Communications to the Editor

Chain Folding in Polyethylene Crystals. The Cooperative Effect of Bond Angle Deformation and Rotational Strain

The folding of a polymer chain in the proximity of the basal surface of a lamellar crystal is certainly connected with the simultaneous deformation of many geometrical parameters from their usual values, in order to minimize the energy. This is a consequence of the fact that the two straight segments of the chain connected with the fold are bound to occupy rather definite relative positions dictated by the crystal structure. More generally, the existence of geometrical constraints is the source of cooperative deviations of the molecular parameters from their unstrained values:[1,2] bond angles and internal rotations around single bonds are especially involved in the strain.

McMahon, McCullough, and Schlegel[3] have studied in some detail the model of chain folding in crystalline polyethylene. They minimized the conformational energy for both the possible folds, A and B (in the 200 and 110 planes, respectively),[4,5] assuming the conformation of a zigzag planar segment as the reference state and allowing for the variation in rotation angles only. Considering as many as seven variable angles, which correspond to one free coordinate once the six conditions of constraint are deducted,[3] they obtain 12.3 and 14.6 kcal/mol for folds A and B only.

We have been stimulated to reinvestigate the problem by the two following considerations: (i) the importance of bond angle deformation should not be neglected in the present problem; (ii) contrary to the case of the previous authors, an optimization routine for functions of several variables (up to 30) is available to us,[6] which allows us to start from models that do not necessarily fulfill the boundary conditions, provided they are close to a minimum in the conformational energy surface.

TABLE I
CALCULATED ENERGY (kcal/mol) OF THE FOLDS

Fold type		EROT	EBE	ENB	ETOT
			This Work		
A[a]	(1)	2.24	1.23	−0.35	3.12
	(2)[b]	1.70	1.09	−0.45	2.34
B[a]	(1)	2.55	1.38	0.33	4.26
	(2)[b]	2.58	1.19	0.23	4.00
			Reference 3[c]		
A[b]		7.79		0.79	8.58
B[b]		10.39		−0.20	10.19

[a] The energy results labeled with (1) correspond to minimization over all rotation and bond angles except the first and last one; (2) labels the results of the minimization procedure over all the angles reported in Table II. [b] The conformation of the fold is given in Table II. [c] According to our calculation procedure, for comparison purposes.

After a preliminary investigation of the most suitable geometrical models, we have assumed as starting conformations for folds A and B (see the figure) the following sequences of internal rotation angles (t = trans, $g_\pm$ = gauche in either sense of rotation): $\ldots ttg_+g_+tg_+g_+tt\ldots$ and $\ldots ttg_+tg_+g_+g_-g_-tt\ldots$, respectively.

From our preliminary calculations the energy involved in the folds A and B is about 3 and 4 kcal/mol, respectively, say about 2.5 times less than the figures obtained by McMahon, *et al.*, recalculated with our procedure (see Table I). The reference, *i.e.*, zero energy, state for a fold involving m methylene units consists of two facing segments of $m/2$ units, in the planar zigzag conformation, with the same relative orientation as the two straight segments which are joined together by the fold. We have performed several minimum-energy calculations, each time allowing for a different number n of consecutive rotation angles to vary, together with $n - 1$ C–C–C angles comprised in between. The largest n values are 12 and 11 for fold types A and B, respectively.

We assumed a threefold rotational barrier around the C—C bonds of 3 kcal/mol,[7] and an elastic constant for the C—C—C angles of 180 kcal/mol rad^{-2}, *i.e.*, close to the value adopted by one of us for the C—C—C bending.[8] As for the H···H, H···C, and C···C interactions between atoms separated by not less than three bonds, we used the parameters suggested by Abe, Jernigan, and Flory,[9] for equations of the exp/6 type. Table I shows the minimum-energy results obtained for either type of fold in the runs where the two largest n values were adopted, considering separately the energy components due to the internal rotation (EROT), to the C–C–C bending (EBE), and to the nonbonded interactions (ENB). Table II also lists the values of the chain parameters obtained after the run where all of them were optimized (see the figure for the labeling of the bonds). The importance of the angle bending, which absorbs a substantial fraction of the total strain energy, is apparent, and the need for

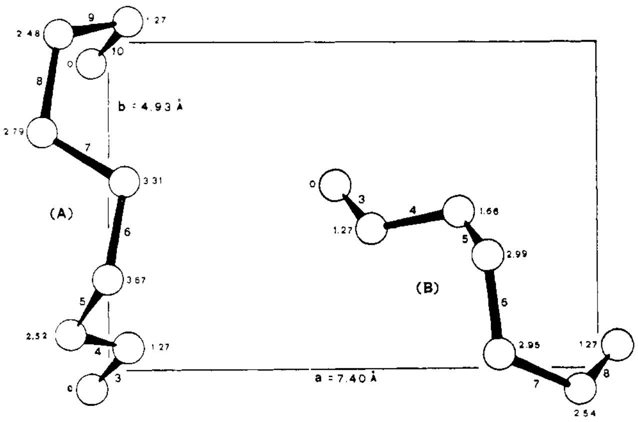

Figure 1. Model of the conformation of folds A (along 200) and B (along 110) seen along the *c* axis of the unit cell of polyethylene. Only bonds 3–10 and 3–8 are shown, respectively. The numbers near the atoms are heights in Ångström units.

---

(1) S. Lifson and A. Warshel, *J. Chem. Phys.*, **49**, 5116 (1968).

(2) P. Corradini, Conference held at the Colloqium on Conformational Analysis, Paris, 1970.

(3) P. E. McMahon, R. L. McCullough, and A. A. Schlegel, *J. Appl. Phys.*, **38**, 4123 (1967).

(4) P. H. Geil, "Polymer Single Crystals," Interscience, New York, N. Y., 1963.

(5) M. I. Bank and S. Krimm, *J. Polym. Sci., Part A-2*, **7**, 1785 (1969).

(6) G. B. Ferraris, *Quad. Ing. Chim. Ital.*, **4**, 171, 1968.

(7) D. R. Herschbach, "Bibliography for Hindered Internal Rotation and Microwave Spectroscopy," Lawrence Radiation Laboratory, University of California, Berkeley, Calif., 1962.

(8) G. Allegra, *Makromol. Chem.*, **110**, 58 (1967).

(9) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966).

TABLE II

FINAL VALUES OF ψ AND θ AFTER THE MINIMIZATION PROCEDURE[a]

Fold type	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6	ψ_7	ψ_8	ψ_9	ψ_{10}	ψ_{11}	ψ_{12}
A[b]	175.6	182.7	158.2	183.9	55.6	56.5	178.0	69.3	58.7	165.6	179.9	173.9
	t	t	t′	t	g+	g+	t	g+	g+	t	t	t
B[b]	184.5	176.7	74.9	174.8	68.4	91.6	−58.4	−64.4	174.4	171.3	180.4	
	t	t	g+	t	g+	g+′	g−	g−	t	t	t	
	$\theta_{1,2}$	$\theta_{2,3}$	$\theta_{3,4}$	$\theta_{4,5}$	$\theta_{5,6}$	$\theta_{6,7}$	$\theta_{7,8}$	$\theta_{8,9}$	$\theta_{9,10}$	$\theta_{10,11}$	$\theta_{11,12}$	
A	114.9	110.3	114.4	112.9	114.5	113.8	113.4	114.6	113.3	113.4	111.8	
B	112.8	112.1	113.6	112.7	114.8	114.8	116.2	114.0	111.4	113.5		
	Data of Reference 3											
A	...ttt 103, 185, 82, 87, 222, 77, 190 ttt...											
B	...ttt 200, 248, 77, 86, 206, 82, 235 ttt...											

[a] The results refer to the calculation labeled (2) of Table I; the ψ's and θ's are labeled according to the figure; angles not explicitly reported were kept fixed ($\psi = 180°$, $\theta = 112°$). The two types of folds A and B are indicated in Figure 1. Trans (t) and gauche ($g_\pm$) bonds with internal rotational angles significantly displaced from the minima of the rotational potential are indicated with a prime (*i.e.*, t′ or $g_\pm$′).
[b] Of course, the enantiomorphous conformations are isoenergetic

introducing a sufficient number of geometrical parameters is also evident, in order to avoid overestimation of the constraints. We wish to emphasize that the introduction as variables of as many as 12 or 11 internal rotation angles and bond angles does not lead to substantial departures from the zigzag conformation of the chain, but in the region of the fold (bonds 5–6–7–8 of fold A and bonds 4–5–6–7 of fold B; see Figure 1). For comparison purposes, the conformational parameters proposed by McMahon, McCullough, and Schlegel,[3] and the corresponding energy values, calculated according to our energy parameters as well as to our reference state, are also given in the tables.

We want to emphasize one particular aspect of the data reported in the Table I: with the energy functions used, practically no repulsive energy between nonbonded atoms appears to be involved in the folded segments, so the fold energy appears to be essentially due to the sum of the torsional and of the bending contributions. We are presently extending our calculations with the main purpose of proving that possible alternative choices of the parameters for the nonbonded interactions have little influence over both the resulting geometry and the energy of the folds. The results already obtained appear to support our present hypothesis. Finally, we want to emphasize that the models given by us are not to be considered as unique, at least in the sense that a wide variability of geometrical models is isoenergetically possible in the neighborhood of each of the studied conformations.

Acknowledgment. The authors gratefully acknowledge the financial support of the LTPR of the National Research Council (Italy).

P. Corradini,* V. Petraccone
Istituto di Chimica dell'Università
Naples, Italy

G. Allegra
Istituto di Chimica dell'Università
Trieste, Italy

Received May 4, 1971