}\Delta\alpha_{CC} + (\sin^2\chi_1 \cos^2\chi_2 - \tfrac{1}{3})\Delta\alpha_{CH} \\ -\sin^2\chi_1 \cos\chi_2 \sin\chi_2 \Delta\alpha_{CH} \\ \cos\chi_1 \sin\chi_1 \sin\chi_2 \Delta\alpha_{CH} \\ -\sin^2\chi_1 \cos\chi_2 \sin\chi_2 \Delta\alpha_{CH} \\ -\tfrac{1}{3}\Delta\alpha_{CC} + (\sin^2\chi_1 \sin^2\chi_2 - \tfrac{1}{3})\Delta\alpha_{CH} \end{bmatrix} \qquad (17) $$

$$ \Gamma = \Delta\alpha_{CC} - 1.95\Delta\alpha_{CH} \qquad (18) $$

Results

Trifunctional Branch Point. Figure 2 shows the results obtained for branched alkanes characterized by $n_1 = n_2 = n_3$, commencing with $n_1 = 2$. Numerical values for σ, ψ, and ω correspond to those appropriate for n-alkanes at 25 °C.[5] The mean-squared optical anisotropies obtained for the corresponding n-alkanes, also shown in Figure 2, are in agreement with the work of Patterson and Flory.[5] Results for the branched alkanes are sensitive to the distinction between σ and τ, and also to the value assigned to $\Delta\phi$.

In Figure 3 the results are replotted using $g_{\gamma 2}$, defined as the ratio of $\langle\gamma^2\rangle_0$ for branched and n-alkanes containing the same number of carbon atoms. Branching is seen to reduce the mean-squared optical anisotropy of alkanes throughout the range shown, with the effect being greatest for small alkanes. The asymptotic limit for $g_{\gamma 2}$ at high molecular weight is unity in each case.

The relationship between $g_{\gamma 2}$ for 3-ethylpentane ($n_1 = n_2 = n_3 = 2$) and 4-propylheptane ($n_1 = n_2 = n_3 = 3$) is seen in Figure 3 to be sensitive to the distinction between σ and τ, and also to the value assigned to $\Delta\phi$. The factors influencing $g_{\gamma 2}$ for these two alkanes are examined further in Figure 4. If $\Delta\phi$ is large (~10°), $g_{\gamma 2}$ for these two alkanes will be nearly identical for any reasonable value of τ/σ. Similarly, $g_{\gamma 2}$ for these two alkanes will be essentially identical if τ/σ is only slightly less than unity, for any reasonable value of $\Delta\phi$. Only if τ/σ is much less than unity, and $\Delta\phi$ is small (0 to ~5°), will $g_{\gamma 2}$ for

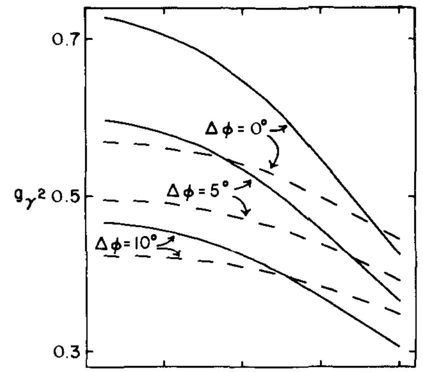

Figure 4. Effect of τ and $\Delta\phi$ at the branch point on $g_{\gamma 2}$ for 3-ethylpentane (solid lines) and 4-propylheptane (dashed lines). The values of σ, ψ, and ω are those appropriate for n-alkanes at 25 °C.[5]

Table II. Optical Anisotropies for the 27 Configurational States Available to 3-Ethylpentane

Statistical wt	No. of states	γ^2 in Å^6 for indicated $\Delta\phi$		
		$\Delta\phi = 0°$	$\Delta\phi = 5°$	$\Delta\phi = 10°$
$\tau^2\psi\omega$	6	0.34	0.39	0.44
$\tau\psi^2$	3	0.41	0.40	0.37
$\tau\psi$	6	0.43	0.40	0.37
$\tau^3\omega^3$	1	0.99	0.99	0.99
$\tau\omega$	3	1.27	1.25	1.22
1	2	1.27	1.03	0.80
ω	6	2.07	1.87	1.65

3-ethylpentane be sufficiently greater than $g_{\gamma 2}$ for 4-propylheptane to permit experimental verification that they are different.

The case of 3-ethylpentane is of particular interest since the three-bond interactions affect its configuration partition function, calculated via (5) and presented in (19), only via the

$$Z = 2 + 6\omega + 3(2\psi + \psi^2 + \omega)\tau + 6\psi\omega\tau^2 + \omega^3\tau^3 \quad (19)$$

statistical weight τ. The origin of the effects of τ/σ and $\Delta\phi$ on the mean-squared optical anisotropy of 3-ethylpentane can be seen from Table II, which contains the optical anisotropies and statistical weights for the 3^3 configurational states available to this molecule. Since ω is much less than unity, those states whose statistical weights contains ω will make only a small contribution to $\langle\gamma^2\rangle_0$. If τ also is much less than unity, the two states which have a statistical weight of unity will provide the dominant contribution to $\langle\gamma^2\rangle_0$. As τ increases, those states which warrant a statistical weight of $\tau\psi^2$ or $\tau\psi$ become more probable. Since these states have smaller optical anisotropies than the states warranting a statistical weight of unity, $\langle\gamma^2\rangle_0$ for 3-ethylpentane decreases as τ increases toward σ, for any reasonable value of $\Delta\phi$.

Table II also shows that the optical anisotropies for all states except one depend on $\Delta\phi$. That state whose optical anisotropy is unaffected by $\Delta\phi$ has a planar trans configuration for ${}_1\mathrm{C}_{n_1-2}$–${}_1\mathrm{C}_{n_1-1}$–${}_1\mathrm{C}_{n_1}$–H, ${}_2\mathrm{C}_2$–${}_2\mathrm{C}_1$–${}_1\mathrm{C}_{n_1}$–H, and ${}_3\mathrm{C}_2$–${}_3\mathrm{C}_1$–${}_1\mathrm{C}_{n_1}$–H. Its statistical weight is $\tau^3\omega^3$, and consequently it makes a negligible contribution to $\langle\gamma^2\rangle_0$. The only states which gain in optical anisotropy as $\Delta\phi$ increases are those meriting a statistical weight of $\tau^2\psi\omega$. The states whose optical anisotropy is most sensitive to $\Delta\phi$ are the two which merit a statistical weight of unity. The optical anisotropies of the nine states meriting a statistical weight of $\tau\psi^2$ or $\tau\psi$ also decrease with an increase in $\Delta\phi$, although not to the same extent as is the case for the two states meriting a statistical weight of unity. Consequently the mean-squared optical anisotropy of 3-ethylpentane decreases with an increase in $\Delta\phi$, for any reasonable value of τ/σ, and the effect is greatest when τ/σ is small.

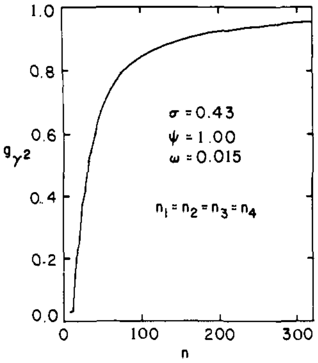

Figure 5. Molecular weight dependence of $g_{\gamma 2}$ for alkanes containing a single tetrafunctional branch point and branches of equal length starting with 3,3-diethylpentane.

Table III. Optical Anisotropies for the 81 Configurational States Available to 3,3-Diethylpentane

γ^2, Å^6	No. of states	Statistical wt
0.01	6	ψ^2
0.03	3	ψ^4
0.79	24	$\psi\omega$
0.80	24	$\psi^2\omega$
1.59	12	$\psi\omega^2$
2.37	12	ω^3

Tetrafunctional Branch Point. The $g_{\gamma 2}$ obtained for the case where the branch point is tetrafunctional, and the branches are of equal length, are shown in Figure 5. As when the branch point is trifunctional, the influence of the tetrafunctional branch point on the mean-squared optical anisotropy disappears at sufficiently large n. However, $\langle\gamma^2\rangle_0$ for alkanes of low molecular weight is depressed to a significantly greater extent by a tetrafunctional branch point than by a trifunctional branch point. The $\langle\gamma^2\rangle_0$ for 3,3-diethylpentane is 0.07 Å^6 ($g_{\gamma 2}$ = 0.028), in excellent agreement with the estimate of 0.1 Å^6 by Patterson and Flory.[5] This molecule is of interest because its configuration partition function, calculated via (10) and presented in (20), is independent of terms reflecting three-bond

$$Z = 6\psi^2 + 3\psi^4 + 24\psi(1 + \psi)\omega + 12\psi\omega^2 + 12\omega^3 \quad (20)$$

interactions. The optical anisotropies of the 3^4 configurational states for 3,3-diethylpentane are shown in Table III. It is apparent that $\langle\gamma^2\rangle_0$ for 3,3-diethylpentane must be extremely small (although not zero) so long as ω is much smaller than ψ.

Comparison of g and $g_{\gamma 2}$. The effect of a trifunctional or tetrafunctional branch point on the mean-squared optical anisotropy of alkanes disappears at sufficiently high molecular weight. This result is in contrast to that obtained for the mean-squared radius of gyration, the asymptotic limit for g being less than unity.[10,12,13] Both g and $g_{\gamma 2}$ for molecules of low to moderate molecular weight deviate from their asymptotic values in a manner determined by the short-range interactions present. The deviations encountered in $g_{\gamma 2}$ for low molecular weight alkanes at 25 °C are more pronounced than the deviations found for g assuming a variety of short-range interactions.[10] The number of bonds required for either g or $g_{\gamma 2}$ to attain its asymptotic limit is greater when the branch point is tetrafunctional than when it is trifunctional.

Table II shows that the squared optical anisotropies for the conformations available to 3-ethylpentane differ by a factor of 4 to 6, depending on $\Delta\phi$. The s^2 for these same conformations differ to a considerably lesser extent. Consequently the value of $g_{\gamma 2}$, but not g,[10] for 3-ethylpentane is sensitive to the distinction between σ and τ.

Comparison with Previous Work. Previous investigations of isotactic vinyl polymers have shown that the computed values for the characteristic ratio,[14,15] strain birefringence coefficient Γ_2,[16] and optical anisotropy[17] decrease as $\Delta\phi$ increases. The present work shows that an increase in $\Delta\phi$ at the trifunctional branch point in an alkane containing three articulated branches also brings about a decrease in $\langle\gamma^2\rangle$. Good agreement between experimental[18] and calculated[17] optical anisotropies for 2,4-dimethylpentane has been obtained when $\Delta\phi = 10°$. The characteristic ratio of isotactic vinyl polymers[14] and the optical rotation for poly[(*S*)-methylhept-1-ene][19,20] become larger as the value assigned to τ decreases. The present work shows that $\langle\gamma^2\rangle$ for an alkane consisting of three articulated branches emanating from a common atom also increases as the value assigned to τ decreases.

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Vacuum Ultraviolet Circular Dichroism of β-Forming Alkyl Oligopeptides

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Abstract: The vacuum ultraviolet circular dichroism, to 140 nm, is reported for films of oligopeptides having the general formula BOC(L-X)$_n$OMe, where X = Ala, Val, Nva and n = 2-7. Substantial amounts of β conformation are indicated at the trimer in the alanine series, the hexamer in the norvaline series, and the heptamer in the valine series. The alanine and valine heptamer conformations are assigned to the antiparallel and parallel sheets, respectively. The norvaline heptamer conformation is assigned to a mixture of parallel and antiparallel sheets, in approximately equal amounts. The assignments are in agreement with published infrared data for these peptides.

The formation of secondary structure in peptides is directed by chemical structure, i.e., the nature of the side chains and the chain length, and by a large number of environmental factors. In recent years work has been carried out in our laboratories on the synthesis and conformational analysis of monodisperse linear homo-oligopeptides,[1b,2] and on the extension of circular dichroism measurements on polypeptides into the vacuum ultraviolet spectral region.[1a,3] In this work we report the vacuum ultraviolet circular dichroism (VUCD)[4] to 140 nm of films of oligopeptides having the general formula BOC(L-X)$_n$OMe, where X = Ala, Val, Nva and n = 2-7.

Palumbo et al.[2] have reported solid state infrared absorption data for the same oligopeptide series. Shifts in the positions of the amide I and V bands indicate that the higher members of all three series are in the β conformation in the solid state. Absorption was found in the deblocked heptamers, HCl·H(L-X)$_7$OMe, of alanine and norvaline at 1694 and 1692 cm^{-1}, respectively, but none was found in the deblocked valine heptamer. It was concluded that the β conformation which develops in the alanine and norvaline heptamers definitely contains antiparallel chains whereas parallel chains are predominant in the case of valine.

Theoret et al.[5] measured the solid state infrared absorption of the zwitterionic alanine dimer through hexamer. Absorption was found in the tetramer through hexamer at 1697 cm^{-1} indicating the presence of the antiparallel β conformation in the solid state of those zwitterionic forms; bands were found in the dimer and trimer at 1685 and 1692 cm^{-1}, respectively. The zwitterionic alanine dimer through hexamer as also studied in the solid state by Sutton and Koenig[6] with Raman spectroscopy. The antiparallel β conformation was indicated in the tetramer through hexamer by the appearance of a band at 1663 cm^{-1}; in the dimer and trimer the band was found at 1680 and 1659 cm^{-1}, respectively. Fujie et al.[7] reported infrared data and x-ray diffraction patterns for the alanine dimer, trimer, tetramer, and nonamer. The tetramer x-ray diffraction pattern is similar to that of the nonamer, but the dimer and trimer patterns are qualitatively different. Komoto et al.[8] observed development of the β conformation in the early stages of solid state polymerization of L-valine *N*-carboxyanhydride.

Of particular importance in the present work is the question of the consistency of infrared absorption and circular dichroism as analytical tools for the detection of the β conformation in solid state oligopeptides and, especially, in their ability to distinguish between the parallel and antiparallel sheets.

Experimental Section

Synthesis. The details of the synthesis and the chemical and optical characterizations of BOC(L-X)$_n$OMe, where X = Val, Nva, Ala and n = 2-7, are reported in ref 9-11.