A Monte Carlo Simulation of Polyethylene Chain

CHANCHAL K. MITRA & GIRJESH GOVIL

Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400005

The application of Monte Carlo procedures to polyethylene chains are discussed. Conformational energy maps for *n*-pentane by the EHT and INDO methods have been used for simulation. The end-to-end distance and radius of gyration are also reported. The agreement with experiment is good for chains generated with 'excluded volume effect' and based on INDO energy map. The simulated chains show a sheet-like structure.

THE statistical mechanical treatment of polymer chains has produced extremely useful results in recent years[1]. The microscopic treatment, though theoretically possible, is physically discouraging; because of the large number of atoms involved (of the order of 10^4-10^5 in a typical polymer). On the other hand, macroscopic properties are statistical mechanical averages (ensemble averages) of the corresponding microscopic variables, whose detailed nature may not be of direct interest. A physical macroscopic structure can be obtained through Monte Carlo procedures without the detailed knowledge of the dynamical structure, viz. the motion of a polymer chain in conformational space.

All macroscopic properties (for man-made polymers in particular) like the elastic behaviour, the size and shape, the molecular weight distribution etc., can be studied conveniently by elementary statistical mechanical formulation in terms of a suitable model. In most cases, the final result rests critically on the choice of the model, rather than on the rigour of the mathematical procedure. The situation is a conflicting one: the model has to be simple to be useful, and at the same time should be close to the actual system in order that it is realistic. On the other hand the actual system is so complex that it evades direct calculation. As a compromise, a model bearing close resemblance to the actual system is chosen and/or some semiempirical parameters are introduced as to give rise to realistic results.

In this paper we have discussed the application of Monte Carlo procedures to polyethylene chains. In the calculation, the bond length and the bond angles were kept fixed — only the torsional angles were changed. This is quite justified because the bond stretching (and bending) energy is one or two order of magnitude higher than the rotational barrier heights. Monte Carlo methods have been used to generate random polyethylene chains (a simulation process) and the end-to-end distance and the radius of gyration have been evaluated. These two quantities can be considered to give the zeroeth order and first order approximation to the shape of the molecule. Chains have been simulated both by considering excluded volume effect and where such effects were neglected.

Conformational Energy Maps

The general approach of the application of Monte Carlo methods to the problems discussed here involves what is known as a 'rotational isomeric state approximation'. This involves replacing the continuum of conformations that may be acquired around each chemical bond due to internal rotations by a discrete set of angles ($\{\phi_3\}$, $\{\phi_4\}$). The probability ($P\{\phi_3,\phi_4\}$) of each state (ϕ_3,ϕ_4) is obtained through the classical Boltzmann distribution

$$P(\phi_3,\phi_4) = \frac{\exp[-E(\phi_3,\phi_4)/RT]}{\Sigma\exp[-E(\phi_3,\phi_4)/RT]}$$

(The denominator assures that P lies between 0 and 1). Here $E(\phi_3,\phi_4)$ is the total molecular energy for the state with torsional angles ϕ_3, ϕ_4 which are conveniently obtained from either classical theories[2] (e.g. classical potential function, CPF) or molecular orbital theories (like EHT, CNDO, INDO, PCILO etc.). Very often there is a strong correlation between adjacent bonds with the result that the conformational state about a particular bond i is dictated to some extent by the torsional angles ϕ_{i-1} and ϕ_{i+1}. For example, in *n*-butane, the C-C rotations give rise to three well-defined isomers —*gauche* (g^+), *trans* (t) and *gauche* (g^-). In a right handed *cis* convention of measuring torsional angles (Fig. 1) the correspond torsional angles ϕ are 60°, 180° and 300° respectively. In case of *n*-pentane, one expects nine state conformers g^+g^+, g^+t, g^+g^-, tg^+, tt, tg^-, g^-g^+, g^-t, g^-g^-.

However, conformations of the type g^+g^- and g^-g^+ are unfavoured because of strong steric repulsions (such steric interactions has often been called pentane effect). Therefore for studying conformational features of long hydrocarbon chains, *n*-pentane becomes the smallest and a reasonable model compound.

The quantum mechanical methods of EHT (extended Huckel theory) and INDO[3] (intermediate neglect of differential overlap) have been used to

calculate the energy of the molecule (*n*-pentane) as a function of the torsional angles. The calculations have been carried out using standard programmes[4] on a CDC-3600 computer. The orbital ex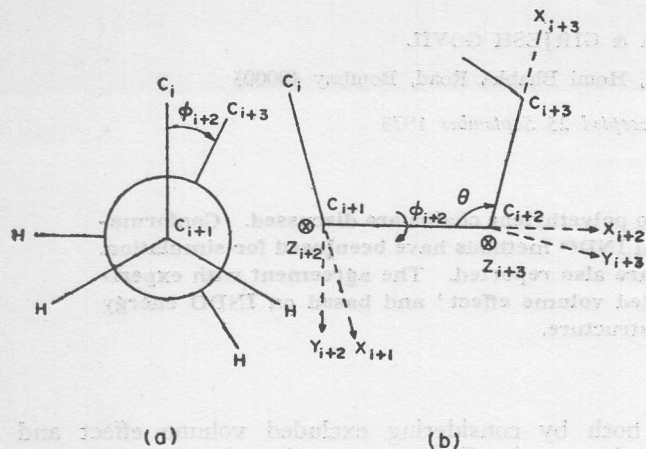ponent and valence shell ionization potentials for different orbitals used in the EHT calculations are listed in an earlier paper[5]. The energy is calculated as a function of two torsional angles ϕ_3 and ϕ_4 of *n*-pentane. In these calculations, the two terminal methyl groups have been kept in staggered conformations. The results are plotted in the form of a isoenergy contours in the two dimensional (ϕ_3, ϕ_4) conformational space (Figs. 2 and 3).

Simulation of Polythene Chains

In the simulation process, the atoms are numbered sequentially. The co-ordinates are calculated using the standard methods of matrix transformation and multiplication. Each time a new carbon atom is added, a local co-ordinate system is set up at that point. The local co-ordinates are then transformed to the proper reference frame (Fig. 1b) by the simple process of rotation and translation. For example, the coordinates of atom ($i+3$) in the

(a)   **(b)**

Fig. 1 — Definition of the torsional angles defining rotations about C-C bonds in polyethylene chain. The angle ϕ_{i+2} decides the relative arrangements of atoms C_i, C_{i+1}, C_{i+2} and C_{i+3} [(a) Looking along the bond joining C_{i+1} and C_{i+2}, the angle ϕ_{i+2} is positive for a clockwise rotation of the far end with respect to the near end. The zero value of ϕ_{i+2} corresponds to a *cis* arrangement of C_i and C_{+3}. (b) The projection perpendicular to the bond being rotated. The diagram depicts the convention followed in choosing a local co-ordinate system. For the ($i+3$)th co-ordinate system, the origin is at the atom no ($i+2$), the x axis is along the bond joining ($i+2$) and ($i+3$) atoms and y axis is perpendicular to the x axis in a sense such that its projection on X_{i+2} is positive Then Z-axes are defined in a right-handed sense. In the drawing, all the Z-axes point downwards. The bond angle θ has been taken as 109·47° in the calculations]

coordinate system ($i+3$) is simply $\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$, taking the bond length as the unit of distance. To bring this to the frame of ($i+2$)th atom, three steps were required: (i) rotation by $-\phi_{i+2}$ about X_{i+2} (ii) rotation by $\pi - \theta$ about Z_{i+2} axis and (iii) translation by the coordinates of ($i+2$)th atom. Thus the coordinates of ($i+3$)th atom in the frame the defined by the first three atoms is given by

$$\underset{\sim}{\mathcal{X}}_{i+3} = \left[\prod_{k=3}^{i+3} \underset{\approx}{\mathcal{T}}(\phi_k) \right] \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \underset{\sim}{\mathcal{X}}_{i+2}$$

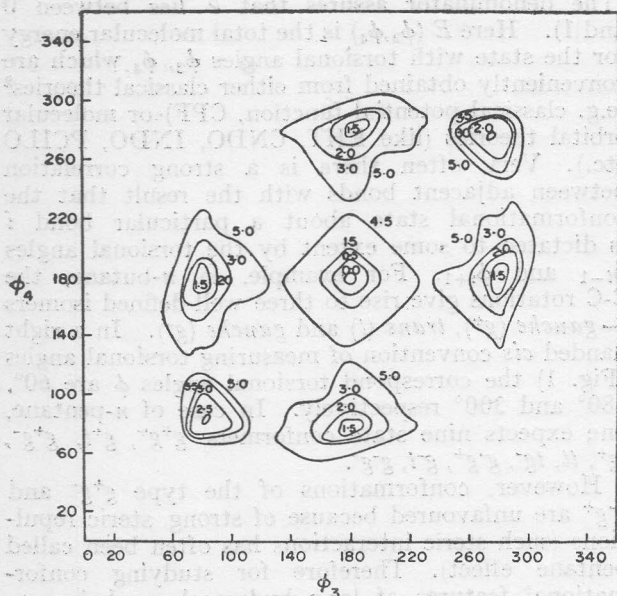where $\underset{\approx}{\mathcal{T}}(\phi)$ has the form

Fig. 2 — Isoenergy contours in the (ϕ_3, ϕ_4) space for *n*-pentane [The relative energies are expressed in kcal mole⁻¹. The energies are obtained by EHT calculations. The global minimum is at (180°, 180°) and the relative energy for such an arrangement is at least 1·5 kcal mole⁻¹ lower than that for other six minima]
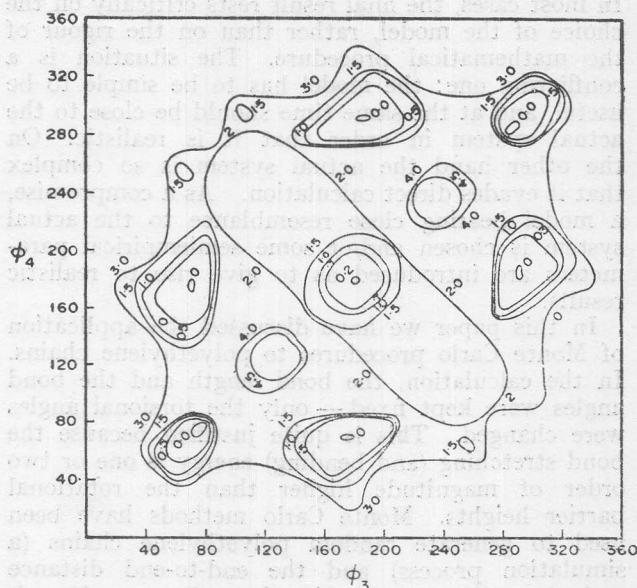

Fig. 3 — Isoenergy contours for *n*-pentane as predicted by INDO [The relative energies are in kcal mole⁻¹. The global minima corresponds to (g^+g^+) arrangement. The next lowest minimum is about 0·200 kcal mole⁻¹ higher]

$$\mathcal{T}(\phi) = \begin{pmatrix} \dfrac{1}{3} & \dfrac{2\sqrt{2}}{3} & 0 \\[2ex] -\dfrac{2\sqrt{2}}{3}\cos\phi & \dfrac{1}{3}\cos\phi & -\sin\phi \\[2ex] -\dfrac{2\sqrt{2}}{3}\sin\phi & \dfrac{1}{3}\sin\phi & \cos\phi \end{pmatrix}$$

($\theta = 109\cdot47°$ and $\cos\theta = 1/3$ been used consistently)

Since the coordinates of the first three atoms are used to define the co-ordinate system, they are known and so by using the above method, the co-ordinates of all the atoms in the chain can be obtained[6].

The value for the torsional angle about the bond $i(\phi_i)$ is chosen using a simple Monte Carlo technique in the rotational isomeric state model. The energy map is divided into 36×36 square blocks — each block (l,m) representing $10°$ variations in ϕ_3 and ϕ_4. A number $\mathsf{P}(l,m)$ is assigned to each block with $\mathsf{P}(l,m) = \exp[-E(l,m)/RT]$, where $E(l,m)$ is the average energy in that block. In practice, $E(l,m)$ were taken as the energy at the centre of the square. Thus the energy map is converted into a probability map — the number in any square telling the relative probability of having a con-formation with the value of (ϕ_3, ϕ_4) at the centre of the square. These relative probabilities are normalized as described below. To initiate the chain, we note that the first three carbon atoms define the co-ordinate system. The next two can be chosen independently with a probability distri-bution as governed by the (ϕ_3, ϕ_4) map. The matrix $\mathscr{P}$ has the elements defined by

$$p(l,m) = \frac{\displaystyle\sum_{n=1}^{l-1}\sum_{k=1}^{36}\mathsf{P}(n,k) + \sum_{k=1}^{m}\mathsf{P}(l,k)}{\displaystyle\sum_{n=1}^{36}\sum_{k=1}^{36}\mathsf{P}(n,k)}$$

The numbers in $\mathscr{P}$ matrix now lie between 0 and 1 in ascending order. A random number (R) between 0 and 1 is generated using the random number generator in the computer. The elements of $\mathscr{P}$ matrix are then sequentially searched for the condition $p(l,m) < R < p(l,m+1)$ to be satisfied. Values of (ϕ_3, ϕ_4) are chosen to correspond to the centre of the block (l,m). From these two torsional angles, using the matrix transformation process, the first five atoms of the chain are simulated.

To continue the chain further, it should be realized that the angle has already been fixed and one has to find ϕ_{i+1} to fix the position of carbon atom $(i+1)$. In other words, the row of the matrix $\mathscr{P}$ is already determined by the value of ϕ_i. Therefore, the matrix $\mathscr{P}$ is modified to normalize row-wise. Thus the elements of the lth row of the matrix $\mathscr{P}$ now contains

$$p(l,m) = \frac{\displaystyle\sum_{k=1}^{m}\mathsf{P}(l,k)}{\displaystyle\sum_{k=1}^{36}\mathsf{P}(l,k)} \quad \text{for all } l$$

For simulation of the atom $(i+1)$, the last torsional angle is taken and the corresponding row (l) is obtained. A random number (R) is called and compared with each block of the particular row

that satisfies $p(l,m) < R < p(l,m+1)$. The value of the torsional angle corresponding to the centre of the column (m) is taken as the new torsional angle. Using this new torsional angle, co-ordinates of the $(i+1)$th atom are generated. This process is used for the sixth carbon atom onwards and is continued until a chain with required number of atoms has been simulated. For each torsional angle, the co-ordinates are calculated by the formula described before. The co-ordinates of the pendant hydrogens are not generated because these are not important for our discussion. Even for considerations of excluded volume effects the errors thus introduced are small and have been taken into account indirectly by assigning a somewhat increased van der Waals radius ($1\cdot85$ Å) for carbon.

For chains where effects of excluded volume are taken into account, the distance of the simu-lated carbon atom $(i+1)$ is checked for close-contacts with all other atoms already in the chains. If there is a bad contact, the whole chains is not rejected, but a new value is sought for ϕ_{i+1} by generating the random number again. This additional cons-traint results in somewhat larger end to end dis-tances. 100 chains of 250 methylene units have been generated both by using the EHT and INDO energy map and both end-to-end distances (r) and their distribution functions have been obtained. The characteristic ratio (C) and mean radius of gyration have also been calculated and are reported in Table 1.

$$\text{Characteristic ratio } C = \frac{<r^2>}{n^2}$$

Radius of gyration g is calculated from $g^2 = \dfrac{1}{n}\sum_{0<i<j<n} r_{ij}^2$ where n is the total number of atoms in the backbone chain and r_{ij} is the distance between the ith and jth atom.

Results and Discussion

Figs. 2 and 3 show the conformational map obtained by EHT and INDO calculations res-pectively. Both the maps show that regions

TABLE 1 — ROOT MEAN SQUARE AVERAGE OF END-TO-END DISTANCE AND THE RADIUS OF GYRATION FOR CHAINS GENERATED USING INDO AND EHT ENERGY MAPS

End-to-end distance $<r^2>^{1/2}$	Charac-teristic ratio $\dfrac{<r^2>}{n}$	Radius of gyration $<g^2>^{1/2}$	$\dfrac{<r^2>}{<g^2>}$
	INDO		
(a) 46·939	8·8	17·057	7·5
(b) 23·229	2·1	10·089	5·9
	EHT		
(a) 175·920	123·7	52·613	11·1
(b) 168·556	113·6	50·126	11·3

(1) All dimensions are in units of bond length, 1·54Å.
(a) Considering excluded volume effect.
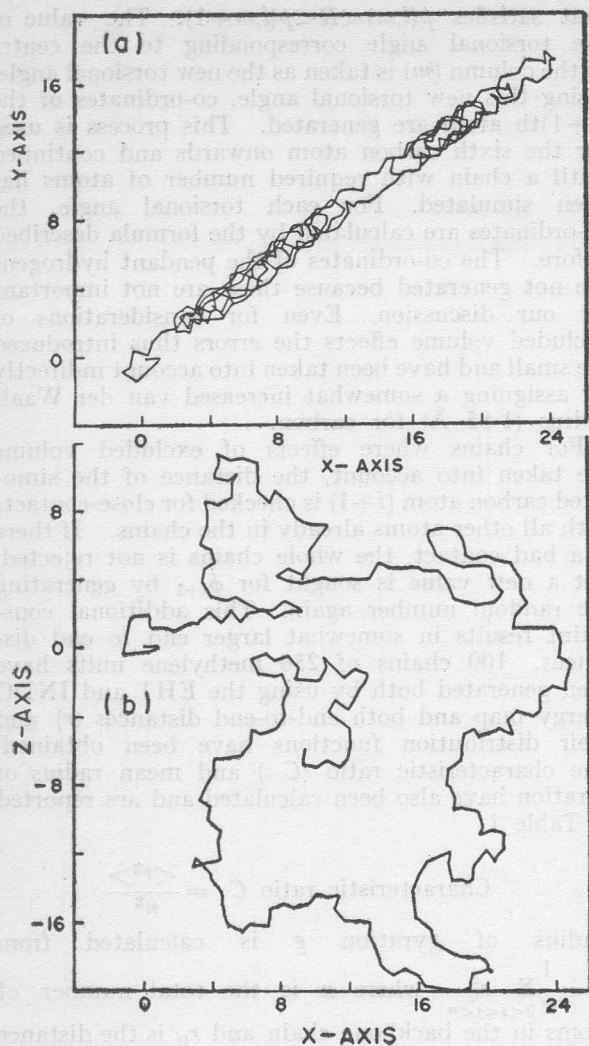(b) Neglecting excluded volume effect.

Fig. 4 — Projection of a typical random chain on the coordinate planes. This particular chain was generated using the INDO potential energy map [(a) Projection on XY plane and (b) projection on XZ plane]

corresponding to g^+g^- and g^-g^+ conformations are unstable. The other seven regions g^+g^+, g^-g^-, g^+t, tg^+, g^-t, tg^-, tt which correspond to the staggered forms about the C-C bonds are found to be stable. However, quantitatively there is a marked difference between the predicted relative stabilizations of these regions by the two theories. In the EHT map the (180°, 180°) region is preferred by about 1·5 to 2·5 cal mole^{-1} over other regions. Obviously, the conformational distribution is heavily weighted in favour of an all *trans* arrangement. In the INDO map the g^+g^+ (or g^-g^-) correspond to a global energy minimum but it is only slightly favoured over the other five low energy regions. The simulated coils based on INDO map thus show a much greater randomness and a lower end-to-end distance.

The calculated end-to-end distance from INDO maps, taking excluded volume effect in consideration is in very good agreement with experimental values. Thus the predicted value C is 8·8 (at 25°). The experimental value at 140° is 6·7 with a temperatured coefficient of $-1·0 \times 10^{-3}$ (ref. 1). The extrapolated value at 25° thus turns out to be 7·6.

Fig. 4 shows the distribution of end-to-end distance and radius of gyration using INDO energy map and correcting for excluded volume. The histograms approach a Gaussian behaviour with a sharp rise and a gradual tailing off. The behaviour illustrates that the statistical sampling based on 100 chains of 250 carbon atoms represents a reasonable macroscopic picture of the system. This is definitely not true for the calculations based on EHT energy maps (Fig. 5). In these cases, the *trans* states are so heavily populated that they do not show the expected tail in the distribution.

Figs. 6a and 6b show a typical projection of the simulated chains from INDO energy maps on the XY and XZ planes. It is interesting to note that long sections of the simulated chains show a sheet-like overall structure which is one of the basic properties of polyethylene. On the other hand, short segments, as may occur in phospholipids (containing 10-20 atoms) are relatively straight.
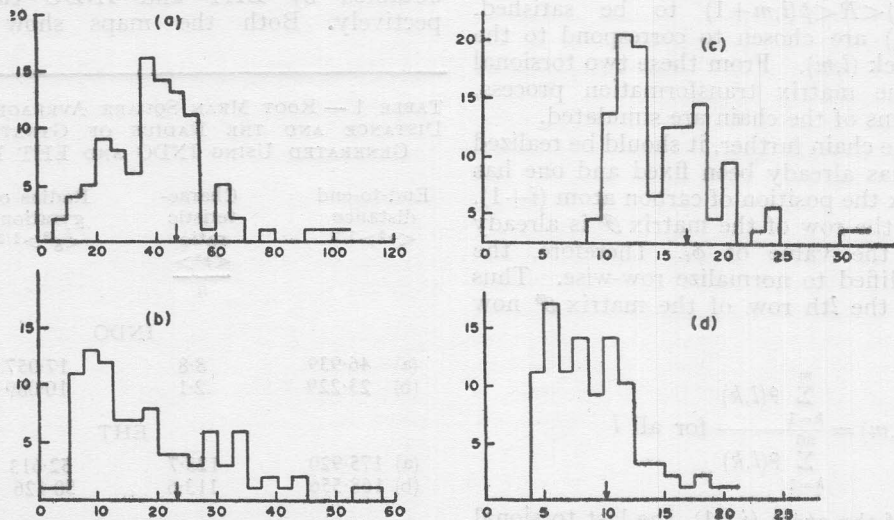
Fig. 5 — Distribution functions for end-to-end distance and radius of gyration for 100 chains of 250 units using INDO energy map. [(a) and (b) are end-to-end distance and radius of gyration respectively with excluded volume effect present. (c) and (d) are the same quantities with excluded volume effect being neglected. The arrow points to the root mean square value of quantity under discussion]
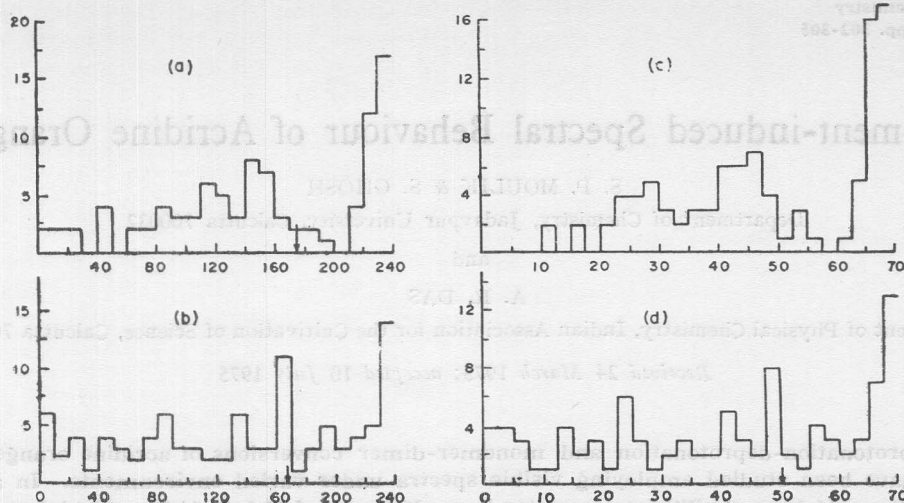
Fig. 6 — The distribution functions using EHT energy map. [(a) End-to-end distance with excluded volume effect (b) mean radius of gyration with excluded volume effect, (c) end-to-end distance without excluded volume effect, (d) mean radius of gyration without excluded volume effect]

The ratio of $<r^2>/<g^2>$ is also found to be close to 6 for chains simulated by INDO maps. This also shows independently that INDO energy map gives better agreement with experiment and theory.

References

1. FLORY, P. J., *Statistical mechanics of chain molecules* (Interscience Publishers, New York), 1969, Chapter VII.

2. LAL, M. & SPENCER, D., *Molec. Phys.*, **22** (1971), 649.

3. POPLE, J. A. & BEVERIDGE, D. L., *Approximate molecular orbital theory* (McGraw-Hill, New York), 1970.

4. The EHT programme was kindly supplied by Prof. R. Hoffman, and INDO programme was obtained from QCPE.

5. GOVIL, G., *J. chem. Soc.*, (A) (1970), 2464.

6. HOPFINGER, A. T., *Conformational properties of macromolecules* (Adacemic Press, New York), 1973, Chapter I.