On the Calculation of Molecular Conformation in Crystalline Polymers.

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Summary. — The stability of helical conformations in simple polymer chains should depend upon intramolecular interactions, which can be described in a first approximation in terms of repulsive forces between nonbonded atoms along the chain plus a small contribution from dispersion forces. Using the same consistent set of interaction parameters as in a previous work on small molecules, the conformational potential energy of isolated polymer chains satisfying the postulate of the conformational equivalence of each monomeric unit has been investigated as a continuous function of skeletal bond angles. The most stable conformations corresponding to the deepest minima of the potential energy plot for polyethylene, polytetrafluoroethylene, polyoxymethylene and polyethylene oxide are in good agreement with the conformations experimentally observed from X-ray diffraction patterns.

1. — Introduction.

It is well known that the conformational properties of small molecules can be obtained in an approximate way from a knowledge of the interaction forces between bond pairs. Stabilities of molecular conformations and barriers to internal rotation around axial bonds can be discussed in terms of forces of this kind \(^{1,2}\).

On theoretical grounds, there is no conceptual difference between the inter-

molecular interaction between two rare gas atoms, say, and the intramolecular interaction between a pair of saturated bonds in a polyatomic molecule.

We can therefore borrow from the theory of intermolecular forces (2) the useful distinction between "short-range" and "long-range" intramolecular forces. There is by no means a clear cut between these two ranges, the distinction being useful mainly for semiempirical purposes.

Short-range intramolecular forces are mainly due to the repulsive interpenetration of the electronic charge distribution between pairs of saturated chemical bonds, appearing as a first-order effect in a series expansion of the interaction energy (4,5).

It can be shown on quantum-mechanical grounds (4) that the interaction between bond pairs exhibits a strong angular dependence through the change of overlap between orbitals belonging to atoms not directly bonded. As a first approximation, the interaction energy varies exponentially with the internuclear distance between nonbonded atoms, but the coefficients of the exponential terms appear to depend upon the rest of the molecule.

Recent theoretical approaches to long-range forces (7) improve the molecular wave function by admitting configuration interaction of the ground state with higher excited states.

In the electrostatic picture useful for semiempirical descriptions, long-range intramolecular forces appear due to the weak attractive interaction between induced dipoles (terms such as $R^{-4}$), between induced dipoles and quadrupoles ($R^{-8}$), between induced quadrupoles ($R^{-10}$) and so on. Higher-order terms give usually negligible contributions and it seems therefore justified to take into account only the first term ($R^{-4}$) in the expansion. On these theoretical grounds it seems worth-while to try to represent the intramolecular interaction between bond pairs in a polyatomic molecule by the simple function

\begin{equation}
E(R) = A \exp[-\beta R] - B \exp[-2\beta R] + CR^{-1} - DR^{-6},
\end{equation}

where $A$, $B$, $C$, $D$, $\beta$ are constants for the pair and $R$ is the internuclear distance between nonbonded atoms. The first two terms represent the repulsive interaction energy between the charge clouds of the bonds, the third term the electrostatic contribution due to the asymmetry of the charge distribution


