C. 7H,16H-Benzo[1'',2'':3,4:4'',5'':3',4']dipyrrolo[2,1-*b*:2',1*b*']diquinazoline-7,9,16,18-tetrone (IV) was obtained by the treatment of II of 240–250° for 2 hr. Yellow crystals melting at 444° were obtained.

Anal. Calcd for $C_{24}H_{10}O_4N_4$: C, 68.89; H, 2.40; N, 13.39. Found: C, 68.23; H, 2.21; N, 13.63.

7. Polymerizations. Typical Preparation of a Poly(amic acid amide) (VI). The low-temperature solution polymerization was carried out by the reaction of MABA with PMDA in NMP. To a solution of purified MABA (4.267 g, 0.015 mol) in NMP (50 ml) was added freshly sublimed PMDA (3.272 g, 0.015 mol) at 22° in a heterogeneous system with rapid stirring in an inert atmosphere. After 10 min, a light yellow, clear solution was obtained and the viscous polymer solution was quenched by pouring it into ethanol after 6 hr. The fibrous polymer was filtered, washed thoroughly with ethanol, and dried under vacuum at 75°. The yield of polymer was nearly quantitative and the inherent viscosity was 2.9 in NMP (0.5% concentration, 25°). The polymer solution was poured onto a glass plate and heated at 75° for 15 hr to afford a transparent, tough film of poly(amic acid amide) (VIb).

Anal. Calcd for $C_{25}H_{18}O_8N_4$: C, 59.76; H, 3.61; N, 11.15. Found: C, 57.21; H, 4.05; N, 10.48.

The poly(amic acid amide) thus obtained was soluble in DMAc, NMP, dimethylformamide, and dimethyl sulfoxide, and concentrated sulfuric acid.

8. Conversion to Poly(amic acid amide) (VIb) and Poly(isoindoloquinazolinedione) (IXb). The poly(amic acid amide) film was heated on a frame in an oven at 150° for 2 hr. The polymer undergoes the first intramolecular dehydration to form a poly(imide amide) (IXb) of high molecular weight.

Anal. Calcd for $(C_{25}H_{14}O_6N_4)_n$: C, 64.38; H, 3.06; N, 12.01. Found: C, 64.06; H, 3.30; N, 11.88.

The dehydration was also effected by treating poly(amic acid amide) film (VIb) with a solvent pair of acetic anhydride and pyridine (1:1). The poly(isoindoloquinazolinedione) (IXb) was obtained by heating the poly(imide amide) (VIIb) or poly(amic acid amide) (IXb) in nitrogen at 250° for 30 min.

Anal. Calcd for $(C_{25}H_{10}O_4N_4)_n$: C, 69.78; H, 2.34; N, 13.02. Found: C, 69.30; H, 2.50; N, 12.78.

Acknowledgment. The author gratefully acknowledges the interest and encouragement of Dr. N. Yoda of Pioneering Research and Development Laboratories, Toray Ind. Inc. The author is indebted to Messrs. T. Mizushima and T. Suzuki for the thermal analyses and the nomenclature of the monomer and polymers, and Dr. A. Ishitani for the measurement and valuable discussion of ultraviolet spectra. Thanks are due to Mr. A. Kobayashi for technical assistance.

Conformational Analysis and Chain Statistics of Poly(isobutylene)[1a]

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Received June 12, 1970

ABSTRACT: The conformational analysis of poly(isobutylene) is performed, with explicit allowance for elastic bending of the chain ∠CCC bond angles. The corresponding effect consists of a drastic flattening of the conformational energy function *vs.* ψ_1 and ψ_2 (the chain rotation angles on the general monomer unit). Furthermore, the differences among the energy minima, calculated either allowing for all H···H, H···C, and C···C nonbonded interactions, or treating the methyl groups as spherically symmetrical bodies and assigning different values to their van der Waals' radius, are very similar; quite the opposite is obtained if the chain bond angles are kept fixed. The chain conformation in the crystalline state is unambiguously verified to be close to that proposed by Wasai, Saegusa, and Furukawa:[5] it corresponds to an 8_3 helix. The chain conformation in the unperturbed state is shown to be satisfactorily described in terms of a statistical sequence of "staggered" (T, G, and G') rotational states. Both the mean-square end-to-end distance and its temperature derivative, evaluated with the conformational energy values obtained for the chain in the crystalline state, are in excellent agreement with experiment.

The problem of the chain conformation of poly(isobutylene), both in the crystalline state and in solution, has aroused considerable controversy.[2-9]

For the crystalline state, Fuller, Frosch, and Pape[2a] first proposed a definite chain conformation, containing eight monomer units in one turn (8_1). Liquori, on the basis of the qualitative distribution of the diffracted X-ray intensities on the fiber spectrum, showed that an 8_1 or an 8_7 conformation is unlikely. He proposed a uniform 8_5 helix,[2b] which should have constant values of the bond angles, and internal rotation angles on the chain backbone equal to 114 and 98°, respectively

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(2) (a) C. S. Fuller, C. J. Frosch, and N. R. Pape, *J. Amer. Chem. Soc.*, **62**, 1905 (1940); (b) A. M. Liquori, 13th International Congress of Pure and Applied Chemistry, Stockholm, 1953; *Acta Crystallogr.*, **9**, 345 (1955).

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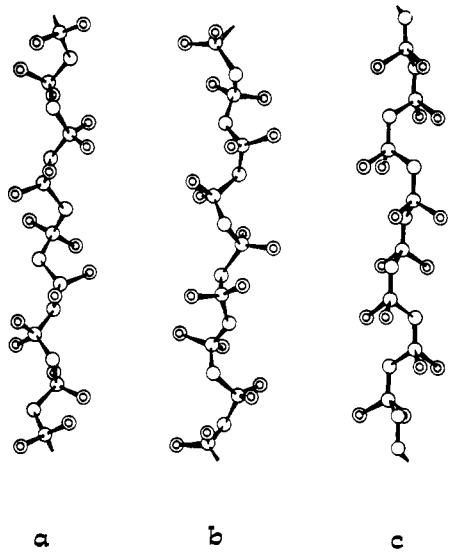

Figure 1. Helical conformation attributed to crystalline poly(isobutylene) by Liquori[2b] (a), Bunn and Holmes[3] (b), and Wasai, Saegusa, and Furukawa[5] (c).

(assuming the trans-planar conformation as 180° (Figure 1a)). Bunn and Holmes later modified this model by taking the $\angle C_2$–CH_2 and $\angle C_2$–$C(CH_3)_2$ bond angles equal to 126 and 107°, respectively, while assuming 77.5 and 129° for the skeletal internal rotation angles around the two bonds of each monomer unit (Figure 1b); adopting this conformation, still represented by a 8_5 helix, a good agreement was claimed by them among calculated and observed X-ray intensities.[3] Finally, Wasai, Saegusa, and Furukawa proposed a helix conformation with 8_3 symmetry, having all the skeletal bond angles equal to 120° and the two internal rotation angles of each monomer unit equal to 180 and 48° (Figure 1c). They concluded that this conformation is energetically more stable than that proposed by Liquori by approximately 50 kcal/monomer unit (mu.).[5]

As for the chain conformational statistics in the unperturbed state, some very approximate treatments have been proposed,[6-8] which give conflicting results for the characteristic ratio $\langle r^2\rangle_0/nl^2$: the experimental value at 24° of this parameter (6.6) has been derived from viscosity measurements in Θ solvents by Fox and Flory.[9]

For all the above, we have been stimulated to reexamine the whole conformational problem of poly(isobutylene) both in the crystalline state and in solution. We have tried to take account as fully as possible of bond angle flexibility, which plays an important role in overcrowded molecules, as it has been recently predicted by Flory,[10] and proved by one of us for syndiotactic poly(α-methylvinyl methyl ether).[11]

Both in the conformational calculations performed by De Santis, Giglio, Liquori, and Ripamonti[4] and in those reported by Wasai, *et al.*,[5] the bond angle flexibility was ignored. On the other hand, the inherent computational difficulties deriving from the existence

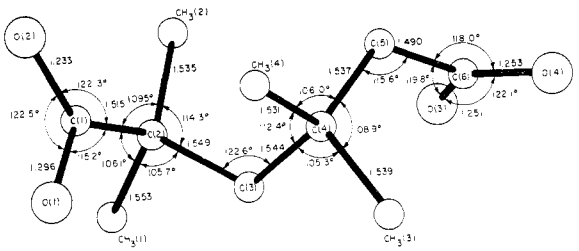

Figure 2. Molecular model of 2,2,4,4-tetramethyladipic acid.[14] Bond lengths (ångströms) and bond angles (degrees) are indicated except for C(1)–C(2)–C(3), C(3)–C(4)–C(5), CH_3(1)–C(2)–CH_3(2), and CH_3(3)–C(4)–CH_3(4), which are 111.8, 114.5, 109.0, and 109.6°, respectively. Average standard deviations are 0.005 Å and 0.2°. (Photograph reproduced from ref 14.)

of a large number of independent bond angles + internal rotation angles per monomer unit, coupled with the uncertainty in the choice of reliable parameters for the calculation of nonbonded interaction energies at short interatomic distances, tend to discourage a thorough investigation in this direction.

However, for several synthetic polymers the minimum energy chain conformations calculated with different sets of nonbonded interaction parameters have not shown big differences;[4,12] this consideration stimulated our confidence that a definite gain in structural knowledge would result from even partial allowance for bond angle deformations, in spite of the uncertainties involved. Furthermore, the X-ray intensity distribution on the fiber spectrum should provide an important check of the accuracy of our results.[11,13] Finally, from the recent X-ray analysis of crystalline 2,2,4,4-tetramethyladipic acid recently performed by us,[14] some interesting geometrical parameters were revealed (Figure 2), the most notable of which being the high value (122.6 ± 0.3°) of the $-C(CH_3)_2$–CH_2–$C(CH_3)_2$–bond angle. Since this molecule must certainly experience intramolecular repulsions similar to those existing in poly(isobutylene), we believe that the assumption of a similar value of this bond angle in the crystalline polymer may be reasonably accepted. We have therefore decided to carry out a conformational analysis of crystalline poly(isobutylene) where, in addition to the chain internal rotation angles, allowance was made for the bond angle flexibility in the main chain only, under the simplifying assumption of perfectly elastic deformations. The type of nonbonded interactions assumed and the value of the corresponding parameters have been chosen according to the following criteria: the minimum energy chain conformation should correspond to either a 8_5 or a 8_3 helix, with a monomer unit repeat of 2.33 Å;[2a] the calculated X-ray intensity distribution from an isolated chain should be in substantial agreement with the intensity observed on the X-ray fiber spectrum; the above conformation should be characterized by a C–CH_2–C bond angle close to 123°.

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As a corollary of the conformational energy calculations performed for the chain in the crystalline state, interesting information was available to us concerning the conformation of the free chain. Consequently, we have developed calculations of the mean-square end-to-end distance for the macromolecule in unperturbed solution: the statistical model, based on the rotational isomeric state approximation, is very simple, and the results are in agreement with the experimental data.

Conformational Calculations in the Crystalline State

The evidence given in favor of a helical conformation for crystalline poly(isobutylene) containing eight monomer residues per chain repeat is compelling.[2b] Accordingly, we will attribute identical internal geometrical parameters to all monomer units of the chain, in agreement with the equivalence postulate.[15]

Under this assumption, the internal coordinates (i.c.) of the macromolecule are 36, corresponding to the independent cartesian coordinates of the 12 atoms of the monomer unit. We will assume the constancy of bond lengths, which reduces the number of the i.c. to 24. Still the full conformational analysis of the problem would be prohibitively lengthy and complicated from a computational point of view; in addition, such a job probably would not be worth the effort, in view of the existing uncertainties in the choice of the parameters for the nonbonded interaction energies, as well as for the strain of bond angles.

We have confined our attention to the four internal coordinates indicated in Figure 3, which we consider to be the most relevant to the problem at hand, namely, two internal rotation angles on the chain skeleton (ψ_1 and ψ_2) and two chain bond angles (θ_1 and θ_2). We have considered the following expression of the intramolecular conformational energy per monomer unit under the assumption that $\psi = 0°$ for the cis conformation. In this expression U_0 is the intrinsic

$$U = {}^1/_2U_0(2 + \cos\psi_1 + \cos\psi_2) + {}^1/_2k[(\theta_1 - \theta_{10})^2 + (\theta_2 - \theta_{20})^2] + \sum_{i<j} U_{nb}(ij) \quad (1)$$

threefold potential for two tetrahedral carbon atoms which rotate around their connecting bond; k is the force constant for the ∠CCC bending, assuming a rigorously elastic deformation; θ_{10} and θ_{20} are the zero-strain values of θ_1 and θ_2, and $U_{nb}(ij)$ is the interaction energy between the nonbonded atoms i and j. In the last summation the index i runs over all the atoms of the monomer unit, while j should be extended to all the chain atoms following i. In practice, the longest range interactions accounted for in our calculations correspond to pairs of carbon atoms—and connected hydrogens—separated by six bonds. Bond and rotation angles not explicitly indicated in eq 1 have been defined as follows: (i) the bond angles around the methyl carbon atoms, as well as the ∠HCH angles on the methylene groups and the $\angle CH_3CCH_3$ angles, are fixed at the tetrahedral value (109.5°); (ii) both the methylene hydrogen and the methyl carbon atoms lie on the plane bisecting the C angle between chain bonds and are placed in symmetrical positions with respect to the plane containing these bonds; (iii) the rotation of the (C)–CH_3 groups with respect to the C—C bond is such that one hydrogen atom lies on the plane containing the CH_3—C—CH_3 bonds, in such a direction as to obtain a quasi-"staggered" conformation (the perfect "staggered" conformation is only possible when the ∠CCC bond angle on the chain equals the tetrahedral value). The assumptions connected with the rigidity of the methyl groups have lead us to propose an alternative treatment, based on a postulated spherical symmetry, as we shall see in the following. All C—C and C—H bond lengths have been assumed 1.54 and 1.10 Å, respectively.

In equation 1 the U_0 barrier has been assumed 3.0 kcal/mu., as it has been found in ethane.[16] The k elastic constant, assumed equal for both the chain ∠CCC bond angles of each monomer unit, has been given the value 0.95 dyn Å/rad² = 136 kcal/mol rad², *i.e.*, close to the values found from ir data for the corresponding diagonal elements of a simplified valence force field matrix, obtained by overlay calculation for linear and branched paraffins.[17] This figure should be probably increased in order to take account of the simultaneous strain of other bond angles, during the deformation of the ∠CCC angle. We have neglected such consideration on the basis that under relatively high angle strain, such as is found in the present polymer, the transferability of such a force constant represents an approximation anyway. θ_{10} and θ_{20} have been taken equal to 110° (*i.e.*, close to the tetrahedral value as in neopentane) and 112° (as on the average in linear hydrocarbons), respectively.

The calculation of the nonbonded interaction energies, represented by the double summation in eq 1, has been carried out in two distinct ways. First, all the H···H, H···C, and C···C interactions have been evaluated adopting 6–12 Lennard-Jones potential functions, whose parameters are reported in Table I.[18] It must be pointed out that the assumed internal rigidity of the methyl groups and their fixed rotational orientation with respect to the main chain must necessarily lead to exaggerate values of the strain energy, in such a crowded

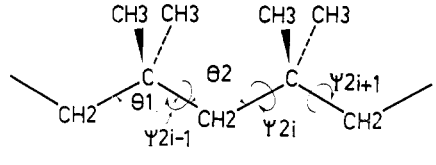

Figure 3. Schematic representation of the poly(isobutylene) chain in the zigzag planar conformation. In the crystalline state it has been assumed $\psi_{2i-1} = \psi_{2i+1} = \cdots = \psi_1$; $\psi_{2i} = \psi_{2i+2} = \cdots = \psi_2$, so that only four internal coordinates per monomer unit have been considered.

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TABLE I
LENNARD-JONES PARAMETERS FOR THE NONBONDED INTERACTIONS ($U_{ab} = A_{ab}/r_{ab}^{12} - B_{ab}/r_{ab}^{6}$)[a]

		A_{ab}	B_{ab}
C···C		2.94×10^5	381
C···H		3.97×10^4	134
H···H		4.71×10^3	49
$CH_3 \cdots CH_3$	Case B[b]	5.64×10^6	2750
	Case C[c]	3.00×10^6	2750
	Case D[d]	2.13×10^6	2750

[a] r_{ab} is expressed in ångströms; U_{ab} is expressed in kcal/mu. [b] van der Waals' radius of CH_3, 2.0 Å. [c] van der Waals radius of CH_3, 1.8 Å. [d] van der Waals' radius of CH_3, 1.7 Å.

system as the one under examination. Consequently a second type of calculation has been performed assuming the methyl group as a spherically symmetrical body, and still adopting potentials of the Lennard-Jones type. The B_{ab} parameters involving the methyl group (see Table I) have been expressed according to the Slater–Kirkwood approximation[19,20] where α_a and α_b

$$B_{ab} = \frac{3\alpha_a\alpha_b eh}{4\pi[(\alpha_a/N_a)^{1/2} + (\alpha_b/N_b)^{1/2}]m_e^{1/2}} \quad (2)$$

are the polarizabilities of the a and b atoms or groups, N_a and N_b are their equivalent outer shell electron numbers, e and m_e are the electron charge and mass, respectively, and h is the Planck constant. N_{CH_3} has been equated to 22, *i.e.*, slightly less than N_{CH_4} = 24,[21] because of the smaller number of electrons contained in the methyl radical than in the methane molecule.[22] The A_{ab} parameters have been derived by imposing $\partial U/\partial r = 0$ at the van der Waals' distance between a and b, expressed as the sum of their van der Waals' radii. The van der Waals' radius of $-CH_3$ (r_{CH_3}) has been treated as an adjustable parameter, as we shall see. The resulting value of all the Lennard-Jones parameters involving the methyl group when its van der Waals' radius is equal to 2.0, 1.8, and 1.7 Å are reported in Table I. The nonbonded interactions between atoms and/or groups separated by only two bonds were neglected, being included in the corresponding bond angle deformations.

The calculation of the conformational energy (equation 1) was carried out by changing ψ_1 and ψ_2 by increments of 20° each, and for each combination changing θ_1 and θ_2 by increments of 2° until the minimum energy value E was found. Since we are interested in finding conformations of minimum energy, only the minimal values of θ_1, θ_2, and E were considered, as functions of ψ_1 and ψ_2. Figure 4 shows the maps of E (Figure 4a) and θ_2 (Figure 4b) represented with level contours *vs.* ψ_1 and ψ_2. No map is reported for θ_1 since its variations from θ_{10} never exceed 2–4° and apparently they do not have a significant effect on the resulting energy.

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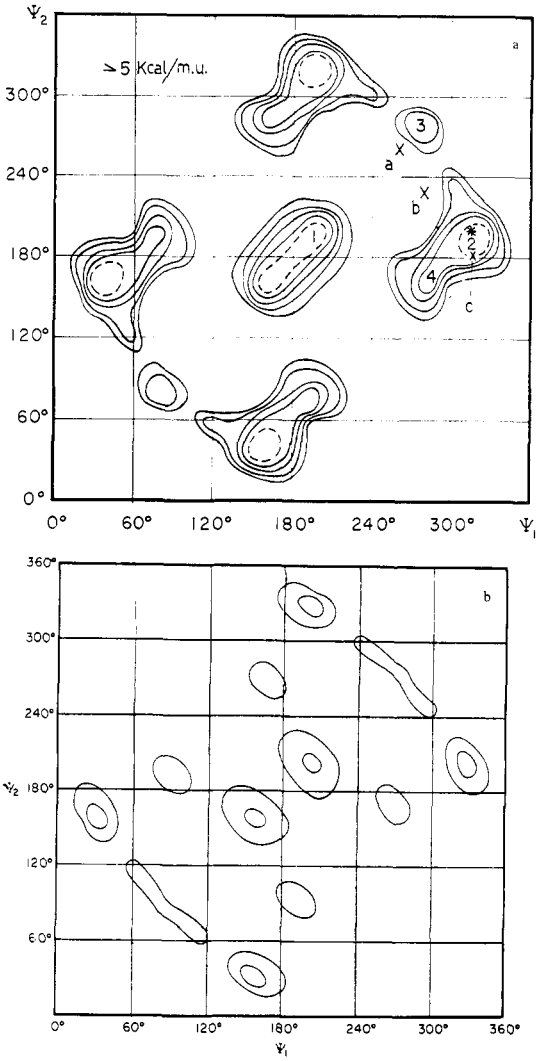

Figure 4. (a) Plot of the conformational potential energy *vs.* ψ_1 and ψ_2, minimized with respect to θ_1 and θ_2 (see Figure 3). Energy levels are drawn at 1 (dashed line), 2, 3, ··· 5 kcal/mu. 1, 2, 3, and 4 correspond to different energy minima, a, b, and c to different models already proposed; the star corresponds to the best conformation (see text). (b) Plot of θ_2, corresponding to minimal energy values, *vs.* ψ_1 and ψ_2. Contours are drawn at θ_2 = 124° (innermost level), 126°···. The two maps have been calculated according to the D set of the parameters for nonbonded inteactions (see Table I).

Results of Conformational Calculations

Referring to Table I and to Figure 3, four different conformational calculations were carried out. First (*case A*) we considered all atom-to-atom nonbonded interactions H···H, H···C, C···C, then we assumed the methyl group as a spherical body, taking r_{CH_3} = 2.0, 1.8, and 1.7 Å (*cases B, C, and D, respectively*).

In each of the four cases the energy map *vs.* ψ_1 and ψ_2 shows four distinct minima, whose positions do not vary appreciably; they are indicated as 1, 2, 3, and 4 in Figure 4a. The energy differences are reported in Table II, which also shows the corresponding values obtained under the assumption of fixed bond angles ($\theta_1 = \theta_{10} = 110°$; $\theta_2 = \theta_{20} = 112°$). The smoothening effect of the bond angle flexibility on the conformational energy is well apparent: the energy differences reported

TABLE II
ENERGY DIFFERENCES[a] AMONG THE FOUR MINIMA (1–4, SEE FIGURE 4a) OF THE CONFORMATIONAL ENERGY OF THE POLY(ISOBUTYLENE) CHAIN

	Case A (all H atoms considered)		Case B r_{methyl} = 2.0 Å		Case C r_{methyl} = 1.8 Å		Case D r_{methyl} = 1.7 Å	
	θ_{var}	θ_{fixed}	θ_{var}	θ_{fixed}	θ_{var}	θ_{fixed}	θ_{var}	θ_{fixed}
$E(2) - E(1)$	0.3	226	0.1	21	0.1	12	0.3	8
$E(3) - E(1)$	1.1	26	2.8	58	2.9	41	3.1	33
$E(4) - E(1)$	0.9	14	2.3	38	1.9	23	1.7	17

[a] In kcal/mu. Four different schemes for calculation of the nonbonded interactions have been considered (see text).

never exceed 4 kcal/mu., while the figures show an increase by two orders of magnitude if the bond angles are assumed as rigid and equal to their zero-strain values (of course, such an increase would be reduced if a higher value were arbitrarily assigned to θ_{20}). Furthermore, in the assumption of rigid bond angles, the energy differences exhibit a much stronger dependence from the nonbonded interaction parameters utilized. The same kind of smoothening effect due to the bond angle flexibility is also observable on the energy barriers between the four different minima; the corresponding values do not change very much within the four different cases from A to D, and they are always lower than 10 kcal/mu. Quite the opposite is observed if the bond angle flexibility is ignored.

In all cases the θ_2 bond angle shows large increases above the unstrained value of 112°. The largest values are obtained for case A (*i.e.*, all hydrogen atoms considered) where θ_2 is never lower than 134°. Only in case D, the minimum values of θ_2 (=124°) are close to the values observed in the model compound 2,2,4,4-tetramethyladipic acid 122.6° (see Figure 2). Accordingly, we have concluded that the best-fitting van der Waals' radius of the methyl group is 1.7 Å, *if the 6–12 interaction potential is adopted, with the parameters proposed for expression 2.* The two maps reported in Figure 4 are based on this value (*case D*). It is interesting that the figure which reproduces the experimental data of the energy difference between the gauche and trans conformations of *n*-butane (0.8 kcal/mu.) is close to the above (1.75 Å[23]). From Figure 4b it can be seen that the minima of θ_2 coincide with the minima of the conformational energy, as it should be expected (*cf.* Figure 4a).

In spite of the different choices of the chain bond angles, we have compared with our results the models proposed by Liquori (see Figure 1a[2b]), Bunn and Holmes (see Figure 1b[3]), and Wasai, Saegusa, and Furukawa (see Figure 1c[5]); the corresponding (ψ_1, ψ_2) values are indicated in Figure 4a with the points labeled as a, b, and c respectively. Assuming for the three models the θ_2 values given in Figure 4b and θ_1 = 110°, the conformational energy of a and b is about 8 and 10 kcal/mu. higher than the minimum of the plot, respectively, and values not very different are obtained for the other choices of the nonbonded energy parameters (cases A, B, and C). It is also evident that model c is very close to minimum 2, and therefore it represents the most satisfactory chain conformation by far. Its conformational energy is only 1 kcal/mu. higher than the minimum, and it can be further reduced with a small shift of both ψ_1 and ψ_2 to the point labeled with a star in Figure 4a; both the helix symmetry (8_3) and the chain repeat per monomer unit remain unchanged. The resulting chain model is reported in Figure 5; the internal angular coordinates are θ_1 = 110°, θ_2 = 124°, ψ_1 = 203.3°, ψ_2 = −47.5°. The similarity with the model reported in Figure 1c is evident.

We have reported in a previous paper[14] that, had we to transfer to poly(isobutylene) the geometrical parameters obtained for the model compound 2,2,4,4-tetramethyladipic acid (see Figure 2), the polymer conformation would correspond to a 2_1 helix with $\psi_1 \simeq \psi_2 \simeq 67°$, and a chain repeat per monomer unit equal to 2.06 Å. In Figure 4a a relative energy minimum (no. 3) is observed at $\psi_1 = \psi_2 \simeq 80°$, *i.e.*, close to the conformation found for the acid; however, its energy is 3.2 kcal/mu. higher than that of the absolute minimum. The apparent inconsistency is explained with the consideration that interactions between methyl group six bonds apart—*i.e.*, belonging to second neighboring units—are responsible for the energy content of this conformation; interactions of this type cannot exist in tetramethyladipic acid, due to the shortness of the molecule. Conformational calculations performed by us by artifically excluding the above contributions have shown that the resulting absolute energy minimum is centered at $\psi_1 = \psi_2 \simeq 65°$, in excellent agreement with the conformation found for crystalline tetramethyladipic acid.

Calculation of the Diffracted Intensity from the Isolated Chain. Comparison with the X-Ray Fiber Intensities

The cylindrical coordinates of the four nonhydrogen atoms of the monomer unit, corresponding to the model represented in Figure 5, are given in Table III. The X-ray intensity scattered by the isolated helix, according to a result first obtained by Cochran,

TABLE III
CYLINDRICAL COORDINATES OF THE NONHYDROGEN ATOMS OF THE MONOMER UNIT[a]

	r, Å	z, Å	φ, deg
C(1)	0.838	0.0	0.0
C(2)	0.600	1.517	7.8
C(3)	1.915	−0.376	−49.8
C(4)	2.175	−0.409	25.6

[a] *Cf.* Figure 5 for symbols and conventions.

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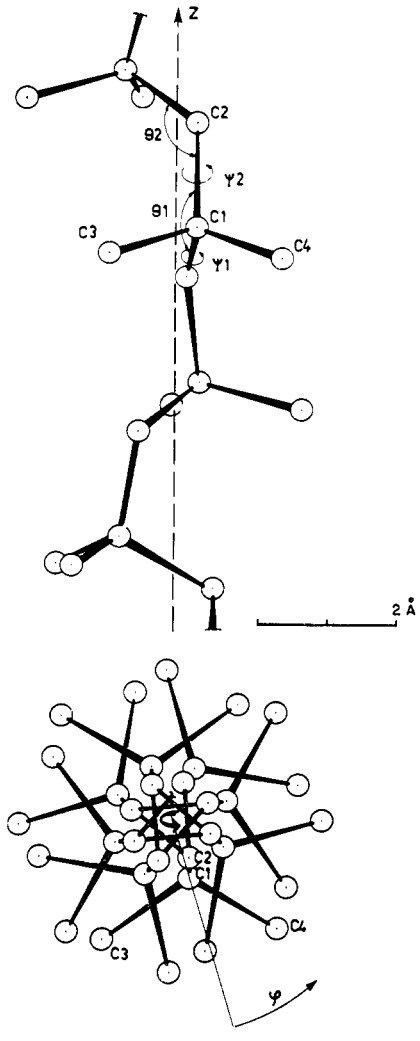

Figure 5. Best conformational model, corresponding to the star reported in Figure 4a, in agreement with both energy and X-ray data. Symbols are consistent with Figure 3 and Table III. Hydrogen atoms are omitted.

Crick, and Vand,[24] subsequently elaborated by Corradini and Pasquon[25] is

$$I(R,l) = \sum_n \left[\sum_i f_i J_n(2\pi R r_i) \cos\left(2\pi \frac{l z_i}{c} - n\varphi_i\right)\right]^2 + \sum_n \left[\sum_i f_i J_n(2\pi R r_i) \sin\left(2\pi \frac{l z_i}{c} - n\varphi_i\right)\right]^2 \quad (3)$$

where l is the index of the reciprocal layer, c is the chain repeat, r_i, z_i, φ_i, and f_i are the (three) cylindrical coordinates and the scattering form factor of the ith atom, respectively, R is the radial reciprocal coordinate (Å^{-1}) and J_n is the Bessel function of integer order n. Possible values of n for the lth layer of a helix containing N monomer units in M turns are given by the relationship

$$l = Mn + Nm \quad (4)$$

where m is any integer, positive or negative, including zero. Table IV reports the lowest values of the Bessel

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TABLE IV
VALUES OF THE LOWEST INDICES OF THE BESSEL FUNCTIONS ALLOWED ON THE RECIPROCAL LAYERS WITH $0 \leqslant l \leqslant 8$ FOR AN 8_3 HELIX[a]

l	n_1	n_2
0	0	±8
1	3	−5
2	−2	6
3	1	−7
4	4	−4
5	−1	7
6	2	−6
7	−3	5
8	0	±8

[a] *Cf.* eq 3 and 4

indices allowed on each layer; for $R \leqslant 0.5$ Å^{-1} Bessel functions with higher indices do not give any appreciable contribution. The calculated intensity (eq 3) for each layer is reported in Figure 6 as a continuous function of the equatorial coordinate; the observed intensities are also reported, in an arbitrary scale. The overall com-

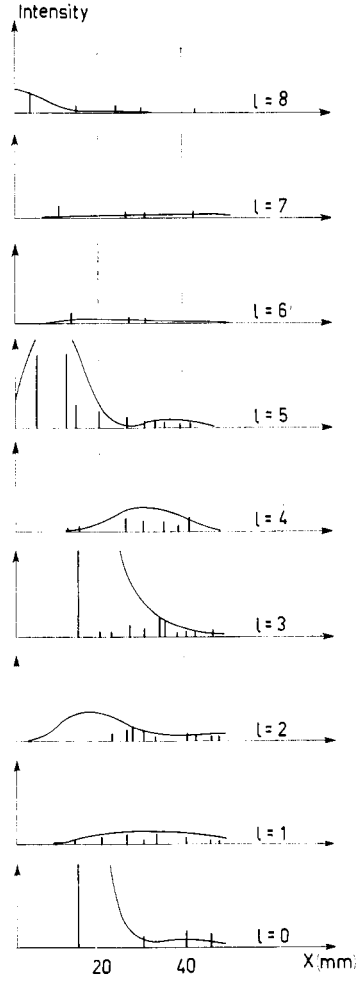

Figure 6. Comparison between observed (vertical segments) and calculated (continuous curves) X-ray intensities: the latter have been corrected for the Lorentz polarization factor. An isotropic thermal factor $B = 8$ Å^2 was applied to all carbon atoms. The x coordinate (millimeters) corresponds to the distance from the meridional line in a fiber spectrum taken with a cylindrical camera with $d = 57.3$ mm. Intensities are given in arbitrary units.

parison between calculated and observed data, from a statistical viewpoint, is quite satisfactory.

The Unperturbed Mean-Square End-to-End Distance. Calculations and Comparison with Experimental Results

The calculations reported above, although strictly applicable to the crystalline state only, indicate that several conformations of comparable energy are accessible to each monomer unit. Since part of the information contained therein may also be applied to the free polymer chain, we have been stimulated to undertake an analysis of the chain statistics in unperturbed solution, with the specific purpose of evaluating the unperturbed mean-square end-to-end distance at different temperatures.

Let us first examine the conformations of chain segments defined by two neighboring rotation angles. Referring to Figure 3, it is apparent that two nonequivalent pairs are to be considered, *i.e.*, (ψ_{2i-1}, ψ_{2i}) and (ψ_{2i}, ψ_{2i+1}). As long as the bond coordination of methyl-substituted carbon atoms is assumed to be perfectly tetrahedral, the first pair defines a chain segment which can be approximated by the 2,2,4,4-tetramethylpentane molecule: the only assumption concerns two methylenes, which are treated as methyl groups. With the same procedure as well as the same parameters used for the calculations reported in Figure 4 we obtained the conformational energy plot of 2,2,4,4-tetramethylpentane (Figure 7). The two internal rotation angles defining the carbon skeleton have been labeled with symbols consistent with Figure 3. A series of equivalent energy minima, markedly elongated in the direction of the main diagonal, are centered at ψ angles equal to $60° + k(120°)$ (k integer); the corresponding value of the CCH_2C angle is 122°. A similar systematic elongation of the minima may be recognized in the plot reported in Figure 4a. Within the rotational isomeric state scheme each broad minimum could be best approximated by two pointlike minima symmetrically shifted by ±10–20° from the center. However, this picture would lead to serious computational complications, insofar as it would involve taking into account correlation among three or four consecutive rotation angles. For the same reason, the technique of expanding the statistical weight into a double Fourier series, recently introduced by one of us,[26] proves too complicated in the present case. A simpler picture is obtained if each energy minimum is approximated by its central point: both ψ_{2i-1} and ψ_{2i} are then confined to the "staggered" values, and any rotational pair has the same statistical weight. In other words, ψ_{2i-1} and ψ_{2i} are statistically independent. Although Figure 7 suggests that small deviations from the staggered conformations should not be treated as independent, we believe this picture to be sufficiently representative of the average conformational properties of the macromolecule.

Let us consider now the (ψ_{2i}, ψ_{2i+1}) pair (see Figure 3); we will use the symbols T, G, and G′ for ψ = 180, 60, and 300°, respectively. The conformational energies associated with the TT, GT, TG... sequences may be approximately derived from the plot of Figure 4a.

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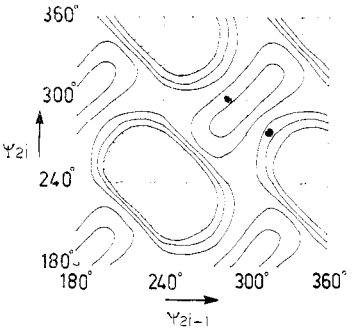

Figure 7. Conformational energy of 2,2,4,4-tetramethylpentane *vs.* the two internal rotation angles defining a sequence of five carbon atoms (see Figure 3). Owing to the threefold symmetry around each rotation angle, $E(\psi_{2i-1}, \psi_{2i}) = E(\psi_{2i-1} + 120°, \psi_{2i}) = E(\psi_{2i-1}, \psi_{2i} + 120°)$, and therefore only one quadrant of the whole plot is shown. Parameters for the calculation are given in the text and in Table I. Levels are drawn at 1, 2, ...5 kcal/mu.: cross-hatched areas correspond to $E > 5$ kcal/mu.

This statement is justified by the consideration that all the ψ angles corresponding to the minima 1–4 do not deviate from the staggered values by more than 20°; however, it has only approximate validity because the plot of Figure 4a has been obtained under the (now) unnecessary restriction that the ψ's sequence is regular (*i.e.*, ... $\psi_1, \psi_2, \psi_1, \psi_2$ ...). In particular, inspection of molecular models shows that the release of the above restriction substantially reduces the dissymmetry of the energy minima close to G′T and to G′G′—or equivalent sequences—with respect to the points with coordinates (300°, 180°) and (300°, 300°). Our assumption that the staggered conformations are sufficient for the chain statistical description seems therefore justified. It may be seen in Figure 4a that the lowest energy of the TT and G′T—or the equivalent GT, TG′, and TG—sequences is about the same: in fact, TT corresponds to minimum 1 as well as to the minimum related to 1 by a center of symmetry, G′T corresponds to the pair of minima 2 and 4. Since TT is represented by two minima with equal (zero) energy, while one of the two minima corresponding to G′T (or any other equivalent sequence) is about 1.5 kcal/mu. higher, we have attributed different statistical weights to TT and to G′T, *i.e.*, 2 and $\eta = 1 + \exp(-E_1/RT)$, respectively, where E_1 will be taken in the range 1–2 kcal/mu. The lowest energy of the G′G′ and GG sequences (E) should be about 3 kcal/mu. higher than zero: it corresponds in fact to the energy of minimum 3 (see also Table II), and will be taken in the range 2–4 kcal/mu. The energy of the GG′ and G′G sequences is very high, and therefore these conformations are forbidden: the validity of this conclusion may be checked by direct inspection of the model.

We are able now to summarize our conclusions concerning the statistical correlation between first neighboring chain rotations. Confining our attention to the T, G, and G′ isomeric states, no apparent correlation is observable between ψ_{2i-1} and ψ_{2i} (see Figure 7); in other words, all the elements of the corresponding 3 × 3 matrix of the statistical weights (correlation matrix) are equal to 1. As for the coupling between ψ_{2i} and ψ_{2i+1}, the correlation matrix has the form

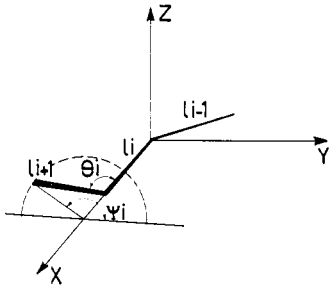

Figure 8. The intrinsic reference frame of one chain bond, consistent with the rotation matrix $\mathbf{T}(\psi_i, \theta_i)$ given in eq 9 of the text.

$$\mathbf{U} = \begin{array}{c|ccc} & \mathrm{T} & \mathrm{G} & \mathrm{G}' \\ \mathrm{T} & 2 & \eta & \eta \\ \mathrm{G} & \eta & \epsilon & 0 \\ \mathrm{G}' & \eta & 0 & \epsilon \end{array} \tag{5}$$

$$\epsilon = \exp\left(-\frac{E}{RT}\right) \qquad E = 2\text{–}4 \text{ kcal/mu.}$$

$$\eta = 1 + \exp\left(\frac{E_1}{RT}\right) \qquad E_1 = 1\text{–}2 \text{ kcal/mu.}$$

It should be stressed that, except for the approximation of neglecting deviations of ± 10–$20°$ from the staggered rotations, the above conclusions take account of the nonbonded interactions between atoms or groups separated by as many as six bonds.

The expression of the mean-square end-to-end distance may be expressed in the form[6]

$$\langle r^2\rangle_0 \simeq 2Nl^2\left\{1 + (1\ 0\ 0)[\langle \mathbf{T}_e\rangle + \langle \mathbf{T}_e\mathbf{T}_c\rangle + \langle \mathbf{T}_e\mathbf{T}_o\mathbf{T}_e\rangle + \langle \mathbf{T}_e\mathbf{T}_c\mathbf{T}_e\mathbf{T}_o\rangle + \ldots + \langle \mathbf{T}_o\rangle + \langle \mathbf{T}_o\mathbf{T}_e\rangle + \langle \mathbf{T}_o\mathbf{T}_e\mathbf{T}_o\rangle + \langle \mathbf{T}_o\mathbf{T}_e\mathbf{T}_o\mathbf{T}_e\rangle + \ldots]\begin{vmatrix}1\\0\\0\end{vmatrix}\right\} \tag{6}$$

where N ($\rightarrow\infty$) is the number of monomer units per chain, l (= 1.54 Å) is the C—C bond length, and the terms in brackets stand for averages of products of matrices which account for the rotations around even bonds, like $2i$ in Figure 3 ($\mathbf{T}_e$), and odd bonds, like $2i + 1$ ($\mathbf{T}_o$). More precisely, these matrices represent the rotation of the internal coordinate system associated with a given bond into that of the following bond. The orientation of the internal system of the general bond is illustrated in Figure 8. From what precedes, we know that the rotation around any odd bond, like ψ_{2i-1} in Figure 3, is uncorrelated with the next rotation (ψ_{2i}): this means that each of the averages in equation 6 can be split into a product of smaller averages. As an example

$$\langle \mathbf{T}_o\mathbf{T}_e\mathbf{T}_o\mathbf{T}_e\rangle = \langle \mathbf{T}_o\rangle\langle \mathbf{T}_e\mathbf{T}_o\rangle\langle \mathbf{T}_e\rangle \tag{7}$$

and consequently eq 6 easily reduces to

$$\langle r^2\rangle_0 = 2Nl^2(1\ 0\ 0)(\mathbf{E} + \langle \mathbf{T}_o\rangle)(\mathbf{E} + \langle \mathbf{T}_e\mathbf{T}_o\rangle + \langle \mathbf{T}_e\mathbf{T}_o\rangle^2 + \langle \mathbf{T}_e\mathbf{T}_o\rangle^3 + \ldots) \tag{8}$$

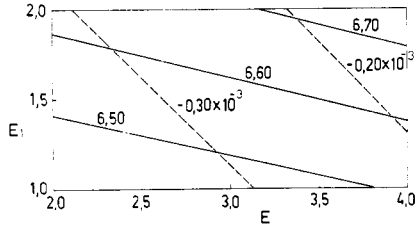

Figure 9. Values of $\langle r^2\rangle_0/2Nl^2$ at 24° (continuous lines) and of d ln $\langle r^2\rangle_0/dT$ (average in the range 0–90°, broken lines) plotted against E and E_1 (kcal/mu.; see text).

$$(\mathbf{E} + \langle \mathbf{T}_e\rangle)\begin{vmatrix}1\\0\\0\end{vmatrix} =$$

$$2Nl^2(1\ 0\ 0)(\mathbf{E} + \langle \mathbf{T}_o\rangle)(\mathbf{E} - \langle \mathbf{T}_e\mathbf{T}_o\rangle)^{-1}(\mathbf{E} + \langle \mathbf{T}_e\rangle)\begin{vmatrix}1\\0\\0\end{vmatrix}$$

The rotation matrix $\mathbf{T}$ for the kth bond is a function of $\psi = \psi_k$ as well as $\theta = \theta_{k,k+1}$ (the bond angle between k and $k + 1$)

$$\mathbf{T}(\psi, \theta) = \begin{vmatrix} -\cos\theta & -\sin\theta & 0 \\ \cos\psi\sin\theta & -\cos\psi\cos\theta & -\sin\psi \\ \sin\psi\sin\theta & -\sin\psi\cos\theta & \cos\psi \end{vmatrix} \tag{9}$$

The bond angles associated to even and odd bonds are assumed to be equal to the tetrahedral value ($\theta_1 = 109.5°$) and to the minimum CCH_2C angle reported in Figure 4b ($\theta_2 = 124°$), respectively. The matrix averages of eq 8 are best evaluated with the introduction of the following matrices (*cf.* equation 5 for the definition of $\mathbf{U}$)

$$\mathbf{R} = (1\ 1\ 1) \times \mathbf{E}_3;\ \zeta_1 = [\mathbf{T}(180°, \theta_1), \mathbf{T}(60°, \theta_1), \mathbf{T}(300°, \theta_1)]$$
$$\zeta_2 = \begin{vmatrix}\mathbf{T}(180°, \theta_2)\\ \mathbf{T}(60°, \theta_2)\\ \mathbf{T}(300°, \theta_2)\end{vmatrix} \qquad \mathbf{U}_3 = \mathbf{U} \times \mathbf{E}_3 \tag{10}$$

where $\mathbf{E}_3$ is the unit matrix of order 3 and $\times$ is the symbol of the direct product. Furthermore, let us define

$$\lambda = \sum_{i,j=1}^{3}\sum U_{ij} = 2 + 2\epsilon + 4\eta \tag{11}$$

It is easy to show that the conformational partition function of the macromolecule is given by $Z = \lambda^N$. The three matrix averages appearing in (8) may now be expressed as

$$\begin{aligned}\langle \mathbf{T}_o\rangle &= \mathbf{R}\mathbf{U}_3\zeta_2/\lambda \\ \langle \mathbf{T}_e\rangle &= \zeta_1\mathbf{U}_3\mathbf{R}/\lambda \\ \langle \mathbf{T}_e\mathbf{T}_o\rangle &= \zeta_1\mathbf{U}_3\zeta_2/\lambda\end{aligned} \tag{12}$$

The characteristic ratio $\langle r^2\rangle_0/2Nl^2$, calculated according to eq 8 at $T = 24°$, is reported in Figure 9 as a function of E and E_1, taken in the range indicated in equation 5. The resulting values are in the range 6.4–6.75, while the experimental figure, from viscosity measurements in Θ solvents, is 6.6.[9] The agreement is good in the whole range, so that the results of our conformational calcu-

lations seem to be fully justified. The average temperature coefficient d ln $\langle r^2\rangle_0/dT$, in the range 0–90°, is also reported in Figure 9: it is always negative and rather small, being in the range from -0.1 to -0.4×10^{-3}. It compares very well with viscosimetric measurements (-0.28×10^{-3} from 30 to 130°),[27] and also with stress–temperature results on rubberlike samples (from -0.08 to -0.27×10^{-3} in the range 18–95°).[28]

Conclusions

We wish to stress particularly a conclusion arising from the present study, concerning the effect of the bond angle flexibility on the potential energy in a crowded molecule (see Table II).

Not only is the conformational energy function strongly flattened by that effect, but energy differences among various conformations are much less dependent on the choice of the nonbonded interaction parameters. Since uncertainty in these parameters is a major factor of error in the conformational results, we can reasonably hope that more reliable conclusions will be reached in the conformational analysis of a crowded molecule if the bond angle deformation will be taken into account explicitly.

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Acknowledgment. The authors are indebted to Professor M. Goodman of the Polytechnic Institute of Brooklyn for useful discussions.

Physical Properties of Poly(β-hydroxy butyrate). II. Conformational Aspects in Solution

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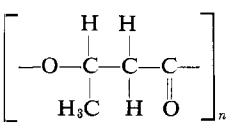
Received April 8, 1970

ABSTRACT: A series of samples of poly(β-hydroxy butyrate) covering a wide range of molecular weights has been studied by means of intrinsic viscosity, sedimentation analysis, and optical rotatory dispersion. The hydrodynamic properties alone suggest a coillike behavior in chloroform, ethylene dichloride, and trifluoroethanol. However, evidence supporting a sharp helix–coil transition has led to a model involving folded helical segments which allows rigid rod behavior but is reconcilable with the hydrodynamic data. A new proof of structure for this natural polyester is provided by the linear Freudenberg plot for molar rotation per residue as a function of degree of polymerization.

This optically active natural polyester poly(β-hydroxy butyrate) (PHB) was discovered by a microbiologist[1] and its structure was shown to be



It occurs as crystalline hydrophobic granules about 0.5 μ in diameter and can be isolated from the cytoplasm of bacteria in a state which still has *in vitro* biological activity.[2] It has clearly been shown to be a carbon reserve[3] and it would seem therefore to occupy, in the bacterial world, a role similar to that of starch in the plant world.

The true study of the solution and molecular properties of this lipidlike polyester started in the early 1950's with papers correlating intrinsic viscosity of PHB and methods of isolation[4] as well as actual molecular weight measurements.[5] In the 1960's, a rapid assay method was developed,[6] the weak negative optical activity of the polymer at 589 mμ was reported,[7] and the biologically active dimer was synthesized.[8] Finally, previous papers of this series[9,10] reported for the first time on the X-ray crystallographic properties.

The present paper aims at a further development of our understanding of the solution properties of PHB by modern methods. In view of the biological origin of this polyester, which crystallizes as a right-handed 2_1 helix,[10] the possibility of retaining the helical conformation in solution was always in mind and several experiments were aimed specifically at examining this possibility.

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