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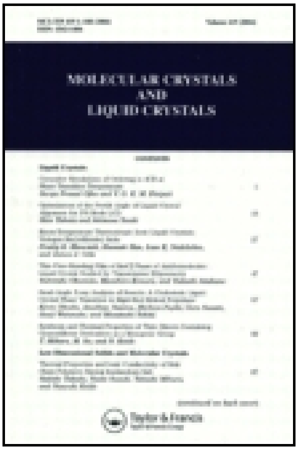

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Anisotropic Dispersion Interactions In Liquid Crystals

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The polarizability and shape anisotropies of a new class of aliphatic liquid crystals, 4,4′-di-*n*-alkyl-bibicyclo[2.2.2]octanes (*n*,*n*-BBCO) have been calculated as a function of the alkyl chain length and its degree of flexibility to inquire about the relative importance of *attractive* and *repulsive* interactions in stabilizing the liquid crystalline phase. The calculated polarizability anisotropies are found to be much smaller than that of conventional mesogens. In the context of the Maier-Saupe theory, this indicates that anisotropic dispersion interactions make only a minor contribution to the stability of this class of liquid crystals. The cylindrical symmetry exhibited by the *n*,*n*-BBCO homologues and their rigid molecular structure suggest that they might be ideally suited for critical testing of existing theories of the nematic-isotropic phase transition.

INTRODUCTION

Liquid crystals provide a unique entrée to the problem of anisotropic intermolecular interactions in condensed fluid phases. Thermodynamics properties of thermotropic liquid crystals exhibit an ill-defined hypersensitivity to ordinarily innocuous chemical substitutions on the mesogen's molecular framework and empirical correlations of these properties with chemical structure are suggestive of a critical balance between *attractive* and *repulsive* intermolecular interactions. Originally, these two interactions were considered separately in general theoretical approaches to modeling the nematic-isotropic phase transition: (1) The mean field model of Maier and Saupe[1] focusses on attractive dispersion interactions parameterized via the magnitude of the anisotropy of the molecular polarizability relative to the average

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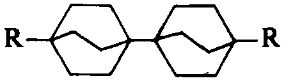
polarizability ($\Delta\alpha/\bar{\alpha}$); (2) The athermal virial expansion by Onsager[2] and Flory's lattice model[3] focus on anisotropic repulsive interactions where the shape anisotropy of the nematogen in terms of its axial ratio is the dominant parameter. These models have been refined and extended since their introduction, and "hybrid" models combining both attractive and repulsive features are currently being considered.[4,5]

In general, however, a critical comparison of existing theories with experimental observations faces a difficulty stemming from the complex structural details of real mesogenic molecules. In most of these models the nematogen is assumed to have prolate, cylindrical symmetry. Moreover in models where this restriction is removed there remain difficulties. For example, in the generalized van der Waals (GVDW) model,[4] a theory including both attractive and repulsive interactions, parameters describing the nematic-isotropic transition are strongly influenced by the shape *biaxiality* of the nematogen "particle"—a quantity that eludes precise definition for complex flexible mesogens. Furthermore conventional mesogens almost always include a number of polarizable units separated spatially in the molecule. Hence, the use of a single point dipole description for the computation of attractive intermolecular interactions is questionable. In short, current models do not permit the inclusion of molecular structural details of the complexity exhibited by conventional mesogens and consequently, the procedure for evaluating theory is severely hampered.

Ideally, spherocylindrically shaped molecules with minimal variation in the polarizability distribution are essential to more critical evaluation of models like the GVDW model and other "hybrid" models in which there is explicit consideration of the relative importance of anisotropic attractive and anisotropic repulsive intermolecular interactions. A new, structurally simple class of totally aliphatic mesogens, 4,4′-di-*n*-alkyl-bibicyclo[2.2.2]octanes (*n*,*n*-BBCO),



R : alkyl

has been recently synthesized.[6] As a step toward demonstrating the plausibility of using the *n*,*n*-BBCO system to test models of the nematic-isotropic transition, we have computed the molecular polarizability and the axial ratio as a function of the length and flexibility of the terminal alkyl chain substituents in the rotational isomeric state (RIS) limit.[7] As anticipated, the calculated values for the ratio $\Delta\alpha/\bar{\alpha}$ are quite small and suggest that the anisotropic dispersion forces are not significant in this class of liquid crystals. A hypothetical mesogen structure based on oligomers of the *n,n*-BBCO core is proposed as an ideal candidate for assessing the relative importance of polarizability and shape anisotropies for stabilizing the liquid crystalline phase.

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RESULTS AND DISCUSSION

The structural parameters employed in the calculation of the polarizability for *n,n*-BBCO homologues are given in Table I. The bicyclo[2.2.2]octane system in *n,n*-BBCO homologues is idealized to possess D_{3h} symmetry with tetrahedral C—C—C bond angles in agreement with the results of diffraction studies.[8,9] Two such bicyclooctane rings are juxtaposed coaxially resulting in a linear BBCO core unit. The C^0—C^1 bond of the pendant alkyl chain (C^0 at a junction with the core) is placed along the para axis of BBCO, hence, the dihedral angle around the C^0—C^1 bond would have three RIS at 120° intervals in which non-bonded interactions between C^2 and core are minimized. The *n,n*-BBCO molecule as a whole consequently exhibits cylindrical symmetry. By placing one of the axes of the molecular-fixed frame (*Z*-axis) along the axis of symmetry, the molecular polarizability tensor will be diagonalized. The calculations were in practice conducted for one-half of the *n,n*-BBCO molecule. This simplification merely assumes that configurational averaging of the two end alkyl chains (separated by the BBCO core) is mutually independent. The tensor obtained for an end alkyl chain was then doubled and added to that for the central BBCO core in the common *XYZ* molecular frame, yielding the final molecular tensor. The details of the computation are given in the appendix.

TABLE I

Structural data for *n,n*-BBCO homologues

Bond	Length (Å)
C—C	1.53
C—H	1.10
Bonds	**Angle (°)**
C—C—C (core)	109.47
(alkyl)	112.5
H—C—H (methylene)	109.0
(methyl)	109.47

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Table II summarizes the principal polarizabilities $\langle \alpha^{\parallel} \rangle$ and $\langle \alpha^{\perp} \rangle$ of the alkyl chain attached to the BBCO core as a function of the chain length (T = 300 K). As shown in recent studies,[10-12] the average configuration of the alkyl chain in liquid crystals is distorted from a "free chain configuration" because of the uniaxial constraints generated by the local mean field. We therefore present in Table II the lower and upper limits of the principal values, which are calculated for the fully-restricted chain and for the free chain, respectively. The former corresponds to averages over "helical" configurations such as $tg^{\pm}tg^{\pm}\ldots$ which minimize the molecular width, *i.e.*, minimize the lateral interactions with the environment. It can be shown on the basis of intrachain geometrical considerations that the principal polarizabilities for such a helical configuration has the same value as that of the all-*trans* configuration.

Since three RIS are assumed around each C—C bond, the homologues with $n \geq 3$ are expected to adopt several distinct end-chain configurations. However some of these configurations become less favorable because of intense intramolecular non-bonded interactions with the bulky BBCO core. Rotation around the C^1—C^2 bond is severely restricted; only the *trans* state is allowed. It follows that in the case of 3,3- and 4,4-BBCO's the free and restricted chain calculations result in identical polarizability values. (For the latter homologue, allowed configurations, *tt*, tg^+ and tg^-, give the same principal polarizabilities).

In Figure 1, we plot the ratio of the polarizability anisotropy $\Delta\alpha = \langle \alpha^{\parallel} \rangle - \langle \alpha^{\perp} \rangle$ to the average polarizability $\bar{\alpha} = (\langle \alpha^{\parallel} \rangle + 2\langle \alpha^{\perp} \rangle)/3$ of n,n-BBCO homologues for unrestricted "free" and all-*trans* pendant chains. It should be noted that 1,1-BBCO has a

TABLE II

Principal polarizabilities $\langle \alpha^{\parallel} \rangle$ and $\langle \alpha^{\perp} \rangle$ of the alkyl C—C_nH_{2n+1} groups attached to the BBCO core (in Å^3)

	Restricted chain		Free chain	
n	$\langle \alpha^{\parallel} \rangle$	$\langle \alpha^{\perp} \rangle$	$\langle \alpha^{\parallel} \rangle$	$\langle \alpha^{\perp} \rangle$
1			2.95	2.21
2			4.66	4.06
3			6.83	5.69
4			8.54	7.55
5	10.70	9.17	10.48	9.29
6	12.42	11.03	12.29	11.12
7	14.58	12.66	14.11	12.89
8	16.29	14.51	15.87	14.72

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$\Delta\alpha/\bar{\alpha}$ value larger than those for the diethyl and other even-numbered homologues ($\Delta\alpha$ itself is also larger for dimethyl than for diethyl derivatives). *If* the forces responsible for the liquid crystal formation could be attributed to the anisotropy in the molecular polarizability alone, then one might expect 1,1-BBCO to exhibit a liquid crystalline phase. The experiment by Reiffenrath and Schneider,[6] however, shows that only *n*,*n*-BBCO homologues with $n \geq 2$ can form liquid crystals. One can also see in Figure 1 that $\Delta\alpha/\bar{\alpha}$ remains in a narrow range between 0.06 and 0.10 for all *n*,*n*-BBCO homologues studied here. These values are quite small compared with the value of 0.42 reported for a typical aromatic-core mesogen (PAA)[13] having a comparatively highly polarizable core—the conjugated azoxy and phenyl groups.

It might be useful in terms of speculating about mesophase existence and stability if one could calculate the molecular polarizabilities of various mesogens simply by adding the tensors for constituent bond groups. One difficulty in such a calculation lies in estimation of the polarizability associated with flexible end chains. Non-bonded interactions of the chain with each specific type of mesogen core and the associated geometrical details of the junction of the chain to the core require corresponding configurational averages to be repeated for each mesogen. However, the maximum range of the principal polarizability can be calculated. Consider an isolated alkyl chain with the molecular-fixed *Z*-axis along the C^0—C^1 bond. The lowest value of $\Delta\alpha$ would be attained when the chain adopts all allowed configura-

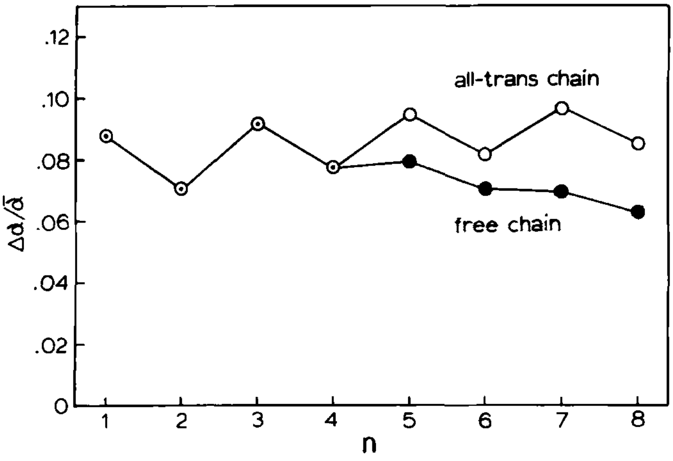

FIGURE 1 Calculated range of $\Delta\alpha/\bar{\alpha}$ of *n*,*n*-BBCO homologues. The upper and lower limits correspond to restricted (or all-*trans*) and free end chain configurations, respectively.

tions. The "free" chain configuration in this case represents a chain free from constraints from *both* the core and the neighboring molecules. The upper limit has already been calculated for the helical (or all-*trans*) configurations of n,n-BBCO's end alkyl chains. Table III summarizes the $\langle \alpha^{\parallel} \rangle$ and $\langle \alpha^{\perp} \rangle$ values in these two extreme conditions. The free-chain calculation ignores non-bonded interactions with the core, hence it gives an exaggerated, but safe, estimation of the lower limit of anisotropy. By applying the values in Table III to n,n-BBCOs ($n \geq 3$), we find that the lower limits of $\Delta\alpha/\bar{\alpha}$ decrease by approximately 0.02 from the exact calculations in Figure 1. Hence, in so far as the approximation of additive group polarizabilities go, the data in Table III may be used to estimate the contribution of alkyl chains to mesogen polarizabilities.

The role of the polarizability anisotropy in stabilizing the liquid crystalline phases has been discussed by Wulf[13] in relation to the Maier-Saupe theory.[1] By denoting the anisotropic and isotropic energies as E_a and E_i, respectively, the Maier-Saupe potential can be written as,

$$U(\theta) = -2E_i - E_a S\left(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\right), \tag{1}$$

where, θ is an angle between the long axis of each molecule and the nematic director and, S is an orientational order parameter defined by $\left\langle \tfrac{3}{2}\cos\theta - \tfrac{1}{2} \right\rangle$. Within the dipole-dipole approximation the ratio of E_a to E_i is given by,

$$E_a/E_i = \frac{2}{5}\left(\frac{\Delta\alpha}{3\bar{\alpha}}\right)^2. \tag{2}$$

TABLE III

Principal polarizabilities $\langle \alpha^{\parallel} \rangle$ and $\langle \alpha^{\perp} \rangle$ of the isolated alkyl C—C_nH_{2n+1} chain (in Å^3)

	Restricted chain		Free chain	
n	$\langle \alpha^{\parallel} \rangle$	$\langle \alpha^{\perp} \rangle$	$\langle \alpha^{\parallel} \rangle$	$\langle \alpha^{\perp} \rangle$
3	6.83	5.69	6.56	5.82
4	8.54	7.55	8.32	7.66
5	10.70	9.17	10.19	9.43
6	12.42	11.03	11.95	11.26
7	14.58	12.66	13.80	13.05
8	16.29	14.51	15.58	14.87

[a] The Z-axis is placed along the first C—C bond

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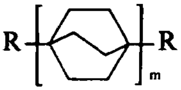
While the phases exhibited by the n,n-BBCO homologues are of the smectic type,[6] it nevertheless is of interest to use eq. 2 for an estimation of the relative importance of attractive interactions in terms of the E_a/E_i value. By introducing the calculated $\Delta\alpha/\bar{\alpha}$ values of 0.06 ~ 0.10 for n,n-BBCOs, we find that the anisotropic energy is negligibly small compared with the isotropic energy:

$$E_a/E_i = 1.6 \sim 4.4 \times 10^{-4}.$$

The corresponding value for PAA calculated from $\Delta\alpha/\bar{\alpha} = 0.42$ is 20 to 50 times larger than the above value. However, even this PAA value has been claimed to be too small to explain the observed temperature of the anisotropic-isotropic transition.[13] We therefore conclude that anisotropic dispersion interactions certainly can not be a dominant mechanism in the stabilization of n,n-BBCO liquid crystalline phases.

In view of these findings and in conjunction with the essentially cylindrical and aliphatic structure of n,n-BBCO homologues, it would appear that extensions of this structure would provide ideal candidates for testing the parameters critical to mesophase stability. Homologues of the type:



where $m \geq 3$ should be explored in this context. It seems reasonable to suggest that in the mesophases of higher homologues, lateral registration between molecules would be unimportant and nematic phases would appear. The polarizability anisotropy $\Delta\alpha/\bar{\alpha}$ remains in the same range of 0.06 ~ 0.10 even when m is increased from 2 to 10, thus no significant changes in the mesophase stability can be expected from this mechanism. On the other hand, the axial ratio, L/D, exhibits a considerable increase with m. For homologues with methyl to propyl end chains D can be identified with the core diameter, and L/D increases linearly with m. By assuming the radii of core CH_2 and alkyl CH_3 groups to be 1.95 Å,[11] L/D is given as,

$$\frac{L}{D} = \frac{4.08\,m + 2.37 + 2\,Z}{6.79} \tag{3}$$

where Z = 1.53, 2.12 and 3.65 Å are the end-chain contribution to the length along the para-axis for methyl, ethyl and propyl derivatives, respectively. According to the refined lattice theory,[5,14] the nematic–isotropic transition temperature rises toward $T_{NI} \rightarrow \infty$ as the

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axial ratio approaches a critical value of 6–8. This value would be attained at $m = 8$–10 for above homologues, hence it would be of interest to see if oligomers in the range $3 \leq m \leq 10$ can be synthesized and if T_{NI} does in fact exhibit the predicted variation.

CONCLUDING REMARKS

Conventional mesogens have a core consisting of one or more aromatic units with pendant groups that may contain hetero atoms. The extent of the electronic conjugation is quite variable and consequently, it is rather difficult to estimate the anisotropy of the polarizability tensor of a single molecule. Moreover, the detailed nature of polarization of such complex mesogens may not be simply represented by a point molecular polarizability tensor because of the specific spatial arrangement of highly polarizable groups. (Interactions between multiple centers may generate higher anisotropies locally than that derived with a single point dipole approximation.) Such problems should be minimized with oligomers of n,n-BBCO, a pure aliphatic compound with cylindrical symmetry. The present calculation estimates a quite small $\Delta\alpha/\bar{\alpha}$ value leading to the conclusion that anisotropic attractive interactions play only a minor role in stabilizing n,n-BBCO liquid crystalline phases. A hypothetical series of homologues employing the bicyclo[2.2.2]octane core are suggested as ideal candidates for critical testing of theories that explicitly include repulsive interactions in modeling the nematic-isotropic transition.

APPENDIX

The molecular polarizabilities of n,n-BBCOs and simple alkanes are calculated by the group polarizability method, which adds the contributions from individual bonds in a rigid subunit of the chain.[15,16] For an alkyl chain with n C—C skeletal bonds, we assume the i-th subunit to consist of the C^i—C^{i+1} bond and two C—H bonds attached to C^i atom. The local frame for the i-th subunit is chosen as follows:

1-axis: H—H vector
2-axis: bisectrix of H—C—H angle
3-axis: vector from C^{i-1} to C^{i+1}.

The polarizability tensors for the C—C and C—H bonds are taken to be cylindrically symmetric about the bond axis, hence they include only two independent parameters, $\alpha^{\parallel}$ and $\alpha^{\perp}$, expressing the polariz-

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abilities parallel and perpendicular to the bond axis, respectively. The transformation of bond polarizability tensors from the bond-fixed frame to the local segmental frame defined above would result in a following expression of the group polarizability tensor for the i-th CH_2C group of the chain $(1 < i < n - 1)$:

$$\boldsymbol{\alpha}^i = \begin{bmatrix} \alpha_{CC}^{\perp} & 0 & 0 \\ 0 & \alpha^{\parallel}\cos^2\theta + \alpha_{CC}^{\perp}\sin^2\theta & \left(\alpha_{CC}^{\parallel} - \alpha_{CC}^{\perp}\right)\sin\theta\cos\theta \\ 0 & \left(\alpha_{CC}^{\parallel} - \alpha_{CC}^{\perp}\right)\sin\theta\cos\theta & \alpha_{CC}^{\parallel}\sin^2\theta + \alpha_{CC}^{\perp}\cos^2\theta \end{bmatrix}$$
$$+2\begin{bmatrix} \alpha_{CH}^{\parallel}\sin^2\phi + \alpha_{CH}^{\perp}\cos^2\phi & 0 & 0 \\ 0 & \alpha_{CH}^{\parallel}\cos^2\phi + \alpha_{CH}^{\perp}\sin^2\phi & 0 \\ 0 & 0 & \alpha_{CH}^{\perp} \end{bmatrix} \tag{A-1}$$

where $\theta = \pi - \frac{1}{2}\angle CCC$ and $\phi = \angle HCH$. The first and last group tensors for alkane include contributions from the terminal methyl groups. The tensor $\boldsymbol{\alpha}^1$ containing excess contributions from the C^0—C^1 bond and the three methyl C—H bonds can be written as,

$$\boldsymbol{\alpha}^1 = 2\begin{bmatrix} \alpha_{CC}^{\perp} & 0 & 0 \\ 0 & \alpha_{CC}^{\parallel}\cos^2\theta + \alpha_{CC}^{\perp}\sin^2\theta & 0 \\ 0 & 0 & \alpha_{CC}^{\parallel}\sin^2\theta + \alpha_{CC}^{\perp}\cos^2\theta \end{bmatrix}$$
$$+2\begin{bmatrix} \alpha_{CH}^{\parallel}\sin^2\phi + \alpha_{CH}^{\perp}\cos^2\phi & 0 & 0 \\ 0 & \alpha_{CH}^{\parallel}\cos^2\phi + \alpha_{CH}^{\perp}\sin^2\phi & 0 \\ 0 & 0 & \alpha_{CH}^{\perp} \end{bmatrix}$$
$$+3\begin{bmatrix} \alpha_{ME}^{\perp} & 0 & 0 \\ 0 & \alpha_{ME}^{\parallel}\cos^2\theta + \alpha_{ME}^{\perp}\sin^2\theta & -\left(\alpha_{ME}^{\parallel} - \alpha_{ME}^{\perp}\right)\sin\theta\cos\theta \\ 0 & -\left(\alpha_{ME}^{\parallel} - \alpha_{ME}^{\perp}\right)\sin\theta\cos\theta & \alpha_{ME}^{\parallel}\sin^2\theta + \alpha_{ME}^{\perp}\cos^2\theta \end{bmatrix} \tag{A-2}$$

with

$$\begin{aligned} \alpha_{ME}^{\parallel} &= \alpha_{CH}^{\parallel}\cos^2\theta_0 + \alpha_{CH}^{\perp}\sin^2\theta_0, \\ \alpha_{ME}^{\perp} &= \tfrac{1}{2}\left\{\alpha_{CH}^{\parallel}\sin^2\theta_0 + \alpha_{CH}^{\perp}\left(1 + \cos^2\theta_0\right)\right\}, \end{aligned} \tag{A-3}$$

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where $\theta_0 = \pi - \angle HC^0C^1$. When the alkyl chain is attached to a mesogen's rigid-core unit, the third tensor in eq. A-2 (representing C—H contributions) will be replaced by an appropriate polarizability tensor. The last group tensor formulated for the CH_2CH_3 group has the form,

$$\alpha^{i-1} = \begin{bmatrix} \alpha_{CC}^{\perp} & 0 & 0 \\ 0 & \alpha_{CC}^{\parallel}\cos^2\theta + \alpha_{CC}^{\perp}\sin^2\theta & \left(\alpha_{CC}^{\parallel} - \alpha_{CC}^{\perp}\right)\sin\theta\cos\theta \\ 0 & \left(\alpha_{CC}^{\parallel} - \alpha_{CC}^{\perp}\right)\sin\theta\cos\theta & \alpha_{CC}^{\parallel}\sin^2\theta + \alpha_{CC}^{\perp}\cos^2\theta \end{bmatrix}$$

$$+2\begin{bmatrix} \alpha_{CH}^{\parallel}\sin^2\phi + \alpha_{CH}^{\perp}\cos^2\phi & 0 & 0 \\ 0 & \alpha_{CH}^{\parallel}\cos^2\phi + \alpha_{CH}^{\perp}\sin^2\phi & 0 \\ 0 & 0 & \alpha_{CH}^{\perp} \end{bmatrix}$$

$$+3\begin{bmatrix} \alpha_{ME}^{\perp} & 0 & 0 \\ 0 & \alpha_{ME}^{\parallel}\cos^2\theta + \alpha_{ME}^{\perp}\sin^2\theta & \left(\alpha_{ME}^{\parallel} - \theta_{ME}^{\perp}\right)\sin\theta\cos\theta \\ 0 & \left(\alpha_{ME}^{\parallel} - \alpha_{ME}^{\perp}\right)\sin\theta\cos\theta & \alpha_{ME}^{\parallel}\sin^2\theta + \alpha_{ME}^{\perp}\cos^2\theta \end{bmatrix} \tag{A-4}$$

The molecular polarizability tensor for a given configuration of the chain is then calculated as a sum of group tensors transformed from the local *123*-frame to the molecular fixed *XYZ*-frame. The elements of the molecular tensor are given by,

$$\alpha_{\alpha\beta}\{\varnothing\} = \sum_{i=1}^{n-1}\sum_{r,\delta}^{1,2,3} 1^i_{\gamma\alpha}\{\varnothing\}\,\alpha^i_{\alpha\beta}1^i_{\delta\beta}\{\varnothing\}, \tag{A-5}$$

where $1^i_{\gamma\alpha}\{\varnothing\}$ is the direction cosine between the γ-axis of the local frame and the α-axis of the molecular frame in configuration $\{\varnothing\}$. On averaging $\alpha_{\alpha\beta}\{\varnothing\}$ over all configurations of the chain we have,

$$\langle\alpha_{\alpha\beta}\rangle = \frac{1}{Z}\sum_{\{\varnothing\}}\alpha_{\alpha\beta}\exp[-E\{\varnothing\}/kT], \tag{A-6}$$

where

$$Z = \sum_{\{\varnothing\}}\exp[-E\{\varnothing\}/kT]. \tag{A-7}$$

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To obtain the energy of each configuration $E\{\varnothing\}$, we calculate the dihedral angle energy and the non-bonded interaction energy with the 3-state RIS scheme[7] including a *trans* state (t) at $\varnothing = 0°$ and two *gauche* states ($g^{\pm}$) at $\varnothing = \pm 112.5°$. The first energy term is calculated by assuming the *gauche* energy to be 0.4 kcal/mol higher than that of the *trans* state, and the second term from the Lennard–Jones 6–12 potential using "united atom" parameters for all pairs of atoms separated by at least four bonds. (The non-bonded interaction parameters have been listed elsewhere.)[11] The bond polarizabilities are taken from the values of Patterson and Flory[16] and Denbigh:[17] $\alpha^{\parallel}_{\mathrm{CC}} = 1.49$, $\alpha^{\perp}_{\mathrm{CC}} = 0.19$, $\alpha^{\parallel}_{\mathrm{CH}} = 0.79$, and $\alpha^{\perp}_{\mathrm{CH}} = 0.58$ (Å^3).

Acknowledgment

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