bond. This process was ignored by Hoffmann[14] because the $^1A_1{}^*$ state is energetically unfavorable. Our limited CI calculations on $^1A_1$ states of CH_2 indicate that the $^1A_1{}^* - {}^1A_1$ energy separation is only 1.92 eV. Thus, the possible role of the $^1A_1{}^*$ state in the reaction cannot be ruled out, particularly when this state seems to be the one that is photochemically produced.

In contrast to the carbene, the nitrenium ion may be produced from the heterolytic cleavage of an $>$N–Cl bond under solvolytic conditions, giving a chloride ion and an electron-deficient species $>N\!:^+$, the nitrenium ion.[3] The ion should be formed in the $^1A_1$ state, with the lone pair in the *N*-chloramine correlating with the $3a_1$ orbital in the nitrenium ion. Gassman[3] has pointed out that the $^1A_1$ state should exhibit carbonium ion like behavior, while the $^3B_1$ state would be expected to resemble a nitrogen cation radical in its chemical reactivity. Using these ideas and the fact that spin–orbit interaction should convert the $^1A_1$ nitrenium ion to the $^3B_1$ ion, he has established the existence of the nitrenium ion by observation of triplet–singlet product ratios as halogenated solvents are added to the reaction. Thus, two states of the nitrenium ion are of particular interest in its chemistry.

Our CI calculations indicate that the $^3B_1 - {}^1A_1$ separation for the NH_2^+ molecule is 1.56 eV. This is about twice as large as the $^3B_1 - {}^1A_1$ separation predicted for CH_2. Our value of 0.88 eV for the singlet–triplet splitting in CH_2 compares quite favorably with the more extensive calculations of O'Neil, Schaefer, and Bender,[7] which predict a separation of 0.96 eV. The experimental value of the ($^3B_1 - {}^1A_1$) separation is not known for either CH_2 or NH_2^+; however, in view of our agreement with Schaefer and Bender for the $^3B_1 - {}^1A_1$ separation in CH_2 and the excellent agreement with the experimental value for the ($^1B_1 - {}^1A_1$) separation in CH_2 (see Table I), we believe the reported value for NH_2^+ is probably accurate to 0.2 eV.

Conclusions

In this paper, nonempirical configuration-interaction results have been reported for the low-lying states of NH_2^+ and CH_2. Analysis of these results suggests several points which are of potential value in understanding and interpreting the chemistry of these and related species. First of all, the singlet–triplet separation ($^1A_1 - {}^3B_1$) for NH_2^+ is predicted to be about twice as big as the singlet–triplet separation for CH_2. Secondly, the $^1A_1{}^*$ state of CH_2 is implicated as the active state in the stereospecific addition of CH_2 to olefins.

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Conformational Characteristics and Flexibility of Branched Polyethylenes

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Abstract: The mean-square unperturbed radii of gyration of branched polyethylenes are calculated in the rotational isomeric state approximation. Tri- and tetrafunctional branching is considered, as well as the effects of branch spacing, type, and distribution on the calculated radii. Regardless of the branching functionality, it is found that the mean-square radius of gyration of the backbone of branched polyethylene is nearly identical with the radius of linear polyethylene of the same degree of polymerization as the branched polymer's backbone, providing the branches are spaced 20 or more bonds apart. This result reduces the calculation of the mean-square unperturbed radii of gyration of branched polyethylenes to the taking of the appropriate sums and differences of the radii of gyration of linear portions of the branched polymer. Since the radius of linear polyethylene has been previously calculated as a function of chain length, it is possible to closely approximate the radius of any given branched polyethylene without specifically conducting any further conformational calculations. Examples of the calculated radii of gyration of several widely differing branched polyethylenes are presented and compared to their freely jointed values. A recent solution–viscosity study of ethyl-branched polyethylenes reports an increase in the backbone flexibility relative to linear polyethylene as the branch content is increased. For reasonable ranges of the rotational state statistical weights, it is possible to predict this observed increase in backbone flexibility only if the rotational states are displaced *ca.* 10° from the symmetric positions 0 and ±120°. Displacements of this magnitude from the threefold symmetric locations are in agreement with spectroscopic measurements and potential energy calculations performed on *n*-butane and higher alkanes.

Chain branching, together with molecular weight distribution, tacticity in vinyl polymers, and degree of cross linking in network polymers, is a molecular parameter knowledge of which is crucial to the understanding of the physical properties of polymers.[1] Many experimental studies[2–12] seeking to determine the

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effect of chain branching on the equilibrium and dynamic physical properties of polymers in dilute solution and in the bulk have been undertaken. In addition, several theoretical investigations[1,13–28] have attempted to relate the degree and type of chain branching to the equilibrium statistical radius of gyration (as measured by light scattering) and to the hydrodynamic radius (as determined from viscosity measurements).

However, all but one[9] of the above studies have failed to deal with the influence of branching on polymer backbone flexibility and the contribution this influence makes to the physical properties of branched polymers. Most of the experimental investigations were complicated by molecular weight and branching heterogeneities and in some cases by intermolecular interactions present in the bulk, and the theoretical calculations were performed either on long, freely jointed chains or on a cubic lattice by Monte Carlo methods.[24] Before the influence of branching on the physical properties of polymers can be predicted (especially for polymers in the bulk), knowledge of how branching affects the properties of individual and isolated polymer chains must be gathered.

The purpose of the present investigation is to determine the conformational characteristics of branched polyethylene. Mean-square unperturbed[26] radii of gyration are calculated in the rotational isomeric state approximation[26,27] for variously branched polyethylenes. The calculated radii are compared with the radii obtained experimentally by Stacey and Arnett[9] for ethyl-branched polyethylenes and those calculated previously[13,22] for long, freely jointed branched polymers.

Methods of Calculation

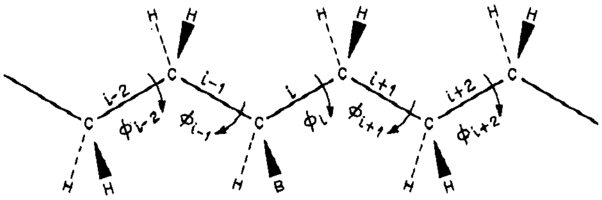

Figure 1. A schematic diagram of a portion of a branched polyethylene in the all-trans or planar-zigzag conformation.

A portion of a branched polyethylene chain in the all-trans or planar-zigzag conformation is depicted in Figure 1. The branch B is of the *n*-alkane type CH_2-$CH_2 \cdots CH_3$. The backbone bond lengths (1.53 Å) and valence angles (112°) are assumed to be rigid.[26,27] The rotational isomeric states of $\varphi = 0°$ (trans (t)) and $\pm 120°$ (gauche (g±)) are adopted, and small displacements away from these threefold symmetric locations are also considered.[26,29] Knowledge of the probabilities of occurrence, or the statistical weights, of the rotational states is necessary[26] to the description of the conformational characteristics of the chain and to the determination of its equilibrium physical properties. The rotational state statistical weights of any nonterminal bond depend only on the rotational states of the nearest neighbor bonds. Consequently, only interactions dependent on a single or pair of adjacent rotation angles need be considered.

Inspection of molecular models makes clear that only the nearest neighbor dependent steric interactions and statistical weights associated with the rotational states of the two backbone bonds preceding and the three backbone bonds succeeding the branch point differ from those in linear polyethylene. As an example of the formulation[30] of statistical weight matrices, we focus attention on the interactions dependent on the pair of rotations about bonds of the type $i - 2$ and $i - 1$ in Figure 1. We seek to determine the following matrix

$$U_{i-1} = \begin{array}{c} \\ \mathrm{t} \\ \mathrm{g}^+ \\ \mathrm{g}^- \end{array} \begin{array}{c} \begin{array}{ccc} \mathrm{t} & \mathrm{g}^+ & \mathrm{g}^- \end{array} \\ \begin{bmatrix} \mu_{\mathrm{tt}} & \mu_{\mathrm{tg}^+} & \mu_{\mathrm{tg}^-} \\ \mu_{\mathrm{g}^+\mathrm{t}} & \mu_{\mathrm{g}^+\mathrm{g}^+} & \mu_{\mathrm{g}^+\mathrm{g}^-} \\ \mu_{\mathrm{g}^-\mathrm{t}} & \mu_{\mathrm{g}^-\mathrm{g}^+} & \mu_{\mathrm{g}^-\mathrm{g}^-} \end{bmatrix} \end{array}$$

whose elements are Boltzmann factors of the energies of each of the nine different pairs of rotational states. The rows of U_{i-1} are indexed by the rotational states of bond $i - 2$ and the columns by the rotational states of bond $i - 1$. For all but the terminal bonds in linear polyethylene[26,28]

$$U = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix}$$

where σ is the statistical weight corresponding to the three-bond trans–gauche energy difference and ω represents the statistical weight of the four-bond pentane interference in the g±g∓ rotational states.

Following Flory, *et al.*,[26,28,29] we break the interactions up into those dependent solely on φ_{i-1} (three-bond interactions) and those dependent on φ_{i-2} and φ_{i-1} (four-bond interactions). The three-bond inter-

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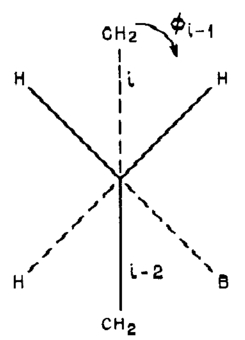

Figure 2. A diagram illustrating the three-bond nonbonded steric interactions dependent on the single rotation angle φ_{i-1} (see Figure 1).

actions dependent upon φ_{i-1} are illustrated in Figure 2. In the trans conformation shown in Figure 2 the CH_2 group attached to bond $i - 2$ is close to the branch B attached to C_{i-1}; rotation of 120° in a clockwise direction results in the g^+ state where the CH_2 group attached to bond $i - 2$ is in close contact with both the CH_2 group attached to bond i and the branch B; and in the g^- state only the two CH_2 groups are in proximity. By analogy to the treatment of linear polyethylene[28] and vinyl polymers,[29] the three-bond statistical weights $\eta\sigma$, $\tau\sigma$, and σ are assigned to the t, g^+, and g^- conformations about bond $i - 1$ and placed in the diagonal matrix $D_{i-1} = \text{diag}(\eta\sigma,\tau\sigma,\sigma)$, or $\text{diag}(\eta,\tau,1)$. The statistical weight σ represents the three-bond interactions between CH_2 groups in the g^- state and τ is the statistical weight for the three-bond interaction involving B and CH_2.

For branches of the n-alkane type and when the rotational states are assumed to be symmetrically located at 0 and ±120°, $\tau = \sigma$. However, theoretical[26,28-31] and experimental[32-34] evidence suggests that $\varphi_{i-1}(\text{t},g^\pm) = -\Delta°, 120°, (-120 + \Delta)°$ and $\varphi_i(\text{t},g^\pm) = \Delta°, (120 - \Delta)°, -120°$, while all other bonds not adjacent to a branch point have $\varphi_\text{t} = 0°$ and $\varphi_{g^\pm} = \pm 120 \mp \Delta°$, where $\Delta \approx 5\text{–}10°$, because of steric repulsions such as those illustrated in Figure 2. However, the steric interactions represented by τ are not alleviated by this displacement, resulting in $0 < \tau < \sigma$.

Four bond interactions involving the rotation angles φ_{i-2} and φ_{i-1} may be summarized by the following matrix

$$V_{i-1} = \begin{array}{rc} i-2 & \overbrace{\begin{array}{ccc}\text{t} & g^+ & g^-\end{array}}^{i-1} \\ \begin{array}{r}\text{t}\\ g^+\\ g^-\end{array} & \begin{bmatrix}1 & 1 & 1\\ 1 & \omega & \omega\\ \omega & \omega & 1\end{bmatrix}\end{array} \qquad (1)$$

where the statistical weight ω represents the interaction of two CH_2 groups as it occurs in the $g^\pm g^\mp$ conformations of linear polyethylene. Elements of unity signify four-bond steric interactions no more severe than in the tt conformation. Finally U_{i-1} is given by

$$U_{i-1} = V_{i-1}D_{i-1} = \begin{bmatrix}\eta & \tau & 1\\ \eta & \tau\omega & \omega\\ \eta\omega & \tau\omega & 1\end{bmatrix} \qquad (2)$$

In a similar fashion we obtain

$$U_{i-2} = \begin{bmatrix}1 & \sigma & \sigma\omega\\ 1 & \sigma & \sigma\omega^2\\ 1 & \sigma\omega & \sigma\omega\end{bmatrix}$$

$$U_i = \begin{bmatrix}\eta\tau^* & 1 & \tau\\ \eta & 1 & \tau\omega\\ \eta & \omega & \tau\end{bmatrix}$$

$$U_{i+1} = \begin{bmatrix}1 & \sigma\omega & \sigma\\ 1 & \sigma & \sigma\omega\\ 1 & \sigma\omega & \sigma\omega\end{bmatrix} \qquad (3)$$

$$U_{i+2} = \begin{bmatrix}1 & \sigma & \sigma\\ \omega & \sigma\omega & \sigma\omega^2\\ 1 & \sigma\omega & \sigma\end{bmatrix}$$

where τ^* denotes the statistical weight corresponding to the additional CH_2–B interaction when the bonds on either side of the branch point are both trans,[26,29] and $\tau^* \approx \tau$ for n-alkane branches.[35] The statistical weight matrices for the bonds adjoining a tetrafunctional branch point are also presented below.

$$U_{i-2} = \begin{bmatrix}1 & \sigma\omega & \sigma\omega\\ 1 & \sigma\omega & \sigma\omega^2\\ 1 & \sigma\omega^2 & \sigma\omega\end{bmatrix}$$

$$U_{i-1} = \begin{bmatrix}1 & 1 & 1\\ \omega & \omega & \omega\\ \omega & \omega & \omega\end{bmatrix}$$

$$U_i = \begin{bmatrix}(\tau^*)^2 & 1 & 1\\ 1 & 1 & \omega\\ 1 & \omega & 1\end{bmatrix} \qquad (4)$$

$$U_{i+1} = \begin{bmatrix}1 & \sigma\omega & \sigma\omega\\ 1 & \sigma\omega & \sigma\omega\\ 1 & \sigma\omega & \sigma\omega\end{bmatrix}$$

$$U_{i+2} = \begin{bmatrix}1 & \sigma & \sigma\\ \omega & \sigma\omega & \sigma\omega^2\\ \omega & \sigma\omega^2 & \sigma\omega\end{bmatrix}$$

The Flory–Jernigan matrix method[26,36] is employed in the calculation of the mean-square radii of gyration. For a chain of n backbone bonds

$$\langle S^2\rangle_\circ = (n + 1)^{-2}\sum_{0 \leq i < j \leq n}\langle r_{ij}{}^2\rangle \qquad (5)$$

where r_{ij} is the distance between the ith and jth chain segments, and

$$\sum_{0 \leq i \leq j \leq n}\langle r_{ij}{}^2\rangle = 2Z^{-1}J^*\left(\prod_{i<1}^{n} G_i\right)J \qquad (6)$$

Hence

$$\langle S^2\rangle_\circ = 2(n + 1)^{-2}Z^{-1}J^*\left(\prod_{i=1}^{n} G_i\right)J \qquad (7)$$

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where J^* is the $1 \times 7\nu$ row $[1,000\cdots0]$, J is the $7\nu \times 1$ column with 6ν zeros followed by ν ones (ν is the number of rotational states)

$$\begin{bmatrix} 0 \\ 0 \\ \cdot \\ \cdot \\ 1 \\ 1 \\ \cdot \\ \cdot \\ 1 \end{bmatrix}$$

$$G_i = \begin{bmatrix} U & U & (U \times l^T)\|T\| & (l^2/2)U & (l^2/2)U \\ 0 & U & (U \times l^T)\|T\| & (l^2/2)U & (l^2/2)U \\ 0 & 0 & (U \times E_3)\|T\| & U \times l & U \times l \\ 0 & 0 & 0 & U & U \\ 0 & 0 & 0 & 0 & U \end{bmatrix}_i \tag{8}$$

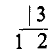
and is $7\nu \times 7\nu$ in size. In this equation U is the statistical weight matrix, l is the bond vector as a column, E_3 is the third order unity matrix, $\|T\|$ is the diagonal array of 3×3 matrices T which transform the representation of a vector in the coordinate system of bond $i + 1$ into its representation in the like coordinate system affixed to bond i (see ref 25), and Z is the configurational partition function

$$Z = K^*\left(\prod_{i=2}^{n-1} U_i\right)K \tag{9}$$

where K^* is the $1 \times \nu$ row vector $[10\cdots0]$ and K is the $\nu \times 1$ column vector

$$\begin{bmatrix} 1 \\ 1 \\ 1 \\ \cdot \\ \cdot \\ \cdot \\ 1 \end{bmatrix}$$

As an example of the applicationof eq 7 and 8 the mean-square radius of the branched polyethylene



is given by

$$\langle S^2\rangle_o = \frac{2}{(a+b+c+1)^2} \times \left[\frac{J^*\left(\prod_{i=1}^{a+c} G_i\right)J}{Z_{ac}} + \frac{J^*\left(\prod_{i=1}^{a+b} G_i\right)J}{Z_{ab}} + \frac{J^*\left(\prod_{i=1}^{b+c} G_i\right)J}{Z_{bc}} - \frac{J^*\left(\prod_{i=1}^{a} G_i\right)J}{Z_{a}} - \frac{J^*\left(\prod_{i=1}^{b} G_i\right)J}{Z_{b}} - \frac{J^*\left(\prod_{i=1}^{c} G_i\right)J}{Z_{c}}\right] \tag{10}$$

where a, b, and c are the numbers of backbone bonds in the segments 1, 2, and 3, respectively, and Z_{ac}, for example, is the partition function for the continuous

Table I. Calculated Unperturbed Radii of Gyration of Trifunctional Branched Polyethylenes of 100 Backbone Bonds

τ^*	τ	$g(5)$[a]	$g(10)$	$g(20)$
0.1	0.1	0.86 (1.01)[b]	0.91 (0.99)	0.95 (1.99)
0.1	0.2	0.86 (1.00)	0.91 (0.99)	0.95 (0.99)
0.1	0.3	0.86 (1.00)	0.91 (0.98)	0.95 (0.99)
0.1	0.4	0.86 (0.99)	0.91 (0.98)	0.95 (0.99)
0.1	0.5	0.86 (0.99)	0.91 (0.97)	0.95 (0.99)
0.2	0.1	0.88 (1.03)	0.92 (1.01)	0.96 (1.00)
0.2	0.2	0.88 (1.02)	0.92 (1.00)	0.96 (1.00)
0.2	0.3	0.87 (1.01)	0.92 (0.99)	0.96 (1.00)
0.2	0.4	0.87 (1.00)	0.92 (0.98)	0.96 (0.99)
0.2	0.5	0.87 (1.00)	0.91 (0.98)	0.95 (0.99)
0.3	0.1	0.89 (1.05)	0.93 (1.02)	0.97 (1.00)
0.3	0.2	0.89 (1.04)	0.93 (1.01)	0.96 (1.00)
0.3	0.3	0.89 (1.03)	0.93 (1.00)	0.96 (1.00)
0.3	0.4	0.88 (1.02)	0.92 (0.99)	0.96 (1.00)
0.3	0.5	0.88 (1.01)	0.92 (0.99)	0.96 (0.99)
0.4	0.1	0.90 (1.07)	0.94 (1.03)	0.97 (1.00)
0.4	0.2	0.90 (1.05)	0.94 (1.02)	0.97 (1.00)
0.4	0.3	0.90 (1.04)	0.93 (1.01)	0.97 (1.00)
0.4	0.4	0.89 (1.03)	0.93 (1.00)	0.96 (1.00)
0.4	0.5	0.89 (1.02)	0.93 (0.99)	0.96 (1.00)
0.5	0.1	0.92 (1.08)	0.95 (1.03)	0.97 (1.00)
0.5	0.2	0.91 (1.06)	0.95 (1.02)	0.97 (1.00)
0.5	0.3	0.90 (1.05)	0.94 (1.01)	0.97 (1.00)
0.5	0.4	0.90 (1.04)	0.94 (1.01)	0.97 (1.00)
0.5	0.5	0.90 (1.03)	0.93 (1.00)	0.96 (1.00)
1.0	0.1	0.97		
1.0	0.2	0.96		
1.0	0.3	0.95		
1.0	0.4	0.94		
1.0	0.5	0.94		

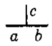
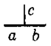
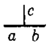
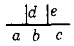
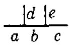
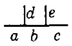
[a] $g = \langle S^2\rangle_{o,B}/\langle S^2\rangle_{o,L}$, and $g(x)$ signifies a branch point every x backbone bonds. [b] $\Delta\varphi = 0°$, $\sigma = 0.54$, and $\omega = 0.088$. All other values correspond to $\Delta\varphi = 10°$, $\sigma = 0.61$, and $\omega = 0.11$.

Table II. Calculated Unperturbed Radii of Gyration of Tetrafunctional Branched Polyethylenes of 100 Backbone Bonds

τ^*	$g(5)$[a]	$g(10)$	$g(20)$
0.1	0.91 (1.05)[b]	0.92 (1.02)	0.95 (1.01)
0.2	0.91 (1.06)	0.92 (1.02)	0.95 (1.01)
0.3	0.91 (1.06)	0.93 (1.03)	0.95 (1.01)
0.4	0.92 (1.07)	0.94 (1.06)	0.96 (1.01)
0.5	0.93 (1.08)	0.94 (1.06)	0.96 (1.01)
1.0	1.0 (1.15)	0.96 (1.08)	0.98 (1.04)

[a] $g = \langle S^2\rangle_{o,B}/\langle S^2\rangle_{o,L}$, and $g(x)$ signifies a branch point every x backbone bonds. [b] $\Delta\varphi = 0°$, $\sigma = 0.54$, and $\omega = 0.088$. All other values correspond to $\Delta\varphi = 10°$, $\sigma = 0.61$, and $\omega = 0.11$.

Table III. Calculated Radii of Gyration of Branched Polyethylenes

Polymer	Branch length	g[a]	g[b]
	$a = b = 100$, $c = 6$	0.958 (0.940)[c]	0.955
	$a = b = 100$, $c = 50$	0.802 (0.790)	0.799
	$a = b = 100$, $c = 100$	0.770 (0.765)	0.768
	$a = b = c = 100$, $d = e = 6$	0.959 (0.935)	0.955
	$a = b = c = 100$, $d = e = 50$	0.755 (0.740)	0.752
	$a = b = c = 100$, $d = e = 100$	0.692 (0.685)	0.690

[a] Correct statistical wt matrices with $\sigma = \tau = \tau^* = 0.54$, $\omega = 0.088$, and $\Delta\varphi = 0°$. [b] Statistical wt matrix appropriate to LPE used for every bond with $\sigma = 0.54$ and $\omega = 0.088$. [c] $\Delta\varphi = 10°$, $\sigma = \tau = \tau^* = 0.61$, and $\omega = 0.11$.

Table IV. Calculated Mean-Square Radii of Gyration of Branched Polyethylenes with Random Distributions of Branch Lengths and Spacings (Cases II and IV)

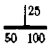
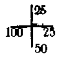
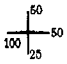
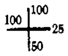
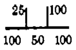
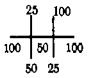
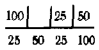
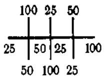
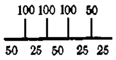
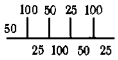
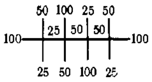
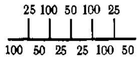
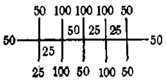
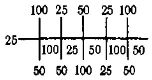
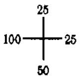
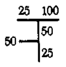
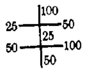
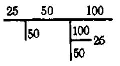
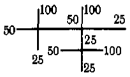
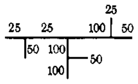
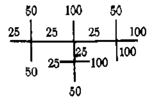
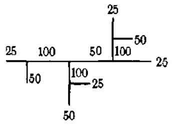
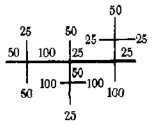
Branching type	Polymer	m^a	f^b	$\langle S^2\rangle_{0,B}/\langle S^2\rangle_{0,L}$ Rotational isomeric state	Freely jointed and long branched polymers
Normal or comb		1	3	0.851	
Normal or comb		1	4	0.725	
Normal or comb		1	4	0.689	
Normal or comb		1	4	0.699	
Normal or comb		2	3	0.727	
Normal or comb		2	4	0.561	
Normal or comb		3	3	0.701	
Normal or comb		3	4	0.493	
Normal or comb		4	3	0.561	0.733
Normal or comb		4	3	0.703	0.733
Normal or comb		4	4	0.444	0.564
Normal or comb		5	3	0.557	0.703
Normal or comb		5	4	0.392	0.534
Normal or comb		5	4	0.511	0.534
Random		1	3	0.851	0.900
Random		1	4	0.725	0.800
Random		2	3	0.786	0.829
Random		2	4	0.517	0.691
Random		3	3	0.673	0.774
Random		3	4	0.507	0.618
Random		4	3	0.680	0.730

Table IV (*Continued*)

Branching type	Polymer	m^a	f^b	$\langle S^2\rangle_{o,B}/\langle S^2\rangle_{o,L}$ Rotational isomeric state	$\langle S^2\rangle_{o,B}/\langle S^2\rangle_{o,L}$ Freely jointed and long branched polymers
Random		4	4	0.396	0.566
Random		5	3	0.678	0.694
Random		5	4	0.438	0.525

^{a} m = number of branch points. ^{b} f = branch functionality.

section of the chain consisting of segments 1 and 3. If this same chain were treated as freely jointed[22,26] and the lengths of segments 1, 2, and 3 are sufficiently long, then

$$\langle S^2\rangle_o = \frac{6l^2}{(a+b+c+1)^2}[(a+b)(a+b+1)^2 + (a+c)(a+c+1)^2 + (b+c)(b+c+1)^2 - a(a+1)^2 - b(b+1)^2 - c(c+1)^2] \quad (11)$$

Results

For articulated branches of the n-alkane type ($B \equiv CH_2-CH_2-\cdots CH_3$), which are primarily under consideration here, the following values of the statistical weights are appropriate[26,28,29] at $T = 140°$: $\eta = 1.0$, $0 < \tau^* \approx \tau < \sigma \leq 0.6$, and $\omega \approx 0.1$. If $B \equiv CH_3$, as in ethylene–propylene copolymers, then $\tau^* = 1.0$. The calculated mean-square unperturbed radii of gyration presented in Tables I and II correspond to these values of the statistical weight parameters and for branches of zero length; *i.e.*, the conformational characteristics of the backbone bonds neighboring a branch point are treated as if a branch were present, but the sums of the mean-square distances between the segments in the same branch, between the segments in different branches, and between the segments in a branch and the backbone are neglected. This method of calculation permits an explicit evaluation of the effect of branching (functionality and spacing) on the flexibility of the polyethylene backbone.

The unperturbed mean-square radii of several branched polyethylenes are calculated using the correct statistical weight matrices derived and presented earlier and then using the matrix appropriate to linear polyethylene for each bond. A display and comparison of these results are made in Table III. The calculated radii of several examples of branched polyethylenes with normal or comb-type branching possessing uniform (case I) and random (case II) distributions[22] of branch lengths and spacings and with random branching and uniform (case III) and random (case IV) distributions of branch lengths and spacings are presented in Tables IV and V. Each radius was calculated using the statistical weight matrix appropriate to linear polyethylene for each bond in the chain. Freely jointed radii are also presented for purposes of comparison.

Discussion

It is clear from the calculated radii of gyration presented in Tables I–III that the backbone flexibility of branched polyethylene is predicted to be nearly the same or slightly greater than linear polyethylene ($\langle S^2\rangle_{o,B} \leq \langle S^2\rangle_{o,L}$), provided $\Delta\varphi \neq 0°$ and the branches are spaced at intervals of 20 or more bonds. The predicted dependence of backbone flexibility upon branching is compared in Table VI to the experimental radii of gyration of ethyl-branched polyethylenes[37] measured by Stacey and Arnett.[9] They find the measured radii to decrease substantially as the number of ethyl branches is increased. The observed reduction in $\langle S^2\rangle_{o,B}$ for the more sparsely branched samples can be reproduced by the calculated radii only if $\tau^* \leq 0.10$. In the range $0 \leq \tau^* \leq 0.5$, it is not obvious[26,29] what precise value should be assigned to τ^* for n-alkane-branched polyethylenes. Unlike most measurements performed on vinyl polymers,[26,29] the data reported by Stacey and Arnett[9] provide an experimental check upon the value of τ^* which is independent of stereoregularity, because of the absence of branch–branch interactions. Hence, one might conclude[38] from the comparison made in Table VI that $\tau = \tau^* \approx 0.10$ is more realistic than $\tau = \tau^* \approx \sigma = 0.5$–$0.6$ for n-alkane-branched polyethylenes.

In any event, the backbone flexibility of sparsely branched polyethylenes (20 or more bonds apart) is seen to vary insignificantly from linear polyethylene. Thus, the mean-square unperturbed radii of gyration of branched polyethylenes may be closely estimated from the radii of gyration previously calculated for linear polyethylene as a function of chain length. Summation of the appropriate known radii of gyration of the linear segments of branched polyethylene (see eq 10) makes possible this estimate of its radius.[39]

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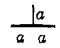
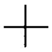
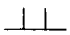
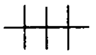
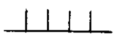
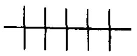
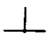
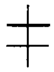
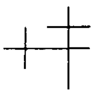
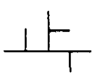
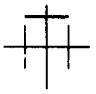
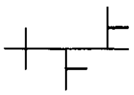
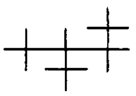
(37) Ethyl-branched polyethylenes were obtained by hydrogenating polybutadienes. The 1,3-diene content detected by infrared spectroscopy prior to hydrogenation was assumed to be the ethyl-branch content subsequent to hydrogenation.

(38) P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 1798 (1967).

(39) Throughout the above comparison of the flexibility of branched and linear polyethylenes, the same temperature has been used in evaluating the rotational state statistical weights for all of the polymers;

Table V. Calculated Mean-Square Radii of Gyration of Branched Polyethylenes with Uniform Distributions of Branch Lengths and Spacing (Cases I and III)

				$(\langle S^2\rangle_{0,B}/\langle S^2\rangle_{0,L})^a$			
Branching type	Polymer	m^b	f^c	$a = 25$	$a = 50$	$a = 100$	Freely jointed with $a = 400$
Normal or comb		1	3	0.737	0.769	0.769	0.776
Normal or comb		1	4	0.568	0.615	0.608	0.626
Normal or comb		2	3	0.684	0.699	0.690	0.715
Normal or comb		2	4	0.520	0.530	0.530	0.548
Normal or comb		3	3	0.654	0.657	0.661	0.670
Normal or comb		3	4	0.479	0.474	0.502	0.498
Normal or comb		4	3	0.619	0.612	0.642	0.638
Normal or comb		4	4	0.445	0.447	0.469	0.465
Normal or comb		5	3	0.602	0.597	0.620	0.617
Normal or comb		5	4	0.416	0.430	0.446	0.443
Random		1	3	0.737	0.769	0.769	0.778
Random		1	4	0.568	0.615	0.608	0.712
Random		2	3	0.684	0.734	0.689	0.712
Random		2	4	0.515	0.557	0.530	0.545
Random		3	3	0.655	0.647	0.674	0.668
Random		3	4	0.479	0.474	0.502	0.496
Random		4	3	0.586	0.604	0.648	0.633
Random		4	4	0.409	0.408	0.439	0.460
Random		5	3	0.609	0.604	0.636	0.605
Random		5	4	0.381	0.395	0.415	0.432

[a] a is the number of bonds in each branch, between branches, or in those portions of the backbone between a branch point and a chain end. [b] The number of branch points. [c] Branch functionality.

Examination of the statistical weight matrices corresponding to the bonds surrounding a branch point (see eq 2–4) leads to a rationalization of the near independence of backbone flexibility upon branching. Bonds $i - 2$ and $i + 1$ (see Figure 1) are less flexible than the backbone bonds in linear polyethylene, while bonds $i - 1$ and i are more flexible and bond $i + 2$ has about the same flexibility, where an increase in bond flexibility over linear polyethylene means the gauche conformations have a higher probability in the branched polymers. This comparison and rationalization may be made quantitative by calculating the *a priori* probability, P_t,

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this assumes that the radii of gyration of branched and linear polyethylenes become unperturbed by excluded volume effects in dilute solution at the same temperature, *i.e.*, at the θ temperature. In fact, this assumption is justified, because it has been shown experimentally (see ref 12 for a summary of the data) that $\theta_B = \theta_L \pm (0\text{–}10°)$ for several different polymer with heavy and light distributions of both short and long branches. Hence, if we remember that for linear polyethylene[26,28] $d \ln \langle r^2\rangle_0/dT = -1.0 \times 10^{-3}\ °C^{-1}$, then $|\theta_B - \theta_L| = 10°$ would result in a 1% difference in their unperturbed radii due solely to the difference in their θ temperatures.

Table VI. Comparison of Calculated and Experimental Radii of Gyration of Ethyl-Branched Polyethylenes

No. of ethyl branches per 100 backbone carbons	$g = \langle S^2\rangle_{0,B}/\langle S^2\rangle_{0,L}$ Expt1[a]	Calcd[b]
5	0.94	0.95–0.97
10	0.89	0.91–0.95
20	0.80	0.86–0.91

[a] Determined from viscosity and light scattering measurements and compared to linear polyethylene with the same degree of polymerization as the backbone of the branched polymer. [b] Branches were assumed to be of zero length and $\Delta\varphi = 10°$, $\sigma = 0.61$, $\omega = 0.11$ with τ^* and τ between 0.1 and 0.5.

Table VII. *A Priori* Bond Rotational State Probabilities

Polymer	P_t[a]	$(P_{g^+} + P_{g^-})$[a]
No branches ($\sigma = 0.54$, $\omega = 0.088$)	0.598	0,402
No branches ($\sigma = 0.61$, $\omega = 0.11$)	0.572	0,428
Trifunctional branch every 5 bonds ($\sigma = 0.54$, $\omega = 0.088$)	0.609–0.654 (0.653–0.684)[b]	0.391–0.346 (0.347–0.316)[b]
Trifunctional branch every 5 bonds ($\sigma = 0.61$, $\omega = 0.11$)	0.594–0.644 (0.639–0.669)[b]	0.406–0.356 (0.361–0.331)[b]
Tetrafunctional branch every 5 bonds ($\sigma = 0.54$, $\omega = 0.5–0.088$)	0.624–0.634 (0.661)[c]	0.376–0.366 (0.339)[c]
Tetrafunctional branch every 5 bonds ($\sigma = 0.61$, $\omega = 0.11$)	0.615–0.625 (0.652)[c]	0.385–0.375 (0.348)[c]

[a] τ and τ^* are between 0.1 and 0.5. [b] $\tau^* = 1.0$, $0.1 \leq \tau \leq 0.5$. [c] $\tau^* = 1.0$.

that any backbone bond in a branched polyethylene is in the trans conformation. The Flory–Jernigan matrix methods[26] were employed to obtain the calculated results given in Table VII. It is clear that the backbones of even these heavily branched polyethylenes have calculated conformational characteristics and flexibilities very similar to linear polyethylene.

Solution and Solid-State Electronic Spectra of Low-Spin Trigonal-Bipyramidal Complexes Containing Nickel(II), Palladium(II), and Platinum(II). Temperature Dependence of the Lowest Energy Ligand-Field Band

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Abstract: Solution and solid-state electronic spectral measurements at 295° and at low temperatures (77° or 100°K) have been carried out on the low-spin trigonal-bipyramidal complexes $[Ni(CN)_2(PhPR_2)_3]$ (R = Me, OEt) and $[MX(L'L_3)]Y$, where M = Ni(II), Pd(II), Pt(II), X = Cl, Br, I, CN, Y = X, ClO_4, BPh_4, and $L'L_3$ represents a potentially quadridentate "tripod-like" ligand $(Me_2AsCH_2CH_2CH_2)_3L'$ (L′ = P, As), $(o\text{-}MeL\cdot C_6H_4)_3P$ (L = S, Se) or $(o\text{-}Ph_2L\cdot C_6H_4)_3L'$ (L′ = L = P, As). The lowest energy band ν_1 is usually asymmetric and even may be split into a double peak at 295°K; on cooling *solutions* of the complexes, band ν_1 exhibits a dramatic increase in extinction coefficient and becomes more symmetrical. This unusual effect is discussed in terms of a Jahn–Teller distortion of the doubly degenerate excited state and a temperature-dependent static distortion of the ground state. By contrast, the two transitions contributing to band ν_1 of the *solid* complexes do not approach one another on cooling but instead become somewhat better resolved, indicating that the asymmetry or splitting of ν_1 is due primarily to a permanent ground-state distortion. The band ν_1 in the solution spectra of the complexes $[MCl(P\cdot As_2P)]Cl$, where M = Pd, Pt and $P\cdot As_2P = (o\text{-}Ph_2As\cdot C_6H_4)_2(o\text{-}Ph_2P\cdot C_6H_4)P$, shows two well-resolved peaks at 100°K, as the three equatorial atoms are no longer the same and the complexes have C_s rather than C_{3v} microsymmetry.

Since the preparation of the first complexes of quadridentate "tripod-like" ligands,[3–5] much work has been carried out on the characterization of this class of complex.[6,7] Structural determinations on certain of the $[MX(L'L_3)]^+$ complexes have shown them to be trigonal-bipyramidal, with the unidentate anion X occupying an axial position trans to the central atom, L′,

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