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AN ALTERNATIVE ANALYTICAL PROCEDURE FOR THE GEOMETRICAL CHARACTERIZATION OF (s1) POLYMER CHAINS

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Abstract—Mathematical procedures are given for correlating the conformational parameters of the structural unit with the geometrical parameters of a polymer chain having s1 symmetry.

MANY papers have been published in the last few years on the geometrical characterization of polymer chains with (s1) helicoidal symmetry.[1,2] Equations have been given in these papers to correlate the helix parameters with the bond lengths, the bond angles and the torsional angles of the structural unit.

Once the identity period (T) along the fibre axis, the number of structural units (p) and the number of pitches (q) within the identity period (T) have been experimentally determined, the conformation of a polymer chain may be assigned with the aid of these equations and the use of the available chemical and structural information.[3,4]

Simple procedures have been developed recently in order to characterize the geometry of polymer chains with some of the possible symmetries different from (s1).[5] A similar treatment is given in this paper for the geometrical characterization of (s1) helices, which, in turn, has proved to be suitable for actual calculations.

Let the independent structural unit be composed of n different chain atoms (P_n): the conformation of the chain will be fixed if n bond lengths (b_n) bond angles (ϕ_n) and n torsional angles (σ_n) are given, the following conditions being imposed by the helicoidal symmetry:

$$b_i = b_{i+kn}; \quad \phi_i = \phi_{i+kn}; \quad \sigma_i = \sigma_{i+kn} \qquad (k \text{ is an integer}).$$

The translation along the helix axis $d=T/p$ and the rotation about the helix axis $\theta=2\pi(q/p)$ which define the geometry of the helix can be derived in the following way.

By referring to Fig. 1 the co-ordinates of the first $i-1, \ldots, 1+2n+1$ atoms of the chain are given by a vector:

$$\mathbf{h}_j = (00b_i)+(00b_{i+1})T_i+(00b_{i+2})T_{i+1}T_i+\ldots+(00b_j)T_{j-1}T_{j-2}\ldots T_{i+1}T_i \qquad (1)$$

where

$$T_j = \begin{vmatrix} \cos\sigma_j & \sin\sigma_j & 0 \\ \cos\phi_j \sin\sigma_j & -\cos\phi_j\cos\sigma_j & \sin\phi_j \\ \sin\phi_j\sin\sigma_j & -\sin\phi_j\cos\sigma_j & -\cos\phi_j \end{vmatrix}.$$

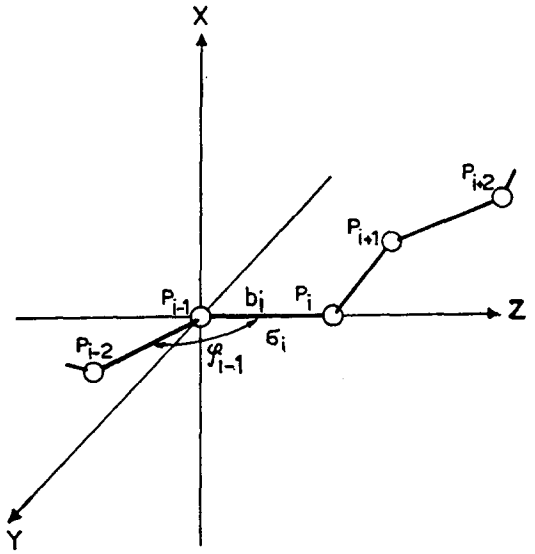

FIG. 1. Right-handed Cartesian co-ordinate system.

The projection of the bonds

$$\mathbf{b}_i = \mathbf{h}_i - \mathbf{h}_{i-1}; \qquad \mathbf{b}_{i+n} = \mathbf{h}_{i+n} - \mathbf{h}_{i+n-1}; \qquad \mathbf{b}_{i+2n} = \mathbf{h}_{i+2n} - \mathbf{h}_{i+2n-1}; \ldots$$

on the chain axis c must, by definition, be equal; that is:

$$\mathbf{b}_i \cdot \mathbf{C} = \mathbf{b}_{i+n} \cdot \mathbf{C} = \mathbf{b}_{i+2n} \cdot \mathbf{C} = \ldots \tag{2}$$

where $\mathbf{C}$ is the unitary vector which defines the direction of the chain axis. The vectors

$$\mathbf{B}_i = \text{vers}\,(\mathbf{b}_i - \mathbf{b}_{i+n}); \qquad \mathbf{B}_{i+n} = \text{vers}\,(\mathbf{b}_{i+n} - \mathbf{b}_{i+2n})^*; \ldots \tag{3}$$

will be therefore perpendicular to $\mathbf{C}$ which can accordingly be fixed in the following way (Fig. 2):

$$\mathbf{C} = \text{vers}\,(\mathbf{B}_i \times \mathbf{B}_{i+n}) \tag{4}$$

Then d and θ are simply given by:

$$d = \mathbf{H}_{i,\,i+n} \cdot \mathbf{C} \tag{5}$$

where $\mathbf{H}_{i,\,i+n}$ is the vector joining the ith and the $(i+n)$th atoms, and

$$\cos\theta = -[\mathbf{B}_i \times \mathbf{B}_{i+n}] \tag{6}$$

When $\mathbf{B}_i \times \mathbf{B}_{i+n} = 0$ in Eqn. (4), which only happens when $\theta = \pi$, then $\mathbf{C} = \text{vers}(\mathbf{b}_i + \mathbf{b}_{i+n})$ and d is calculated as in Eqn. (5).

If $\mathbf{b}_i - \mathbf{b}_{i+n} = 0$ in (3) the same deductions may be drawn provided that bonds $\mathbf{b}_{i+1}$; $\mathbf{b}_{i+n+1}$; $\mathbf{b}_{i+2n+1}$ be considered for which $\mathbf{b}_{i+1} - \mathbf{b}_{i+n+1} \neq 0$ if $\phi_i \neq \pi$.

From Eqns. (5) and (6) the same expressions for the simple cases of one-atom and two-atom chains may be obtained as those reported.[2]

However, this analytical procedure, which uses an algorism indubitably more simple

* Given a vector $\mathbf{A}$, we take vers $\mathbf{A} = \mathbf{A}/|\mathbf{A}|$.

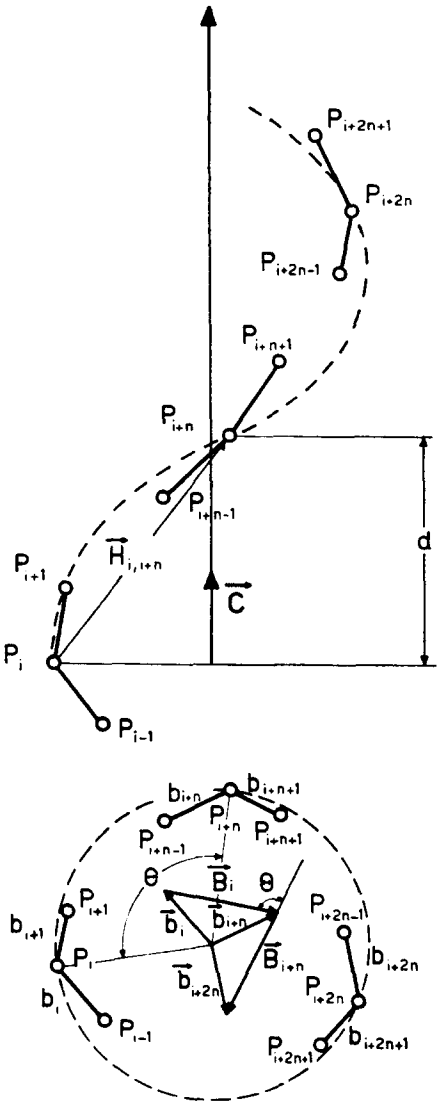

FIG. 2. Side and end view of three segments of a polymer chain related by the helicoidal s1 symmetry (translation d and rotation θ).

than the previous ones, affords an easy method for the determination of the chain geometry in the more complex cases.

This method has been applied to the precise determination of the geometry of the chain in the case of some isotactic polymers[6] and in the conformational analysis of polydimethylketene in which the structural unit is composed of four chain atoms.[7]

A programme has been written for the IBM 1620.

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Résumé—On report les procedures matematiques pour faire une corrélation entre les paramètres conformationals de la unite structurale et les paramètres géometriques de la chaine polymerique avec une symétrie sl.

Sommario—Viene descritto un procedimento matematico che mette in relazione i parametri conformazionali dell'unità strutturale con i parametri geometrici di una catena polimerica avente simmetria sl.

Zusammenfassung—Es wird ein mathematisches Vefahren mitgeteilt, dadurch die Konformationsparameter der Struktureinheit und die geometrischen Parameter der durch sl Symmetrie charakterisierten Polymerkette zueinander in Beziehung gesetzt werden.