Conformational Properties of a Molecule Consisting of Three Branches Emanating from a Common Atom, Evaluated Using Rotational Isomeric State Theory[1]

Wayne L. Mattice

Department of Biochemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

Received July 22, 1975

ABSTRACT: Expressions for the unperturbed mean-square radius of gyration, unperturbed mean-square dipole moment, and unperturbed mean-square optical anisotropy have been obtained for a molecule consisting of three branches which emanate from a common atom, using rotational isomeric state theory. The results are equally valid for homopolymers and copolymers, and for molecules in which the branches are of identical or different lengths. With the exception of a matrix occurring at the branch point, the dimensions of the generator matrices are no larger than those required for a linear molecule. The procedure adopted can be extended to treat more highly branched molecules.

The radius of gyration of branched macromolecules has been treated using random flight statistics.[2-10] In some cases allowance has been made for chain stiffness.[7-9] However, the effect of short-range interactions arising from a particular covalent structure has not been evaluated by the rigorous application of rotational isomeric state theory. A previous communication[11] described the procedures required in order to obtain the configuration partition function, evaluated using the rotational isomeric state approximation, for a macromolecule containing any number of branches. Expressions were also obtained for the a priori probability that a bond (or pair of adjacent bonds) would be in a particular rotational state (or combination of rotational states). The present goal is to utilize the configuration partition function for a macromolecule consisting of a main chain and one branch (3-star) in order to obtain expressions for the unperturbed mean-square radius of gyration, mean-square dipole moment, and mean-square optical anisotropy. The procedure adopted will be similar to that used by Flory[12] in the treatment of a linear molecule. Subsequent communications will present numerical results computed for various covalent structures, and provide a comparison of the results so obtained with predictions based on random flight statistics.

Structure Treated

A diagrammatic representation of the molecule under consideration is shown in Figure 1. The symbols ${}_jA_i$, ${}_j\mathbf{l}_i$, and ${}_j\mathbf{U}_i$ represent atom, bond vector and statistical weight matrix i in branch j, respectively, and n_j is the number of bonds in branch j. The atom from which branching occurs is considered to be the last atom in branch 1. The configuration partition function, Z, for this molecule is (1).[11]

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

Terms such as ${}_1\mathbf{U}_1{}^{(n_1)}$ represent the product of n_1 successive matrices, commencing with ${}_1\mathbf{U}_1$.[12] Terminal matrices are defined in eq 2–4.[12] The symbol ⊗ denotes the direct

$${}_1\mathbf{U}_1 = \mathrm{row}(1,0,\ldots,0) \quad (2)$$

$${}_2\mathbf{U}_{n2} = \mathrm{col}(1,1,\ldots,1) \quad (3)$$

$${}_3\mathbf{U}_{n3} = \mathrm{col}(1,1,\ldots,1) \quad (4)$$

product, and ${}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1$ is the rectangular matrix defined in ref 11.

Configuration-Dependent Quantities for a Specified Conformation

Chain Displacement Vector. The chain displacement vector, $\mathbf{r}_{hk}$, connecting atom h with k in a linear molecule, has been treated by Flory.[12,13] A change in notation will be required for a branched molecule because $\mathbf{r}_{hk}$ is ambiguous if a branch point occurs between atoms h and k. This ambiguity can be resolved by the selection of an appropriate chain (which may consist of more than one branch), with the atoms and bonds in the chain numbered in succession, and the specification of the sequence of the branches which constitute the chain. The sequence of branches which constitute the chain will be written as subscripts preceeding $\mathbf{r}$. Thus the chain displacement vector connecting ${}_1A_h$ with ${}_iA_k$ (i = 2 or 3) will be written as ${}_{1,i}\mathbf{r}_{h,n_1+k}$.

Following the procedures utilized for a linear molecule,[12,13] we obtain (5) for ${}_{ij}\mathbf{r}_{hk}$. The first pseudo row and

$${}_{ij}\mathbf{r}_{hk} = ({}_{ij}\mathbf{A}_{[h+1})({}_{ij}\mathbf{A}_{h+2}{}^{(k-h-2)})({}_{ij}\mathbf{A}_{k]}) \quad (5)$$

$$k - h \geq 2$$

$${}_{ij}\mathbf{A}_h = {}_{ij}\begin{bmatrix} \mathbf{T} & \mathbf{l} \\ \mathbf{0} & 1 \end{bmatrix}_h \quad (6)$$

last column of ${}_{ij}\mathbf{A}_h$ are denoted by ${}_{ij}\mathbf{A}_{[h}$ and ${}_{ij}\mathbf{A}_{h]}$, respectively, and the subscripts preceeding $\mathbf{A}_h$ have the same significance as the subscripts preceeding $\mathbf{r}_{hk}$. The transformation matrix and bond vector for bond h in the chain formed from branches i and j are denoted by ${}_{ij}\mathbf{T}_h$ and ${}_{ij}\mathbf{l}_h$, respectively. The elements in ${}_{ij}\mathbf{T}_h$ and ${}_{ji}\mathbf{T}_{n_i+n_j+1-h}$ are not necessarily identical (even though these transformation matrices are associated with the same bond in the molecule) because, while ${}_{ij}\phi_h = {}_{ji}\phi_{n_i+n_j+1-h}$, it is not necessarily true that ${}_{ij}\theta_h = {}_{ji}\theta_{n_i+n_j+1-h}$. In contrast, ${}_{ij}\mathbf{l}_h = {}_{ji}\mathbf{l}_{n_i+n_j+1-h}$ because the length of the bond is the only nonzero element. Elements of ${}_{ij}\mathbf{T}_1$ are assigned as for $\mathbf{T}_1$ in the linear molecule.[12] Rectangular null matrices of the appropriate dimensions are represented by $\mathbf{0}$. The chain displacement vector connecting the free end of branch i with the free end of branch j is ${}_{ij}\mathbf{r}_{0,n_i+n_j}$.

Square of the Magnitude of the Chain Vector. Proceeding in analogy to the treatment of a linear molecule,[12,14] we obtain (7) for ${}_{ij}r_{hk}{}^2 = {}_{ji}r_{n_i+n_j+1-k,n_i+n_j+1-h}{}^2$.

$${}_{ij}r_{hk}{}^2 = ({}_{ij}\mathbf{G}_{[h+1})({}_{ij}\mathbf{G}_{h+2}{}^{(k-h-2)})({}_{ij}\mathbf{G}_{k]}) \quad (7)$$

$$k - h \geq 2$$

$${}_{ij}\mathbf{G}_h = {}_{ij}\begin{bmatrix} 1 & 2\mathbf{l}^{\mathrm{T}}\mathbf{T} & l^2 \\ 0 & \mathbf{T} & \mathbf{l} \\ 0 & 0 & 1 \end{bmatrix}_h \quad (8)$$

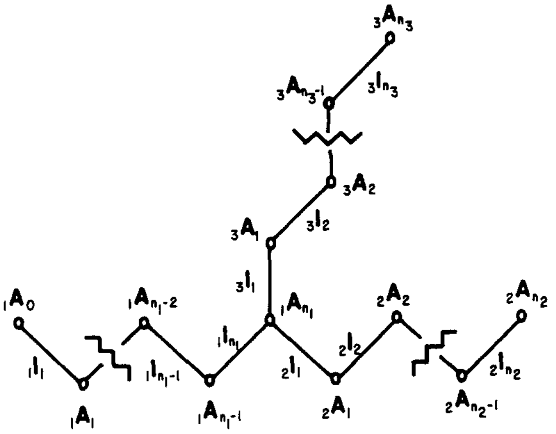

Figure 1. Diagrammatic representation of a molecule consisting of three branches emanating from a common atom.

The square of the distance between the free ends of branches i and j is obtained from (7) when $h = 0$ and $k = n_i + n_j$. The postsubscripts $[h + 1$ and $k]$ signify the first row and last column, respectively, of the indicated generator matrix.

Dipole Moment. The dipole moment, μ, can be obtained through replacement of ${}_{ij}\mathbf{l}_h$ by ${}_{ij}\mathbf{m}_h$, which contains the dipole contribution of group h.[12] This vector shares with the transformation matrix the property that ${}_{ij}\mathbf{m}_h$ is not necessarily equal to ${}_{ji}\mathbf{m}_{n_i+n_j+1-h}$, even though the bond referred to is the same in each case. The dipole moment is the sum of the moments associated with each bond, as shown in (9), which is equivalent to (10). Subtraction of the last sum in

$$\mu = \sum_{1\leq h\leq n_1+n_2} {}_{1,2}\mathrm{T}_1{}^{(h-1)}{}_{1,2}\mathbf{m}_h + \sum_{n_1<h\leq n_1+n_3} {}_{1,3}\mathbf{T}_1{}^{(h-1)}{}_{1,3}\mathbf{m}_h \tag{9}$$

$$\mu = \sum_{i=2,3} \sum_{1\leq h\leq n_1+n_i} {}_{1,i}\mathbf{T}_1{}^{(h-1)}\,{}_{1,i}\mathbf{m}_h - \sum_{1\leq h\leq n_1} {}_{1,2}\mathbf{T}_1{}^{(h-1)}{}_{1,2}\mathbf{m}_h \tag{10}$$

(10) is required because the group dipole moments in branch 1 are each counted twice in the double sum. Evaluation of the sums in (10) can be accomplished using the procedure appropriate for a linear molecule.[12,13] The substitution of ${}_{ij}\mathbf{m}_h$ for each ${}_{ij}\mathbf{l}_h$ is required for each ${}_{ij}\mathbf{A}_h$.

$$\mu = \sum_{i=2,3} ({}_{1,i}\mathbf{A}_{[1})({}_{1,i}\mathbf{A}_2{}^{(n_1+n_i-2)})({}_{1,i}\mathbf{A}_{n_1+n_i]}) - ({}_{1,2}\mathbf{A}_{[1})({}_{1,2}\mathbf{A}_2{}^{(n_1-2)})({}_{1,2}\mathbf{A}_{n_1]}) \tag{11}$$

Squared Magnitude of the Dipole Moment. The square of the magnitude of the dipole moment, μ^2, is obtained from (12). The subtraction is required because each

$$\mu^2 = \sum_{1\leq i<j\leq 3}\left\{\sum_{1\leq h\leq n_i+n_j} {}_{ij}m_h{}^2 + 2\sum_{0<h<k\leq n_i+n_j} ({}_{ij}\mathbf{m}_h{}^{\mathrm{T}})({}_{ij}\mathbf{T}_h{}^{(k-h)})({}_{ij}\mathbf{m}_k)\right\} - \sum_{\substack{1\leq i\leq 3\\ j\neq i}}\left\{\sum_{1\leq h\leq n_i} {}_{ij}m_h{}^2 + 2\sum_{0<h<k\leq n_i} ({}_{ij}\mathbf{m}_h{}^{\mathrm{T}})({}_{ij}\mathbf{T}_h{}^{(k-h)})({}_{ij}\mathbf{m}_k)\right\} \tag{12}$$

$\mathbf{m}_h\cdot\mathbf{m}_k$ in which h and k are in the same branch has been counted twice in the summations involving chains. Use of the methods appropriate for a linear chain[12,14] produces (13).

$$\mu^2 = \sum_{1\leq i<j\leq 3} ({}_{ij}\mathbf{G}_{[1})({}_{ij}\mathrm{G}_2{}^{(n_i+n_j-2)})({}_{ij}\mathbf{G}_{n_i+n_j]}) - \sum_{\substack{1\leq i\leq 3\\ j\neq i}} ({}_{ij}\mathbf{G}_{[1})({}_{ij}\mathbf{G}_2{}^{(n_i-2)})({}_{ij}\mathbf{G}_{n_i]}) \tag{13}$$

The Squared Optical Anisotropy. As in the case of a linear molecule,[12,15] $\hat{\alpha}$, the anisotropic part of the molecular polarizability tensor, α, will be treated as the sum of contributions $\hat{\alpha}_i$ from the various units. The 9×1 column vector $\hat{\alpha}^{\mathrm{C}}$ has the elements of $\hat{\alpha}$ in "reading order", and $\hat{\alpha}^{\mathrm{R}}$ is the row form of $\hat{\alpha}^{\mathrm{C}}$.[12] The squared optical anisotropy, γ^2, for the branched molecule, when the molecules are independent and uncorrelated, is given by (14). The subtraction occurs for reasons similar to those required in (12). As with ${}_{ij}\mathbf{m}_h$, ${}_{ij}\hat{\alpha}_h{}^{\mathrm{C}}$ and ${}_{ji}\hat{\alpha}_{n_i+n_j+1-h}{}^{\mathrm{C}}$ are not necessarily identical, even though they refer to the same bond in the branched macromolecule. Evaluation of (14) via generator matrices[12,16] yields (15). The first row and last column of $\mathbf{P}_h$ are denoted by the postsubscripts $[h$ and $h]$, respectively.

$$\gamma^2 = \sum_{0<i<j\leq 3}\left\{{}^3\!/_2\sum_{1\leq h\leq n_i+n_j} {}_{ij}\hat{\alpha}_h{}^2 + 3\sum_{0<h<k\leq n_i+n_j} \times ({}_{ij}\hat{\alpha}_h{}^{\mathrm{R}})({}_{ij}(\mathbf{T}\otimes\mathbf{T})_h{}^{(k-h)})({}_{ij}\hat{\alpha}_k{}^{\mathrm{C}})\right\} - \sum_{\substack{0<i\leq 3\\ j\neq i}}\left\{{}^3\!/_2\sum_{1\leq h\leq n_i} {}_{ij}\hat{\alpha}_h{}^2 + 3\sum_{0<h<k\leq n_i} ({}_{ij}\hat{\alpha}_h{}^{\mathrm{R}})({}_{ij}(\mathbf{T}\otimes\mathbf{T})_h{}^{(k-h)})({}_{ij}\hat{\alpha}_k{}^{\mathrm{C}})\right\} \tag{14}$$

$$\gamma^2 = {}^3\!/_2\left\{\sum_{0<i<j\leq 3} ({}_{ij}\mathbf{P}_{[1})({}_{ij}\mathbf{P}_2{}^{(n_i+n_j-2)})({}_{ij}\mathbf{P}_{n_i+n_j]}) - \sum_{\substack{0<i\leq 3\\ j\neq i}} ({}_{ij}\mathbf{P}_{[1})({}_{ij}\mathbf{P}_2{}^{(n_i-2)})({}_{ij}\mathbf{P}_{n_i]})\right\} \tag{15}$$

$${}_{ij}\mathbf{P}_h = {}_{ij}\begin{bmatrix} 1 & 2\hat{\alpha}^{\mathrm{R}}(\mathbf{T}\otimes\mathbf{T}) & \hat{\alpha}^2 \\ 0 & \mathbf{T}\otimes\mathbf{T} & \hat{\alpha}^{\mathrm{C}} \\ 0 & 0 & 1 \end{bmatrix}_h \tag{16}$$

Squared Radius of Gyration. The squared radius of gyration, s^2, for a chain containing $n + 1$ atoms, not necessarily of the same mass, is given by (17). In this section m_h represents the mass of atom h, a usage different from that encountered in the section concerning the squared magnitude of the dipole moment. Indices h and k range independently from 0 to n in the sum involving m_hm_k in (17).

$$s^2 = \left(\sum_{h,k} m_hm_k\right)^{-1}\sum_{0\leq h<k\leq n} m_hm_kr_{hk}{}^2 \tag{17}$$

The squared radii of gyration of the atoms in the three branches of the molecule in Figure 1 are given by (18) and (19). The squared radii of gyration of the chains formed from branch 1 and branch i (i = 2 or 3) are shown in (20). It will be convenient to use a slightly different expression, (21), for $s_{23}{}^2$ because the atom at the branch point is considered to belong to branch 1. An alternative form for $s_{23}{}^2$ is (22), in which ${}_{2,3}m_{n_2}$, the mass of the atom at the branch

$$s_1{}^2 = \left\{\sum_{0\leq h\leq n_1}\sum_{0\leq k\leq n_1} ({}_{1,2}m_h)({}_{1,2}m_k)\right\}^{-1} \times \sum_{0\leq h<k\leq n_1} ({}_{1,2}m_h)({}_{1,2}m_k)({}_{1,2}r_{hk}{}^2) \tag{18}$$

$$s_i{}^2 = \left\{\sum_{0\leq h<n_i}\sum_{0\leq k<n_i} ({}_{ij}m_h)({}_{ij}m_k)\right\}^{-1}\sum_{0\leq h<k<n_i} ({}_{ij}m_h)({}_{ij}m_k)({}_{ij}r_{hk}{}^2) \qquad i = 2,3;\ j \neq i \tag{19}$$

$$s_{1i}^{2} = \left\{ \sum_{0 \le h \le n_1 + n_i} \sum_{0 \le k \le n_1 + n_i} ({}_{1i}m_h)({}_{1i}m_k) \right\}^{-1} \times \sum_{0 \le h < k \le n_1 + n_i} ({}_{1i}m_h)({}_{1i}m_k)({}_{1i}r_{hk}^{2}) \quad (20)$$

$$i = 2,3$$

point, is assigned the value of zero. The squared radius of gyration of the entire molecule, s^2, can be obtained from

$$s_{23}^{2} = \left\{ \sum_{\substack{0 \le h \le n_2 + n_3 \\ h \ne n_2}} \sum_{\substack{0 \le k \le n_2 + n_3 \\ k \ne n_2}} ({}_{2,3}m_h)({}_{2,3}m_k) \right\}^{-1} \times \sum_{\substack{0 \le h < k \le n_2 + n_3 \\ h \ne n_2,\, k \ne n_2}} ({}_{2,3}m_h)({}_{2,3}m_k)({}_{2,3}r_{hk}^{2}) \quad (21)$$

the above radii using a procedure related to that adopted for μ^2. The indices h and k in the first term in (23) are un-

$$s_{23}^{2} = \left\{ \sum_{0 \le h \le n_2 + n_3} \sum_{0 \le k \le n_2 + n_3} ({}_{2,3}m_h)({}_{2,3}m_k) \right\}^{-1} \times \sum_{0 \le h < k \le n_2 + n_3} ({}_{2,3}m_h)({}_{2,3}m_k)({}_{2,3}r_{hk}^{2}) \quad (22)$$

$${}_{2,3}m_{n_2} = 0$$

derstood to range independently over all of the $n_1 + n_2 + n_3 + 1$ atoms in the molecule.

$$s^2 = \left(\sum_{h,k} m_h m_k\right)^{-1} \left\{ \sum_{0 < i < j \le 3} \left(\sum_{0 \le h \le n_i + n_j} \sum_{0 \le k \le n_i + n_j} ({}_{ij}m_h)({}_{ij}m_k) \right) s_{ij}^{2} - \right.$$

$${}_{2,3}m_{n_2} = 0$$

$$\left(\sum_{0 \le h \le n_1} \sum_{0 \le k \le n_1} ({}_{1,2}m_h)({}_{1,2}m_k) \right) s_1^{2} - \left. \sum_{\substack{i=2,3 \\ j \ne i}} \left(\sum_{0 \le h < n_i} \sum_{0 \le k < n_i} ({}_{ij}m_h)({}_{ij}m_k) \right) s_i^{2} \right\} \quad (23)$$

The double sums involving r_{hk}^{2} in eq 18–20 and 22 are obtained by a procedure analogous to that used for a linear

$$s_1^{2} = \left\{ \sum_{0 \le h \le n_1} \sum_{0 \le k \le n_1} ({}_{1,2}m_h)({}_{1,2}m_k) \right\}^{-1} ({}_{1,2}\mathbf{S}_{[1})({}_{1,2}\mathbf{S}_2^{(n_1-2)})({}_{1,2}\mathbf{S}_{n_1]}) \quad (24)$$

$$s_i^{2} = \left\{ \sum_{0 \le h < n_i} \sum_{0 \le k < n_i} ({}_{ij}m_h)({}_{ij}m_k) \right\}^{-1} ({}_{ij}\mathbf{S}_{[1})({}_{ij}\mathbf{S}_2^{(n_i-3)})({}_{ij}\mathbf{S}_{n_i-1]}) \quad (25)$$

$$i = 2,\ 3;\ j \ne i$$

$$s_{1,i}^{2} = \left\{ \sum_{0 \le h \le n_1 + n_i} \sum_{0 \le k \le n_1 + n_i} ({}_{1,i}m_h)({}_{1,i}m_k) \right\}^{-1} \times ({}_{1,i}\mathbf{S}_{[1})({}_{1,i}\mathbf{S}_2^{(n_1+n_i-2)})({}_{1,i}\mathbf{S}_{n_1+n_i]}) \quad (26)$$

$$i = 2,\ 3$$

$$s_{23}^{2} = \left\{ \sum_{0 \le h \le n_2 + n_3} \sum_{0 \le k \le n_2 + n_3} ({}_{2,3}m_h)({}_{2,3}m_k) \right\}^{-1} \times ({}_{2,3}\mathbf{S}_{[1})({}_{2,3}\mathbf{S}_2^{(n_2+n_3-2)})({}_{2,3}\mathbf{S}_{n_2+n_3]}) \quad (27)$$

$${}_{2,3}m_{n_2} = 0$$

chain (see Appendix) and are presented in eq 24–27, respectively. The generator matrix ${}_{ij}\mathbf{S}_h$ is presented in (28). Substitution of eq 24–27 into (23) gives s^2.

$${}_{ij}\mathbf{S}_h = {}_{ij}\begin{bmatrix} 1 & m_{h-1}\mathbf{G}_{[h} & m_{h-1}l_h^{2}m_h \\ 0 & \mathbf{G}_h & \mathbf{G}_{h]}m_n \\ 0 & 0 & 1 \end{bmatrix} \quad (28)$$

$$s^2 = \left(\sum_{h,k} m_h m_k\right)^{-1} \left\{ \sum_{0 < i < j \le 3} ({}_{ij}\mathbf{S}_{[1})({}_{ij}\mathbf{S}_2^{(n_i+n_j-2)})({}_{ij}\mathbf{S}_{n_i+n_j]}) - ({}_{1,2}\mathbf{S}_{[1})({}_{1,2}\mathbf{S}_2^{(n_1-2)})({}_{1,2}\mathbf{S}_{n_1]}) - \sum_{\substack{i=2,3 \\ j \ne i}} ({}_{ij}\mathbf{S}_{[1})({}_{ij}\mathbf{S}_2^{(n_i-3)})({}_{ij}\mathbf{S}_{n_i-1]}) \right\} \quad (29)$$

$${}_{2,3}m_{n_2} = 0$$

Statistical Mechanical Averages Over Configuration Space

Alternative Expressions for the Configuration Partition Function. The statistical mechanical average of a configuration-dependent molecular property f can be obtained from the expression for that property in a specified conformation of the branched molecule by procedures closely related to those appropriate for linear molecules.[12] It will be necessary to be able to write the configuration partition function in a fashion where the statistical weight matrices occur in the order appropriate for the chain under consideration. The expression for Z in (1) is appropriate if the chain under consideration is branch 1 followed by branch i (i = 2 or 3). However, if the chain is branch 2 followed by branch 3, the statistical weight matrices in (1) will not appear in the order corresponding to the sequential arrangement of the bonds in the chain.

Since the configuration partition function is a property of the molecule, and is independent of which branch we choose to label "branch 1", we can obtain expressions analogous to (1) in which either branch 2 or 3 is allowed to play the role of branch 1. When the chain under consideration is branch i followed by branch j, the configuration partition function will be written as (30a) or (30b). The expression in

$$Z = {}_{ij}\mathbf{U}_1^{(n_i)}({}_{ij}\mathbf{U}_{n_i+1} \ominus {}_{ik}\mathbf{U}_{n_i+1})\{({}_{ij}\mathbf{U}_{n_i+2}^{(n_j-1)}) \otimes ({}_{ik}\mathbf{U}_{n_i+2}^{(n_k-1)})\} \quad (30a)$$

$$Z = {}_{ij}\mathbf{U}_1^{(n_i)}({}_{ik}\mathbf{U}_{n_i+1} \ominus {}_{ij}\mathbf{U}_{n_i+1})\{({}_{ik}\mathbf{U}_{n_i+2}^{(n_k-1)}) \otimes ({}_{ij}\mathbf{U}_{n_i+2}^{(n_j-1)})\} \quad (30b)$$

(1) is obtained from (30a) when $i = 1$, $j = 2$, and $k = 3$, and it is also obtained from (30b) when $i = 1$, $j = 3$, and $k = 2$.

As was the case with the transformation matrix, we find that ${}_{ij}\mathbf{U}_h$ and ${}_{ji}\mathbf{U}_{n_i+n_j+1-h}$ may differ, even though they are each associated with the same bond in the molecule. These statistical weight matrices will not necessarily have the same dimensions. The number of columns must be the same in each case. It is determined by the number of rotational states available to the bond in question, which is independent of the end of the chain at which numbering commences. The number of rows, however, depends upon the number of rotational states available to the preceeding bond; the bond considered the "preceeding" bond clearly depends on the end of the chain at which numbering begins. A convenient intermediate step in the formulation of the rectangular matrix ${}_{ik}\mathbf{U}_{n_i+1} \ominus {}_{ij}\mathbf{U}_{n_i+1}$ is to assemble ${}_{ij}\mathbf{U}_{n_i+1}$ as an array consisting of rows, columns, and layers.[11] The dimensions of this array may also depend on the sequence of branches viewed as constituting the chain of interest at the moment.

Generator Matrices. In analogy to the case of the linear molecule,[12] the generator matrix of order s involved in the serial multiplication for the property of interest, f, will be written as ${}_{ij}\mathbf{F}_h$. The generator matrix for $\langle f\rangle$ will be ${}_{ij}\boldsymbol{F}_h$, which is formulated by a procedure analogous to that required for the linear molecule.[12] The objective will be to properly combine the statistical weights for bond h in chain ij being in state α and the generator matrix ${}_{ij}\mathbf{F}_h(\alpha)$ appropriate for the bond in the given state. Considerations analogous to those for the linear molecule yield the following:

$$ {}_{ij}\boldsymbol{F}_{[1} = [{}_{ij}\mathbf{F}_{[1}\ 0] \tag{31}$$

$$ {}_{ij}\boldsymbol{F}_h = ({}_{ij}\mathbf{U}_h \otimes \mathbf{E}_s)\Vert{}_{ij}\mathbf{F}_h\Vert \tag{32}$$

$$1 < h \leq n_i \text{ or } n_i + 1 < h < n_i + n_j$$

$$ {}_{ij}\boldsymbol{F}_{n_i+1} = \{({}_{ij}\mathbf{U}_{n_i+1} \ominus {}_{ik}\mathbf{U}_{n_i+1}) \otimes \mathbf{E}_s\}(\Vert{}_{ij}\mathbf{F}_{n_i+1}\Vert \otimes_{s,s} \mathbf{E}_{{}_{ik}\nu_{n_i+1}}) \tag{33a}$$

$$ {}_{ij}\boldsymbol{F}_{n_i+1} = \{({}_{ik}\mathbf{U}_{n_i+1} \ominus {}_{ij}\mathbf{U}_{n_i+1}) \otimes \mathbf{E}_s)\}(\mathbf{E}_{{}_{ik}\nu_{n_i+1}} \otimes \Vert{}_{ij}\mathbf{F}_{n_i+1}\Vert) \tag{33b}$$

$$ {}_{ij}\boldsymbol{F}_{n_i+n_j]} = \mathrm{col}({}_{ij}\mathbf{F}_{n_i+n_j]}\ {}_{ij}\mathbf{F}_{n_i+n_j]}\ \cdots\ {}_{ij}\mathbf{F}_{n_i+n_j]}) \tag{34}$$

The diagonal array of generator matrices ${}_{ij}\mathbf{F}_h(\alpha), \ldots, {}_{ij}\mathbf{F}_h(\nu)$ is denoted by $\Vert{}_{ij}\mathbf{F}_h\Vert$. This pseudodiagonal matrix must be expanded whenever the rectangular matrix occurring immediately after the branch point is required. The manner in which the expansion is effected is determined by the pattern formed by the statistical weights in this rectangular matrix. The statistical weights for the ith rotational state about the first bond in branch 3 occur in columns i, $i + {}_3\nu_1$, $i + 2({}_3\nu_1), \ldots, i + ({}_2\nu_1 - 1)({}_3\nu_1)$ of $({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1)$.[11] Consequently the desired expansion for (33b) is effected by the operation $(\mathbf{E}_{{}_{ik}\nu_{ni+1}} \otimes \Vert{}_{ij}\mathbf{F}_{n_i+1}\Vert)$, where $\mathbf{E}_{{}_{ik}\nu_{ni+1}}$ is the identity matrix of order identical with the number of rotational states about bond $n_i + 1$ in the chain formed from branches i and k. In contrast, the statistical weights for the ith rotational state about the first bond in branch 2 occur in columns $1 + (i - 1){}_3\nu_1$, $2 + (i - 1){}_3\nu_1, \ldots, (i){}_3\nu_1$ of $({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1)$.[11] The appropriate expansion for (33a) will have ${}_{ij}\mathbf{F}_{n_i+1}(\alpha)$ written ${}_{ik}\nu_{n_i+1}$ times along the diagonal, followed by ${}_{ik}\nu_{n_i+1}$ copies of ${}_{ij}\mathbf{F}_{n_i+1}(\beta)$, etc. The resultant pseudodiagonal matrix will be symbolized by $\Vert{}_{ij}\mathbf{F}_{n_i+1}\Vert \otimes_{s,s} \mathbf{E}_{{}_{ik}\nu_{ni+1}}$, and can be viewed as a modification of $\Vert{}_{ij}\mathbf{F}_{n_i+1}\Vert \otimes \mathbf{E}_{{}_{ik}\nu_{ni+1}}$ in which each ${}_{ij}\mathbf{F}_{n_i+1}$ in $\Vert{}_{ij}\mathbf{F}_{n_i+1}\Vert$ plays the role of a single element. In general, a submatrix consisting of a rows and b columns will play the role of an element of $\mathbf{B}$ in $\mathbf{B} \otimes_{a,b} \mathbf{C}$. For example, if $\mathbf{B}$ is a row consisting of four elements, and $\mathbf{C}$ is a row consisting of two elements, the result obtained from $\mathbf{B} \otimes_{1,2} \mathbf{C}$ is:

$$[b_1c_1\ b_2c_1\ b_1c_2\ b_2c_2\ b_3c_1\ b_4c_1\ b_3c_2\ b_4c_2]$$

The customary direct product corresponds to the case where $a = b = 1$. It will be understood that $a = b = 1$ unless specification is made to the contrary.

Additional generator matrices which will prove useful are shown in eq 35–38b.

The only cases in which the above generator matrices exceed the dimensions of those required for a linear molecule are (33a), (33b), (36a), (36b), (38a), and (38b), i.e., whenever the rectangular matrix immediately following the branch point is required.

Mean-Square Dipole Moment. The pseudodiagonal matrix $\Vert{}_{ij}\mathbf{F}_h\Vert$ is constructed from ${}_{ij}\mathbf{G}_h$, with ${}_{ij}\mathbf{m}_h$ replacing ${}_{ij}\mathbf{l}_h$. Evaluation proceeds via (13), yielding (39). The subtraction of the last three terms is required in order to correct for the double counting of the contribution of each branch during the evaluation of the contributions from the chains in the first three terms.

$$ {}_{ij}\boldsymbol{F}_{[h+1} = {}_{ij}\mathbf{U}_{h+1}\Vert{}_{ij}\mathbf{F}_{[h+1}\Vert \tag{35}$$

$$1 < h < n_i \text{ or } n_i < h < n_i + n_j$$

$$ {}_{ij}\boldsymbol{F}_{[n_i+1} = ({}_{ij}\mathbf{U}_{n_i+1} \ominus {}_{ik}\mathbf{U}_{n_i+1})(\Vert{}_{ij}\mathbf{F}_{[n_i+1}\Vert \otimes_{1,s} \mathbf{E}_{{}_{ik}\nu_{n_i+1}}) \tag{36a}$$

$$ {}_{ij}\boldsymbol{F}_{[n_i+1} = ({}_{ik}\mathbf{U}_{n_i+1} \ominus {}_{ij}\mathbf{U}_{n_i+1})(\mathbf{E}_{{}_{ik}\nu_{n_i+1}} \otimes \Vert{}_{ij}\mathbf{F}_{[n_i+1}\Vert) \tag{36b}$$

$$ {}_{ij}\boldsymbol{F}_{h]} = {}_{ij}\mathbf{U}_h \otimes {}_{ij}\mathbf{F}_{h]} \tag{37}$$

$$1 < h \leq n_i \text{ or } n_i + 1 < h < n_i + n_j$$

$$ {}_{ij}\boldsymbol{F}_{n_i+1]} = ({}_{ij}\mathbf{U}_{n_i+1} \ominus {}_{ik}\mathbf{U}_{n_i+1}) \otimes {}_{ij}\mathbf{F}_{n_i+1]} \tag{38a}$$

$$ {}_{ij}\boldsymbol{F}_{n_i+1]} = ({}_{ik}\mathbf{U}_{n_i+1} \ominus {}_{ij}\mathbf{U}_{n_i+1}) \otimes {}_{ij}\mathbf{F}_{n_i+1]} \tag{38b}$$

$$\begin{aligned}\langle\mu^2\rangle_0 = {} & ({}_{1,2}\boldsymbol{F}_{[1})({}_{1,2}\boldsymbol{F}_2{}^{(n_1)})\{(({}_{1,2}\boldsymbol{F}_{n_1+2}{}^{(n_2-2)})({}_{1,2}\boldsymbol{F}_{n_1+n_2]})) \otimes_{s,1} \\ & ({}_{1,3}\mathbf{U}_{n_1+2}{}^{(n_3-1)})\}/Z + ({}_{1,3}\boldsymbol{F}_{[1})({}_{1,3}\boldsymbol{F}_2{}^{(n_1)})\{({}_{1,2}\mathbf{U}_{n_1+2}{}^{(n_2-1)}) \otimes \\ & (({}_{1,3}\boldsymbol{F}_{n_1+2}{}^{(n_3-2)})({}_{1,3}\boldsymbol{F}_{n_1+n_3]}))\}/Z + \\ & ({}_{2,3}\boldsymbol{F}_{[1})({}_{2,3}\boldsymbol{F}_2{}^{(n_2)})\{(({}_{2,3}\boldsymbol{F}_{n_2+2}{}^{(n_3-2)})({}_{2,3}\boldsymbol{F}_{n_2+n_3]})) \otimes_{s,1} \\ & ({}_{2,1}\mathbf{U}_{n_2+2}{}^{(n_1-1)})\}/Z - ({}_{1,2}\boldsymbol{F}_{[1})({}_{1,2}\boldsymbol{F}_2{}^{(n_1-2)})({}_{1,2}\boldsymbol{F}_{n_1]}) \times \\ & ({}_{1,2}\mathbf{U}_{n_1+1} \ominus {}_{1,3}\mathbf{U}_{n_1+1})\{({}_{1,2}\mathbf{U}_{n_1+2}{}^{(n_2-1)}) \otimes \\ & ({}_{1,3}\mathbf{U}_{n_1+2}{}^{(n_3-1)})\}/Z - ({}_{1,2}\mathbf{U}_1{}^{(n_1)}) \times \\ & ({}_{1,2}\boldsymbol{F}_{[n_1+1})\{(({}_{1,2}\boldsymbol{F}_{n_1+2}{}^{(n_2-2)})({}_{1,2}\boldsymbol{F}_{n_1+n_2]})) \otimes_{s,1} \\ & ({}_{1,3}\mathbf{U}_{n_1+2}{}^{(n_3-1)})\}/Z - ({}_{1,3}\mathbf{U}_1{}^{(n_1)})({}_{1,3}\boldsymbol{F}_{[n_1+1}) \times \\ & \{({}_{1.2}\mathbf{U}_{n_1+2}{}^{(n_2-1)}) \otimes (({}_{1,3}\boldsymbol{F}_{n_1+2}{}^{(n_3-2)})({}_{1,3}\boldsymbol{F}_{n_1+n_3]}))\}/Z\end{aligned} \tag{39}$$

Mean-Square Optical Anisotropy. In this case ${}_{ij}\mathbf{P}_h$ is used to form $\Vert{}_{ij}\mathbf{F}_h\Vert$. Evaluation of $\langle\gamma^2\rangle_0$ via (15) yields an expression nearly identical with (39). It is only necessary to substitute $\langle\gamma^2\rangle_0$ for $\langle\mu^2\rangle_0$ on the left side and multiply the right side by 1.5.

Mean-Square Radius of Gyration. The mean-square radius of gyration requires that the pseudodiagonal matrix $\Vert{}_{ij}\mathbf{F}_h\Vert$ be constructed from ${}_{ij}\boldsymbol{S}_h$. Evaluation of $\langle s^2\rangle_0$ proceeds via (29), yielding (40). The first three terms in (40)

$$\begin{aligned}\langle s^2\rangle_0 = {} & \Big(\sum_{h,k} m_h m_k\Big)^{-1} Z^{-1} \times \\ & [({}_{1,2}\boldsymbol{F}_{[1})({}_{1,2}\boldsymbol{F}_2{}^{(n_1)})\{(({}_{1,2}\boldsymbol{F}_{n_1+2}{}^{(n_2-2)})({}_{1,2}\boldsymbol{F}_{n_1+n_2]})) \otimes_{s,1} \\ & ({}_{1,3}\mathbf{U}_{n_1+2}{}^{(n_3-1)})\} + ({}_{1,3}\boldsymbol{F}_{[1})({}_{1,3}\boldsymbol{F}_2{}^{(n_1)})\{({}_{1,2}\mathbf{U}_{n_1+2}{}^{(n_2-1)}) \otimes \\ & (({}_{1,3}\boldsymbol{F}_{n_1+2}{}^{(n_3-2)})({}_{1,3}\boldsymbol{F}_{n_1+n_3]}))\} + ({}_{2,3}\boldsymbol{F}_{[1})({}_{2,3}\boldsymbol{F}_2{}^{(n_2)}) \times \\ & \{(({}_{2,3}\boldsymbol{F}_{n_2+2}{}^{(n_3-2)})({}_{2,3}\boldsymbol{F}_{n_2+n_3]})) \otimes_{s,1} ({}_{2,1}\mathbf{U}_{n_2+2}{}^{(n_1-1)})\}_{({}_{2,3}m_{n_2}=0)} - \\ & ({}_{1,2}\boldsymbol{F}_{[1})({}_{1,2}\boldsymbol{F}_2{}^{(n_1-2)})({}_{1,2}\boldsymbol{F}_{n_1]})({}_{1,2}\mathbf{U}_{n_1+1} \ominus \\ & {}_{1,3}\mathbf{U}_{n_1+1})\ \{({}_{1,2}\mathbf{U}_{n_1+2}{}^{(n_2-1)}) \otimes ({}_{1,3}\mathbf{U}_{n_1+2}{}^{(n_3-1)})\} - \\ & ({}_{1,2}\mathbf{U}_1{}^{(n_1)})({}_{1,2}\mathbf{U}_{n_1+1} \ominus {}_{1,3}\mathbf{U}_{n_1+1})\{(({}_{1,2}\boldsymbol{F}_{[n_1+2})({}_{1,2}\boldsymbol{F}_{n_1+3}{}^{(n_2-3)}) \times \\ & ({}_{1,2}\boldsymbol{F}_{n_1+n_2]})) \otimes_{s,1} ({}_{1,3}\mathbf{U}_{n_1+2}{}^{(n_3-1)})\} - ({}_{1,3}\mathbf{U}_1{}^{(n_1)})({}_{1,2}\mathbf{U}_{n_1+1} \ominus \\ & {}_{1,3}\mathbf{U}_{n_1+1})\{({}_{1,2}\mathbf{U}_{n_1+2}{}^{(n_2-1)}) \otimes (({}_{1,3}\boldsymbol{F}_{[n_1+2}) \times \\ & ({}_{1,3}\boldsymbol{F}_{n_1+3}{}^{(n_3-3)})({}_{1,3}\boldsymbol{F}_{n_1+n_3]})))]\end{aligned} \tag{40}$$

represent the contributions from the three possible chains, ignoring the atom at the branch point in the chain formed by branches 2 and 3, and the last three terms correct for the double counting of the r_{hk}^2 when h and k are in the same branch.

The expressions in (39) and (40) permit the evaluation of $\langle\gamma^2\rangle_0$, $\langle\mu^2\rangle_0$, and $\langle s^2\rangle_0$ for a macromolecule consisting of three branches which emanate from a common atom. The general procedures outlined here can also be applied to more highly branched molecules. In such cases it is sufficient to simply evaluate the contribution to the desired property from all possible chains, with proper consideration of the branch point, and then subtract the appropriate terms in order to compensate for multiple counting.

Acknowledgment. The author wishes to thank Dr. P. J. Flory for his helpful advice during the course of this work.

Appendix

Generator Matrix for the Radius of Gyration of a Linear Molecule in which the Atoms are of Different Mass. The generator matrix employed for the radius of gyration of a linear molecule in which all of the atoms are of the same mass is shown in (A1).[12] Information concerning the length of bond i enters $\mathbf{S}_i$ through l_i, $\mathbf{l}_i$, and $\mathbf{l}_i^T$, and the transformation matrix contains information concerning the bond angle and dihedral angle.[12] No information is provided concerning the mass of the atoms at the ends of bond i. Consequently the computation of s^2 for a particular conformation via (A3)[12] corresponds to the case

$$\mathrm{S}_i = \begin{bmatrix} 1 & \mathbf{G}_{[} & l^2 \\ 0 & \mathbf{G} & \mathbf{G}_{]} \\ 0 & 0 & 1 \end{bmatrix}_i \tag{A1}$$

$$\mathbf{G}_i = \begin{bmatrix} 1 & 2\mathbf{l}^T\mathrm{T} & l^2 \\ 0 & \mathrm{T} & \mathbf{l} \\ 0 & 0 & 1 \end{bmatrix}_i \tag{A2}$$

$$s^2 = (n+1)^{-2}\mathbf{S}_{[1}\mathbf{S}_2^{(n-2)}\mathbf{S}_{n]} \tag{A3}$$

where the $n + 1$ atoms are treated as though they are of equal mass.

In cases where it is desirable to be able to treat chains in which the effective masses associated with the atoms are not identical, the appropriate effective mass for atom i will be denoted by m_i. It may be the actual mass of an atom, or group of atoms, or it may represent an effective scattering factor, depending upon the application. The square of the radius of gyration for a particular conformation is then given by (17). Substitution of the relationship in (A4) for r_{ij}^2 in (17) produces (A5). The appropriate generator matrix can be formed from (A5) in analogy to the manner[12] in which (A1) is constructed from (A6). The result is (A7),

$$r_{ij}^2 = \mathbf{G}_{[i+1}\mathbf{G}_{i+2}^{(j-i-2)}\mathbf{G}_{j]} \qquad j - i > 2 \tag{A4}$$

$$s^2 = \Big(\sum_{0\leqslant i\leqslant n}\sum_{0\leqslant j\leqslant n} m_i m_j\Big)^{-1}\Big[\sum_{0\leqslant i<j-1<n} \times m_i\mathbf{G}_{[i+1}\mathbf{G}_{i+2}^{(j-i-2)}\mathbf{G}_{j]}m_j + \sum_{0<i\leqslant n} m_{i-1}l_i^2 m_i\Big] \tag{A5}$$

$$s^2 = (n+1)^{-2}\Big[\sum_{0\leqslant i<j-1<n}\mathbf{G}_{[i+1}\mathbf{G}_{i+2}^{(j-i-2)}\mathbf{G}_{j]} + \sum_{0<i\leqslant n} l_i^2\Big] \tag{A6}$$

$$\boldsymbol{S}_i = \begin{bmatrix} 1 & m_{i-1}\mathbf{G}_{[i} & m_{i-1}l_i^2 m_i \\ 0 & \mathbf{G}_i & \mathbf{G}_{i]}m_i \\ 0 & 0 & 1 \end{bmatrix} \tag{A7}$$

and the corresponding radius of gyration is calculated via (A8). Averaging over configurations to obtain $\langle s^2\rangle_0$ can be accomplished using procedures described by Flory[12] to obtain $\langle s^2\rangle_0$ for a linear molecule in which the atoms are of identical mass.

$$s^2 = \Big(\sum_{0\leqslant i\leqslant n}\sum_{0\leqslant j\leqslant n} m_i m_j\Big)^{-1}\mathbf{S}_{[1}\mathbf{S}_2^{(n-2)}\mathbf{S}_{n]} \tag{A8}$$

References and Notes

(1) Supported by Grant No. BMS 72-02416 A01 from the National Science Foundation.
(2) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).
(3) H. Benoit, *J. Polym. Sci.*, 11, 507 (1953).
(4) M. Kurata and M. Fukatsu, *J. Chem. Phys.*, **41**, 2934 (1964).
(5) W. C. Forsman, *Macromolecules*, 1, 349 (1968).
(6) K. Solc, *Macromolecules*, **6**, 378 (1973).
(7) K. Kajiwara and C. A. M. Ribeiro, *Macromolecules*, **7**, 121 (1974).
(8) W. Burchard, *Macromolecules*, **7**, 836 (1974).
(9) W. Burchard, *Macromolecules*, **7**, 841 (1974).
(10) S. K. Gupta and W. C. Forsman, *Macromolecules*, **7**, 853 (1974).
(11) W. L. Mattice, *Macromolecules*, **8**, 644 (1975).
(12) P. J. Flory, *Macromolecules*, **7**, 381 (1974).
(13) P. J. Flory, *Proc. Natl. Acad. Sci. U.S.*, **70**, 1819 (1973).
(14) P. J. Flory and Y. Abe, *J. Chem. Phys.*, **54**, 1351 (1971).
(15) R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, **47**, 1999 (1967).
(16) P. J. Flory, *J. Chem. Phys.*, **56**, 862 (1972).