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General Method for Calculating Helical Parameters of Polymer Chains from Bond Lengths, Bond Angles, and Internal-Rotation Angles

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Synopsis

Helical conformations of infinite polymer chains may be described by the helical parameters, d and θ (the translation along the helix axis and the angle of rotation about the axis per repeat unit), ρ_i (the distance of the ith atom from the axis), d_{ij} and θ_{ij} (the translation along the axis and the angle of rotation, respectively, on passing from the ith atom to the jth). A general method has been worked out for calculating all those helical parameters from the bond lengths, bond angles, and internal-rotation angles. The positions of the main chain and side chain atoms with respect to the axis may also be calculated. All the equations are applicable to any helical polymer chain and are readily programmed for electronic computers. A method is also presented for calculating the partial derivatives of helical parameters with respect to molecular parameters.

Introduction

Two helical parameters, d and θ, may be used for describing the spatial arrangement of repeat units of helical polymer chains; d and θ are the translation along the axis and the rotation about the axis, respectively, on passing from an atom of a unit to the corresponding atom of the adjacent unit. General mathematical expressions for these parameters have been derived by Shimanouchi and Mizushima[1] in terms of molecular parameters including bond lengths r, bond angles ϕ, and internal-rotation angles τ. For the polymer chains $(\text{—M—})_p$, $(\text{—M}_1\text{—M}_2\text{—})_p$, $(\text{—M}_1\text{—M}_2\text{—M}_3\text{—})_p$, ..., $(\text{—M}_1\text{—M}_2\text{—M}_3\text{—M}_4\text{—M}_5\text{—M}_6\text{—})_p$, general expressions for d and θ have been rewritten by Miyazawa[2] into explicit equations in terms of bond lengths, half the bond angles ($\phi/2$), and half the internal-rotation angles ($\tau/2$). Also, for the polymer chains $(\text{—M—})_p$, $(\text{—M}_1\text{—M}_2\text{—})_p$, and $(\text{—M}_1\text{—M}_2\text{—M}_3\text{—})_p$, all the helical parameters (d_{ij}, θ_{ij}, and ρ_i) have been given in explicit equations;[2] however, if the repeat unit of a helical main chain is made up of more than three atoms, the equations become somewhat complicated for calculating the helical parameters. In the present study, therefore, a general method was worked out so that all the helical parameters of any polymer chain may be calculated from the bond lengths, bond angles, and internal-rotation angles. The new equations are expressed in matrix representations and are readily programmed for computers. The derivatives of the helical parameters, with respect to the molecular parameters, were also derived in matrix representations.

Helical Parameters

For a helical main chain made up of p atomic repeat units, the bond lengths r_{ij}, bond angles ϕ_i, and internal-rotation angles τ_{ij} are shown in Figure 1*a* ($p = 3$ as an example), where the ith atom of the mth unit is denoted by M_i^m. Right-handed Cartesian coordinates, $\mathbf{X}(x, y, z)$, are set up with the origin on the atom M_1^m. The x axis is parallel to the vector from the atom M_1^m to M_2^m while the y axis lies in the plane M_p^{m-1}—M_1^m—M_2^m and makes an acute angle with the bond M_1^m—M_p^{m-1}. The helical parameters[2] (ρ_i, d_{ij}, and θ_{ij}) are shown in Figure 1*b*. Right-handed Cartesian coordinates, $\boldsymbol{\xi}(\xi, \eta, \zeta)$, are also set up, with the origin on the helix axis (Fig. 1*b*). The ξ axis is perpendicular to the helix axis and points to the atom M_1^m while the ζ axis is parallel to the helix axis.

The position vector ($\mathbf{X}_i^m$) for the ith atom of the mth unit is now given as[1–3]

$$\mathbf{X}_i^m = \mathbf{B}_{12} + \mathbf{A}_{12}\mathbf{B}_{23} + \mathbf{A}_{12}\mathbf{A}_{23}\mathbf{B}_{34} + \cdots + \mathbf{A}_{12}\mathbf{A}_{23}\cdots\mathbf{A}_{i-2,i-1}\mathbf{B}_{i-1,i} \qquad i > 2 \qquad (1)$$

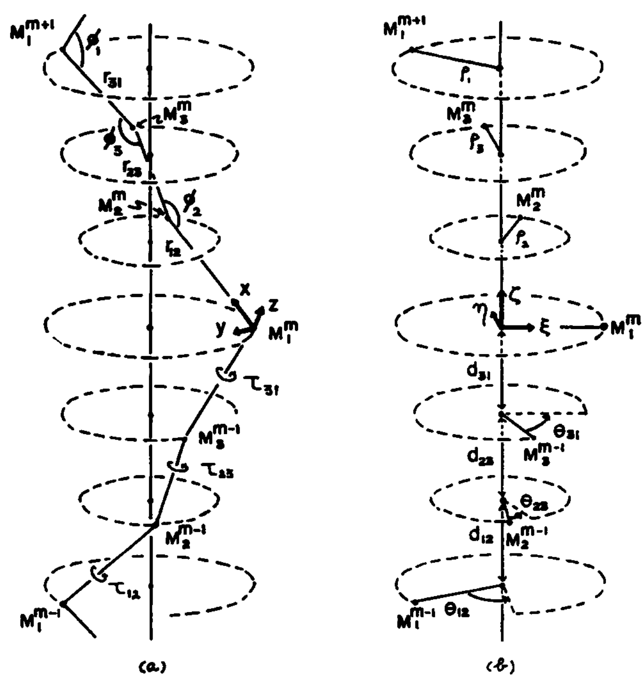

Fig. 1. Schematic representations of (*a*) the bond lengths (r_{ij}), bond angles (ϕ_i), and internal-rotation angles (τ_{ij}) and the right-handed Cartesian coordinates (x, y, z); (*b*) the helical parameters (ρ_i, d_{ij}, and θ_{ij}) and the right-handed Cartesian coordinates (ξ, η, ζ).

where

$$\mathbf{A}_{ij} = \mathbf{A}_{ij}^{\tau}\mathbf{A}_j^{\phi} = \begin{bmatrix} -\cos\phi_j & -\sin\phi_j & 0 \\ \sin\phi_j\cos\tau_{ij} & -\cos\phi_j\cos\tau_{ij} & -\sin\tau_{ij} \\ \sin\phi_j\sin\tau_{ij} & -\cos\phi_j\sin\tau_{ij} & \cos\tau_{ij} \end{bmatrix} \quad (2)$$

and

$$\mathbf{B}_{ij} = \begin{bmatrix} r_{ij} \\ 0 \\ 0 \end{bmatrix} \quad (3)$$

The notations, $\mathbf{A}_{ij}^{\tau}$, $\mathbf{A}_j^{\phi}$, and $\mathbf{B}_{ij}$, have been introduced previously.[2] For simplicity, new matrices $\mathbf{A}^{(i)}$ will be defined as

$$\mathbf{A}^{(0)} = \mathbf{E}$$
$$\mathbf{A}^{(i)} = \mathbf{A}_{12}\mathbf{A}_{23}\cdots\mathbf{A}_{i,i+1} \qquad (0 < i < p) \quad (4)$$

together with the $\mathbf{A}$ matrix.[1]

$$\mathbf{A} = \mathbf{A}_{12}\mathbf{A}_{23}\cdots\mathbf{A}_{p-1,p}\mathbf{A}_{p,1} \quad (5)$$

Then, the position vector $\mathbf{X}_i^m$ is now written as

$$\mathbf{X}_i^m = \sum_{n=1}^{i-1} \mathbf{A}^{(n-1)}\,\mathbf{B}_{n,n+1} \quad (6)$$

Also the vector ($\mathbf{B}$) from the atom M_1^m to M_1^{m+1} is expressed as

$$\mathbf{B} = \mathbf{X}_1^{m+1} = \sum_{n=1}^{p-1} \mathbf{A}^{(n-1)}\,\mathbf{B}_{n,n+1} + \mathbf{A}^{(p-1)}\,\mathbf{B}_{p,1} \quad (7)$$

Accordingly, the position vector of the ith atom in the m + 1st unit is given as

$$\mathbf{X}_i^{m+1} = \mathbf{A}\mathbf{X}_i^m + \mathbf{B} \quad (8)$$

or

$$\mathbf{X}_i^m = \tilde{\mathbf{A}}(\mathbf{X}_i^{m+1} - \mathbf{B}) \quad (8a)$$

where $\tilde{\mathbf{A}}$ is the transpose of the $\mathbf{A}$ matrix. Therefore, the vector ($\mathbf{B}''$) from the atom M_1^{m+1} to M_1^{m+2} is

$$\mathbf{B}'' = \mathbf{X}_1^{m+2} - \mathbf{X}_1^{m+1} = \mathbf{A}\mathbf{X}_1^{m+1} + \mathbf{B} - \mathbf{X}_1^{m+1} = \mathbf{A}\mathbf{B} \quad (9)$$

and the vector ($\mathbf{B}'$) from the atom M_1^{m-1} to M_1^m is

$$\mathbf{B}' = \mathbf{X}_1^m - \mathbf{X}_1^{m-1} = \mathbf{X}_1^m - \tilde{\mathbf{A}}(\mathbf{X}_1^m - \mathbf{B}) = \tilde{\mathbf{A}}\mathbf{B} \quad (10)$$

since $\mathbf{X}_1^m$ is a null vector.

Now two vectors, **C** and **C′**, will be constructed as follows (see also Fig. 2),

$$\mathbf{C} = \mathbf{B}' - \mathbf{B} = (\tilde{\mathbf{A}} - \mathbf{E})\mathbf{B} \qquad (11)$$

$$\mathbf{C}' = \mathbf{B} - \mathbf{B}'' = (\mathbf{E} - \mathbf{A})\mathbf{B} \qquad (12)$$

It may readily be recognized that these vectors are perpendicular to the helix axis. Also the lengths of the **B** and **C** vectors are given as

$$B = (\tilde{\mathbf{B}}\mathbf{B})^{1/2} = (\mathbf{B}\cdot\mathbf{B})^{1/2} \qquad (13)$$

$$C = (\tilde{\mathbf{C}}\mathbf{C})^{1/2} = (\mathbf{C}\cdot\mathbf{C})^{1/2} \qquad (14)$$

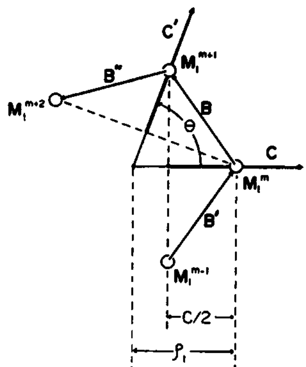

Fig. 2. The **B**, **B′**, **B″**, **C**, and **C′** vectors and the helical parameters, θ and ρ_1.

where the dot $(\cdot)$ denotes scalar products of vectors. Then, as seen in Figure 2, the helical parameters, $\cos\theta$, ρ_1, $d(>0)$ and $\sin\theta$, may be successively calculated as follows:

$$\cos\theta = (\mathbf{C}\cdot\mathbf{C}')/C^2 \qquad (15)$$

$$\rho_1(1 - \cos\theta) = C/2 \qquad (16)$$

$$d^2 + 2\rho_1^2(1 - \cos\theta) = B^2 \qquad (17)$$

$$d\sin\theta = \mathbf{B}\cdot(\mathbf{C}\times\mathbf{C}')/C^2 \qquad (18)$$

where the times sign $(\times)$ denotes vector products.

The unit vectors, $\mathbf{e}_\xi$, $\mathbf{e}_\eta$ and $\mathbf{e}_\zeta$, along the ξ, η, and ζ axes are obtained as

$$\mathbf{e}_\xi = \mathbf{C}/C \qquad (19)$$

$$\mathbf{e}_\eta = \mathbf{e}_\zeta \times \mathbf{e}_\xi \qquad (20)$$

$$\mathbf{e}_\zeta = (\mathbf{C}\times\mathbf{C}')/C^2\sin\theta \qquad (21)$$

and the x, y, and z components of these unit vectors are readily calculated from the components of the **C** and **C′** vectors. Then the transformation from the Cartesian coordinates **X** to the other Cartesian coordinates **ξ** is given by

$$\boldsymbol{\xi} = \mathbf{TX} + \mathbf{L} \tag{22}$$

where

$$\mathbf{T} = \begin{bmatrix} (\mathbf{e}_\xi)_x & (\mathbf{e}_\xi)_y & (\mathbf{e}_\xi)_z \\ (\mathbf{e}_\eta)_x & (\mathbf{e}_\eta)_y & (\mathbf{e}_\eta)_z \\ (\mathbf{e}_\zeta)_x & (\mathbf{e}_\zeta)_y & (\mathbf{e}_\zeta)_z \end{bmatrix} \tag{23}$$

and

$$\mathbf{L} = \begin{bmatrix} \rho_1 \\ 0 \\ 0 \end{bmatrix} \tag{24}$$

Accordingly, the $\boldsymbol{\xi}_i^m$ vector for the ith atom in the mth unit is calculated, by the use of eq. (22), from the $\mathbf{X}_i^m$ vector. The $\boldsymbol{\xi}_i^{m+s}$ vector for the ith atom of the $m + s$th unit is calculated as

$$\boldsymbol{\xi}_i^{m+s} = \mathbf{N}^s\boldsymbol{\xi}_i^m + s\mathbf{D} \tag{25}$$

where

$$\mathbf{N} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{26}$$

and

$$\mathbf{D} = \begin{bmatrix} 0 \\ 0 \\ d \end{bmatrix} \tag{27}$$

From these **ξ** vectors, the helical parameters, ρ_i, d_{ij}, $\cos\theta_{ij}$, and $\sin\theta_{ij}$ are calculated by the use of eqs. (28)–(31).

$$\rho_i = [(\xi_i^m)^2 + (\eta_i^m)^2]^{1/2} \tag{28}$$

$$d_{ij} = \zeta_j^m - \zeta_i^m \tag{29}$$

$$\cos\theta_{ij} = (\xi_i^m\xi_j^m + \eta_i^m\eta_j^m)/\rho_i\rho_j \tag{30}$$

$$\sin\theta_{ij} = (\xi_i^m\eta_j^m - \eta_i^m\xi_j^m)/\rho_i\rho_j \tag{31}$$

All these equations are formulated in convenient forms for calculating the helical parameters as well as the positions, of the main chain atoms (with respect to the helix axis) from the bond lengths, bond angles, and internal-rotation angles. Also, for treating the side-chain atoms, eq. (6) may also be used for calculating the position vector **X**. Then, through the transformation to the **ξ** vector [eq. (22)], the atomic positions (ξ_i, η_i, ζ_i) as referred to the helix axis are obtained; furthermore, the helical parameters (ρ_i, d_{ij}, and θ_{ij}) are also calculated, by the use of eqs. (28)–(31), even for the side-chain atoms. These treatments are applicable to any helical polymer chain and are readily programmed for electronic computers.

Differential Coefficients of Helical Parameters

The partial derivatives of helical parameters (d, $\cos\theta$, $\sin\theta$, ρ_i, d_{ij}, $\cos\theta_{ij}$, and $\sin\theta_{ij}$) with respect to molecular parameters (r_{ij}, ϕ_i, and τ_{ij}) may also be used for studying helical chain conformations. By the use of computers, these derivatives may readily be calculated by numerical differentiation. However, it is also useful to inquire into the analytical forms of the partial derivatives. Then, first, the derivatives of the $\mathbf{A}_{ij}$ and $\mathbf{B}_{ij}$ elements are obtained as,

$$(\partial/\partial r_{kl})\mathbf{A}_{ij} = \mathbf{0} \tag{32}$$

$$\begin{aligned}(\partial/\partial r_{kl})\mathbf{B}_{ij} &= \begin{bmatrix}1\\0\\0\end{bmatrix} = \mathbf{\Delta}_r \qquad \text{For } kl = ij \\ &= \mathbf{0} \qquad \text{For } kl \neq ij\end{aligned} \tag{33}$$

$$\begin{aligned}(\partial/\partial \phi_k)\mathbf{A}_{ij} &= \mathbf{A}_{ij}\mathbf{\Delta}_\phi \qquad \text{For } k = j \\ &= \mathbf{0} \qquad \text{For } k \neq j\end{aligned} \tag{34}$$

$$(\partial/\partial \phi_k)\mathbf{B}_{ij} = \mathbf{0} \tag{35}$$

$$\begin{aligned}(\partial/\partial \tau_{kl})\mathbf{A}_{ij} &= \mathbf{\Delta}_\tau\mathbf{A}_{ij} \qquad \text{For } kl = ij \\ &= \mathbf{0} \qquad \text{For } kl \neq ij\end{aligned} \tag{36}$$

$$(\partial/\partial \tau_{kl})\mathbf{B}_{ij} = \mathbf{0} \tag{37}$$

where

$$\mathbf{\Delta}_\phi = \begin{bmatrix}0 & 1 & 0\\ -1 & 0 & 0\\ 0 & 0 & 0\end{bmatrix} \tag{38}$$

and

$$\mathbf{\Delta}_\tau = \begin{bmatrix}0 & 0 & 0\\ 0 & 0 & -1\\ 0 & 1 & 0\end{bmatrix} \tag{39}$$

Substituting eqs. (32)–(39) into eqs. (4)–(7), we have

$$(\partial/\partial r_{kl})\mathbf{A} = \mathbf{0} \tag{40}$$

$$(\partial/\partial r_{kl})\mathbf{B} = \mathbf{A}^{(k-1)}\mathbf{\Delta}_r \tag{41}$$

$$\begin{aligned}(\partial/\partial r_{kl})\mathbf{X}_i^m &= \mathbf{A}^{(k-1)}\mathbf{\Delta}_r \qquad \text{For } l \leqq i \\ &= \mathbf{0} \qquad \text{For } l > i\end{aligned} \tag{42}$$

$$(\partial/\partial \phi_k)\mathbf{A} = \mathbf{A}^{(k-1)}\mathbf{\Delta}_\phi\tilde{\mathbf{A}}^{(k-1)}\mathbf{A} \tag{43}$$

$$(\partial/\partial\phi_k)\mathbf{B} = \mathbf{A}^{(k-1)}\mathbf{\Delta}_\phi\tilde{\mathbf{A}}^{(k-1)}(\mathbf{B} - \mathbf{X}_k{}^m) \tag{44}$$

$$(\partial/\partial\phi_k)\mathbf{X}_i{}^m = \mathbf{A}^{(k-1)}\mathbf{\Delta}_\phi\tilde{\mathbf{A}}^{(k-1)}(\mathbf{X}_i{}^m - \mathbf{X}_k{}^m) \quad \text{For } k + 1 \leqq i$$
$$= \mathbf{0} \quad \text{For } k + 1 > i \tag{45}$$

$$(\partial/\partial\tau_{kl})\mathbf{A} = \mathbf{A}^{(k-1)}\mathbf{\Delta}_\tau\tilde{\mathbf{A}}^{(k-1)}\mathbf{A} \tag{46}$$

$$(\partial/\partial\tau_{kl})\mathbf{B} = \mathbf{A}^{(k-1)}\mathbf{\Delta}_\tau\tilde{\mathbf{A}}^{(k-1)}(\mathbf{B} - \mathbf{X}_l{}^m) \tag{47}$$

$$(\partial/\partial\tau_{kl})\mathbf{X}_i{}^m = \mathbf{A}^{(k-1)}\mathbf{\Delta}_\tau\tilde{\mathbf{A}}^{(k-1)}(\mathbf{X}_i{}^m - \mathbf{X}_l{}^m) \quad \text{For } l + 1 \leqq i$$
$$= \mathbf{0} \quad \text{For } l + 1 > i \tag{48}$$

The derivatives for helical parameters may now be obtained by the differentiation of the relevant equations and by the substitution of eqs. (40)–(48).

After the completion of the present work, the authors were informed of the unpublished studies by H. Kijima, T. Sato, M. Tsuboi, and A. Wada (the University of Tokyo) in which the analytical expressions for the elements of the **T** matrix were derived.

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