Conformational and Orientational Characteristics of Chain Molecules Placed in Nematic Fields. Part II

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Abstract. — Deuterium NMR quadrupolar splittings and $^2\text{H} - {}^2\text{H}$ dipolar couplings observed from perdeuterated 1,6-dimethoxyhexane ($CD_3O(CD_2)_6OCD_3$) dissolved in a liquid crystal 4'-methoxybenzylidene-4-n-butylaniline (MBBA) were analyzed using the single-ordering-matrix (SOM) and the Photinos-Samulski-Toriumi (P-S-T) models. Within the framework of the rotational isomeric state approximation, intramolecular interactions up to the third-order (between atoms and groups separated by five bonds) were considered. The geometrical parameters and intramolecular interaction energies determined from *ab initio* molecular orbital calculations were employed. The two simulation models yielded fair agreement between theory and experiment, but were found to give quite different images of the solute chain: (the SOM model), the solute becomes rigid and extended to conform itself to the nematic field; (the P-S-T model), the solute has almost the same degree of flexibility as in the free state, but populations of the anisotropic conformers are selectively enhanced. To reveal the true conformational characteristics of chain molecules in nematic fields, experimental techniques to enable direct and quantitative measurements of the bond conformations are necessary.

1. Introduction

In a previous study [1] the author carried out the conformational analysis of n-decane and 1,6-dimethoxyhexane (1,6-DMH) dissolved in a nematic solvent 4'-methoxybenzylidene-4-n-butylaniline (MBBA); ^2H-NMR quadrupolar splittings and $^2\text{H}-{}^2\text{H}$ dipolar couplings observed from these perdeuterated solutes were analyzed using the single-ordering-matrix (SOM) [2] and the Photinos-Samulski-Toriumi (P-S-T) [3] models. Then the intramolecular interaction energies of 1,4-dimethoxybutane (1,4-DMB) [4] and n-alkanes [5] were substituted for those of 1,6-DMH: $E_\rho = 1.0$, $E_{\sigma 1} = -0.2$ or -0.1, $E_{\sigma 2} = 0.3$, $E_{\sigma 3} = 0.5$, $E_{\omega 1} = 0.47$, and $E_{\omega 2} = 2.0$ kcal mol^{-1} (for the definition of the statistical weight parameters, see Fig. 1). The second-order-interaction energy $E_{\omega 1}$, which represents the intramolecular (C–H)$\cdot\cdot$ O interaction, was assumed to be 0.47 kcal mol^{-1} This value, being estimated from the semiempirical potential energy calculations, has been employed for a series of α, ω-dimethoxyalkanes [4, 6]

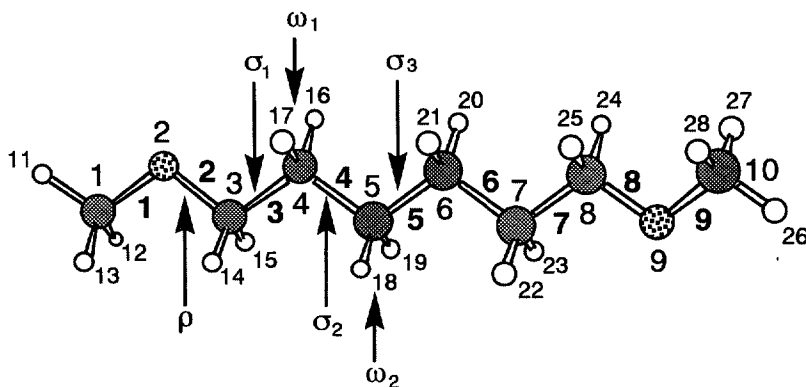(*) e-mail: ysasanuma@ccmail.nimc.go.jp

Fig. 1. — Schematic representation of 1,6-dimethoxyhexane (1,6-DMH) in its all-trans conformation with the definition of statistical weights. The atoms and skeletal bonds are numbered as indicated.

and 1,2-dimethoxypropane (1,2-DMP) [7] and the related polyethers. However, recent *ab initio* molecular orbital (MO) calculations for 1,2-dimethoxyethane (1,2-DME) [8,9] have indicated that the second-order interaction is attractive. The stabilization energy was reported to amount to -1.2 to -1.4 kcal mol^{-1}. Similar attractive interactions have been found for 1,2-DMP and poly(propylene oxide) (PPO), and the conformational characteristics of PPO have been satisfactorily elucidated in terms of the $(C-H)\cdots O$ attractions [10]. In addition, our MO calculations on α,ω-dimethoxyalkanes [11] have suggested that the stabilization due to the $(C-H)\cdots O$ interaction depends on the number of methylene units between the two oxygen atoms.

On these grounds the author reanalyzed the ^{2}H-NMR data [1] from 1,6-DMH in MBBA, using the geometrical parameters and intramolecular interaction energies of 1,6-DMH itself, determined from the *ab initio* MO computations. The results are reported and discussed in this paper.

2. Models

2.1. STATISTICAL WEIGHT MATRICES OF 1,6-DMH IN THE FREE STATE. — Using the rotational isomeric state (RIS) scheme [12,13] with first- (between atoms and groups separated by three bonds), second- (by four bonds), and third-order (by five bonds) interactions, the statistical weight matrices U_js of the skeletal bonds js of 1,6-DMH in the free state may be expressed as follows:

$$U_2 = \begin{array}{c} \\ \\ \\ \end{array}\begin{pmatrix} \overset{t}{1} & \overset{g^+}{\rho} & \overset{g^-}{\rho} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{1}$$

$$U_3 = \begin{array}{c} t \\ g^+ \\ g^- \end{array}\begin{pmatrix} \overset{t}{1} & \overset{g^+}{\sigma_1} & \overset{g^-}{\sigma_1} & \overset{t}{0} & \overset{g^+}{0} & \overset{g^-}{0} & \overset{t}{0} & \overset{g^+}{0} & \overset{g^-}{0} \\ 0 & 0 & 0 & 1 & \sigma_1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \sigma_1 \end{pmatrix} \tag{2}$$

$$
U_4 = \begin{array}{c}
 \\
tt \\ tg^+ \\ tg^- \\ g^+t \\ g^+g^+ \\ g^+g^- \\ g^-t \\ g^-g^+ \\ g^-g^-
\end{array}
\begin{array}{ccccccccc}
t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \\
\left(\begin{array}{ccccccccc}
1 & \sigma_2 & \sigma_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_2 & \sigma_2\omega_1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & \sigma_2\omega_1 & \sigma_2 \\
1 & \sigma_2 & \sigma_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_2 & \sigma_2\omega_1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \sigma_2 \\
1 & \sigma_2 & \sigma_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_2 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & \sigma_2\omega_1 & \sigma_2
\end{array}\right)
\end{array} \tag{3}
$$

$$
U_5 = \begin{array}{c}
 \\
tt \\ tg^+ \\ tg^- \\ g^+t \\ g^+g^+ \\ g^+g^- \\ g^-t \\ g^-g^+ \\ g^-g^-
\end{array}
\begin{array}{ccccccccc}
t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \\
\left(\begin{array}{ccccccccc}
1 & \sigma_3 & \sigma_3 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_3 & \sigma_3\omega_2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & \sigma_3\omega_2 & \sigma_3 \\
1 & \sigma_3 & \sigma_3 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_3 & \sigma_3\omega_2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \sigma_3 \\
1 & \sigma_3 & \sigma_3 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_3 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & \sigma_3\omega_2 & \sigma_3
\end{array}\right)
\end{array} \tag{4}
$$

$$
U_6 = \begin{array}{c}
 \\
tt \\ tg^+ \\ tg^- \\ g^+t \\ g^+g^+ \\ g^+g^- \\ g^-t \\ g^-g^+ \\ g^-g^-
\end{array}
\begin{array}{ccccccccc}
t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \\
\left(\begin{array}{ccccccccc}
1 & \sigma_2 & \sigma_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_2 & \sigma_2\omega_2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & \sigma_2\omega_2 & \sigma_2 \\
1 & \sigma_2 & \sigma_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_2 & \sigma_2\omega_2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \sigma_2 \\
1 & \sigma_2 & \sigma_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & \sigma_2\omega_2 & \sigma_2
\end{array}\right)
\end{array} \tag{5}
$$

$$
U_7 = \begin{array}{c}
 \\
tt \\ tg^+ \\ tg^- \\ g^+t \\ g^+g^+ \\ g^+g^- \\ g^-t \\ g^-g^+ \\ g^-g^-
\end{array}
\begin{array}{ccccccccc}
t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \\
\left(\begin{array}{ccccccccc}
1 & \sigma_1 & \sigma_1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_1 & \sigma_1\omega_1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & \sigma_1\omega_1 & \sigma_1 \\
1 & \sigma_1 & \sigma_1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_1 & \sigma_1\omega_1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \sigma_1 \\
1 & \sigma_1 & \sigma_1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & \sigma_1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & \sigma_1\omega_1 & \sigma_1
\end{array}\right)
\end{array} \tag{6}
$$

and

$$U_8 = \begin{array}{r} \\ \text{tt} \\ \text{tg}^+ \\ \text{tg}^- \\ \text{g}^+\text{t} \\ \text{g}^+\text{g}^+ \\ \text{g}^+\text{g}^- \\ \text{g}^-\text{t} \\ \text{g}^-\text{g}^+ \\ \text{g}^-\text{g}^- \end{array} \begin{array}{ccccccccc} \text{t} & \text{g}^+ & \text{g}^- & \text{t} & \text{g}^+ & \text{g}^- & \text{t} & \text{g}^+ & \text{g}^- \\ \left(\begin{array}{ccccccccc} 1 & \rho & \rho & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & \rho & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \rho \\ 1 & \rho & \rho & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & \rho & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \rho \\ 1 & \rho & \rho & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & \rho & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \rho \end{array}\right) \end{array}. \tag{7}$$

Here the rows and columns of these matrices are indexed to rotational states for the preceding and current bonds. The Greek letters stand for the statistical weights. These parameters are related to the intramolecular interaction energies through the Boltzmann factor [12]. The statistical weight factor is assigned to the *gauche* state of the bond, the weight of unity being given to the *trans* state (see Fig. 1). For the terminal bonds 1 and 9, a threefold symmetric rotational potential is assumed.

2.2. THE SINGLE-ORDERING-MATRIX (SOM) MODEL. — Boden *et al.* [14] have related the quadrupolar splitting $\Delta\nu_i$ to the ordering matrix as follows:

$$\Delta\nu_i = \frac{3}{2}\frac{e^2qQ}{h}\left\{S_{ZZ}\frac{3\,\overline{\cos^2\theta_{Z_i}}-1}{2} + (S_{XX}-S_{YY})\frac{\overline{\cos^2\theta_{X_i}}-\overline{\cos^2\theta_{Y_i}}}{2}\right\} \tag{8}$$

where $S_{\alpha\beta}$ is the $\alpha\beta$ component of the ordering matrix, θ_{α_i} is the angle between the α axis and the C–D bond of the i-th carbon atom (hereafter referred to as the C_i–D bond), and the bar denotes the average over all allowed conformations of the solute molecule. Equation (8) was obtained by assuming that the orientational order parameters $S_{\alpha\beta}$s are identical for all the conformers (the single-ordering-matrix approximation). When the Z axis is set so as to lie in the direction of the greatest molecular length, the magnitude of the biaxiality $S_{XX} - S_{YY}$ is negligibly small. In this treatment, the *longest* principal axis of inertia is defined as the Z axis. Accordingly, equation (8) may be simplified to

$$\Delta\nu_i = \frac{3}{2}\frac{e^2qQ}{h}S_{ZZ}\frac{3\,\overline{\cos^2\theta_{Z_i}}-1}{2} \tag{9}$$

(the cylindrical-symmetry approximation). Then the quadrupolar splitting ratio $\Delta\nu_i/\Delta\nu_k$ is free from the S_{ZZ} value. Therefore, we have

$$\frac{\Delta\nu_i}{\Delta\nu_k} = \frac{3\,\overline{\cos^2\theta_{Z_i}}-1}{3\,\overline{\cos^2\theta_{Z_k}}-1} \tag{10}$$

Similarly, we obtain

$$\frac{D_{DD_i}}{D_{DD_k}} = \frac{\overline{P_2(\cos\theta_{(DD)_i})}}{\overline{P_2(\cos\theta_{(DD)_k})}}. \tag{11}$$

To facilitate the analysis, k is assigned to the central methylene units. In the SOM model it is assumed that the chain molecules in nematic fields can be treated by the RIS scheme; the statistical weight matrices obtained as above may be applied to 1,6-DMH dissolved in MBBA,

if values of the statistical weight parameters are adjusted for the uniaxial environment. On the expectation that second-order interactions $g^{\pm}g^{\mp}$ rarely occur in nematic fields, the weights ω_1 and ω_2 are set equal to zero. The average $\overline{\cos^2\theta_{Z_i}}$ required in equation (10) can be obtained from

$$\overline{\cos^2\theta_{Z_i}} = \frac{\sum_n \cos^2\theta_{Z_i} \left(\prod_{j=2}^{N-1} z_j\right)_n}{\sum_n \left(\prod_{j=2}^{N-1} z_j\right)_n} \tag{12}$$

where z_j represents the weight for bond j, i.e., 1, ρ, σ_1, σ_2, or σ_3. It should be noted that values of the statistical weight parameters differ from those of the free chain. In a similar manner, $\overline{P_2(\cos\theta_{(DD)_i})}$ can be calculated.

The simulation using the SOM model is carried out by varying the z_j values until the best agreement between the calculated and observed quadrupolar splitting ratios is attained. The iterative convergence is performed by e.g. the simplex method [15]. The convergence of the iteration can be monitored by the reliability factor,

$$R(\%) = 100 \times \frac{\left\{\sum_i \left(|\Delta\nu_{i,\text{obsd}}/\Delta\nu_{k,\text{obsd}}| - |\Delta\nu_{i,\text{calcd}}/\Delta\nu_{k,\text{calcd}}|\right)^2\right\}^{1/2}}{\sum_i |\Delta\nu_{i,\text{obsd}}/\Delta\nu_{k,\text{obsd}}|} \tag{13}$$

2.3. THE PHOTINOS-SAMULSKI-TORIUMI (P-S-T) MODEL. — In this treatment, the potential $V(\Omega, n)$ of the mean torque for a conformer n is assumed to be expressed as

$$V(\Omega, n) = -\widetilde{w}_0 \sum_{j=1}^{N} P(\mathbf{s}_j, \mathbf{s}_j) - \widetilde{w}_1 \sum_{j=1}^{N-1} P(\mathbf{s}_j, \mathbf{s}_{j+1}) \tag{14}$$

where Ω represents the orientation of the molecular frame relative to the nematic director, N is the number of skeletal bonds, and $P(\mathbf{s}_j, \mathbf{s}_{j+m}) = (3\cos\theta_j \cos\theta_{j+m} - \mathbf{s}_j \cdot \mathbf{s}_{j+m})/2$, θ_j being the angle between the j-th bond vector $\mathbf{s}_j$ and the nematic director. The coefficients $\widetilde{w}_0$ and $\widetilde{w}_1$, being termed the intermolecular (solvent-solute) coupling constants, are measures of the orientational energies of the bond and chord (a line joining the midpoints of adjacent bonds), respectively. In the P-S-T model the correlation between bond orientations is incorporated by the alignment of the chords. The orientational distribution function $f(\Omega, n)$ for a given orientation and conformation of the molecule is written as

$$f(\Omega, n) = \frac{1}{\zeta} G(n) \, e^{\frac{-E(n)+V(\Omega, n)}{kT}} \tag{15}$$

where ζ is the normalization factor, k is the Boltzmann constant, T is the absolute temperature, $G(n)$ is the conformer rotational kinetic energy factor (set equal to unity in this study), and $E(n)$ is the internal (intramolecular interaction) energy in the free state. Therefore, $E(n)$ is given as a function of $E_\rho, E_{\sigma 1}, E_{\sigma 2}, E_{\sigma 3}, E_{\omega 1}$, and $E_{\omega 2}$ of the free chain and evaluated from equations (1–7) for each conformer. The thermal average $\langle F \rangle$ of a quantity $F(\Omega, n)$ is obtained by averaging over all orientations and conformations of the solute molecule; that is,

$$\langle F \rangle = \sum_n \int d\Omega \, F(\Omega, n) \, f(\Omega, n) . \tag{16}$$

Therefore, the ^{2}H-NMR quadrupolar splitting $\Delta\nu_i$ of the C_i–D bond is given by

$$\Delta\nu_i = \frac{3}{2}\frac{e^2qQ}{h}\langle P_2(\cos\theta_{(CD)_i})\rangle \tag{17}$$

where e^2qQ/h is the quadrupolar coupling constant (=163 kHz [16]), and $P_2(\cos\theta_{(CD)_i}) = (3\cos^2\theta_{(CD)_i} - 1)/2$, $\theta_{(CD)_i}$ being the angle between the C_i–D bond and the nematic director. The D–D dipolar coupling D_{DD_i} for the i-th carbon site is given by

$$D_{DD_i} = -\frac{\gamma_D^2 h}{4\pi^2 r_{DD}^3}\langle P_2(\cos\theta_{(DD)_i})\rangle \tag{18}$$

where $\gamma_D^2 h/4\pi^2 = 2.830 \times 10^3 \text{Å}$, r_{DD} is the D–D distance, and $\theta_{(DD)_i}$ is the angle between the nematic director and the interdeuteron vector at the i-th carbon site. The probability $p^{(n)}$ of the n-th conformer is obtained from

$$p^{(n)} = \frac{\zeta^{(n)}}{\zeta}\,e^{-\frac{E(n)}{kT}} \tag{19}$$

where

$$\zeta^{(n)} = \int e^{-\frac{V(\Omega,n)}{kT}}\,d\Omega\,. \tag{20}$$

The trans fraction f_{t_j} of the j-th bond is evaluated from

$$f_{t_j} = \sum_{n_{t_j}} p^{(n_{t_j})} \tag{21}$$

where n_{t_j} stands for the conformer whose j-th bond takes the trans state. As a measure of the orientational order of the whole chain, the quantity S_{chain} was introduced:

$$S_{\text{chain}} = \frac{\langle V(\Omega,n)\rangle}{V^*} \tag{22}$$

where V^* is the $V(\Omega,n)$ value of the most extended (all-trans) conformer oriented in the nematic direction.

According to the bond-length scaling theorem [17], the intermolecular coupling constants are related to each other by

$$\widetilde{w}_0(C-O) = \left(\frac{l_{C-O}}{l_{C-C}}\right)^2 \widetilde{w}_0(C-C) \tag{23}$$

$$\widetilde{w}_1(C-O,O-C) = \left(\frac{l_{C-O}}{l_{C-C}}\right)^2 \widetilde{w}_1(C-C,C-C) \tag{24}$$

$$\widetilde{w}_1(O-C,C-C) = \frac{l_{C-O}}{l_{C-C}}\,\widetilde{w}_1(C-C,C-C) \tag{25}$$

where $\widetilde{w}_0(a)$ and $\widetilde{w}_1(a,b)$ are the intermolecular coupling constants associated with bond a and adjoining bond pair a and b respectively, l_{C-O} and l_{C-C} denote the C–O and C–C bond lengths respectively. Under these conditions, the number of variables is reduced to two: $\widetilde{w}_0(C-C)$ and $\widetilde{w}_1(C-C,C-C)$ (the two-parameter approximation). For alkyl chains in nematic fields, the following relation was found [17]:

$$\widetilde{w}_0(C-C,C-C) = 0.85\,\widetilde{w}_0(C-C)\,. \tag{26}$$

Table I. — *Geometrical parameters of the all-trans 1,6-DMH, optimized by the ab initio MO calculation at the HF/6-311+G* level* [a].

Bond Length (Å)		Bond angle (deg.)		Dihedral angle (deg.)	
$C^1 - O^2$	1.389				
$O^2 - C^3$	1.395	$\angle C^1 O^2 C^3$	114.51		
$C^3 - C^4$	1.517	$\angle O^2 C^3 C^4$	109.09	$C^1 O^2 - C^3 C^4$	180.0
$C^4 - C^5$	1.528	$\angle C^3 C^4 C^5$	112.71	$O^2 C^3 - C^4 C^5$	180.0
$C^5 - C^6$	1.529	$\angle C^4 C^5 C^6$	112.98	$C^3 C^4 - C^5 C^6$	180.0
$C^1 - H^{11}$	1.081	$\angle O^2 C^1 H^{11}$	107.74	$C^3 O^2 - C^1 H^{11}$	180.0
$C^1 - H^{12,13}$	1.089	$\angle O^2 C^1 H^{12,13}$	111.46	$C^3 O^2 - C^1 H^{12,13}$	∓ 60.68
$C^3 - H^{14,15}$	1.091	$\angle O^2 C^3 H^{14,15}$	109.85	$C^1 O^2 - C^3 H^{14,15}$	∓ 58.82
$C^4 - H^{16,17}$	1.087	$\angle C^3 C^4 H^{16,17}$	108.52	$O^2 C^3 - C^4 H^{16,17}$	∓ 57.70
$C^5 - H^{18,19}$	1.089	$\angle C^4 C^5 H^{18,19}$	109.60	$C^3 C^4 - C^5 H^{18,19}$	∓ 58.03

[a] For the atom numbers (see Fig. 1).

If equation (26) is assumed to be valid for 1,6-DMH, only $\tilde{w}_0(C-C)$ is the independent variable (the single-parameter approximation). In the P-S-T simulation, therefore, the intermolecular coupling constant(s), $\tilde{w}_0(C-C)$ or $\tilde{w}_0(C-C)$ and $\tilde{w}_1(C-C, C-C)$ are treated as adjustable parameter(s), and the R factor of equation (13) is calculated using $\Delta\nu_i$s instead of $(\Delta\nu_i/\Delta\nu_k)$s.

3. *Ab initio* Molecular Orbital Computation

Ab initio MO calculations were carried out by using the Gaussian94 program [18] installed on the cluster of IBM RS/6000 computers in the Research Information Processing Station (RIPS), Tsukuba. For eight conformers tttttt, g^+tttttt, tg$^+$ttttt, ttg$^+$tttt, tttg$^+$ttt, g^+g^-tttttt, tg$^+g^-$tttt, and ttg$^+g^-$ttt *in vacuo*, their molecular structures were fully optimized at the Hartree-Fock (HF) level with the 6-311+G* basis set (HF/6-311+G*). In this paper, for example, the notation tg$^+g^-$tg$^+g^-$t denotes that bonds 2 to 8 take the t, g^+, g^-, t, g^+, g^-, and t states, respectively (for the bond numbers, see Fig. 1). Default convergence criteria were used for the self-consistent-field and geometrical optimizations. With the geometries determined, single-point computations using the second Møller-Plesset (MP) perturbation and 6-311+G* basis set (MP2/6-311+G*//HF/6-311+G*) were carried out. Vibrational frequencies for the equilibrium geometries were evaluated at the HF/6-31+G* level and scaled by 0.893 to correct overestimation of the frequencies. Zero-point and thermal vibrational energy corrections were performed using the scaled frequencies. From the entropy change from 0 to 298.15 K concomitantly computed, the free energy at 298.15 K of each conformer was evaluated. It is assumed that the free energies thus obtained are free from temperature dependence within the temperature range treated here.

4. Results and Discussion

In Table I the geometrical parameters optimized for the all-trans 1,6-DMH are listed [19]. In both SOM and P-S-T simulations, the bond lengths and bond angles were assumed common

Table II. — *Dihedral angles for the gauche plus and minus states of the skeletal bonds, used in the simulations.*

Conformation	Bond no.			
	2	3	4	5
$g^{\pm}$ [a]	∓ 80.34	∓ 63.88	∓ 65.98	∓ 65.13
$tg^{\pm}g^{\mp}tttt$ [b]		∓ 68.62	± 76.88	
$ttg^{\pm}g^{\mp}ttt$ [c]			∓ 97.65	± 63.37

[a] Determined from the geometrical optimization at the HF/6-311+G* level for the $g^{+}tttttt$, $tg^{+}ttttt$, $ttg^{+}tttt$, and $tttg^{+}ttt$ states.

[b] Determined for the $tg^{+}g^{-}tttt$ state. Conformers having the ω_1 interaction were assumed to take these angles.

[c] Determined for the $ttg^{+}g^{-}ttt$ state. Conformers having the ω_2 interaction were assumed to take these angles.

Table III. — *Free energies (ΔG) relative to the all-trans conformation, evaluated from ab initio MO calculations at MP2/6-311+G*//HF/6-311+G* level* [a].

Conformation	Statistical weight(s)	ΔG (kcal mol^{-1})
ttttttt	1	0.00
$g^{+}tttttt$	ρ	1.286
$tg^{+}ttttt$	σ_1	-0.461
$ttg^{+}tttt$	σ_2	0.665
$tttg^{+}ttt$	σ_3	0.583
$tg^{+}g^{-}tttt$	$\sigma_1\sigma_2\omega_1$	0.400
$ttg^{+}g^{-}ttt$	$\sigma_2\sigma_3\omega_2$	2.634

[a] From the ΔG values, the intramolecular interaction energies E_{ρ}, $E_{\sigma 1}$, $E_{\sigma 2}$, $E_{\sigma 3}$, $E_{\omega 1}$, and $E_{\omega 2}$ were determined to be 1.29, -0.46, 0.67, 0.58, 0.20, and 1.39 kcal mol^{-1}, respectively.

to all possible conformers. Dihedral angles for the g^{+} and g^{-} states of bonds 2 to 5 were taken from those of the $g^{+}tttttt$, $tg^{+}ttttt$, $ttg^{+}tttt$, $tttg^{+}ttt$ conformers respectively, being summarized in Table II. When the $g^{\pm}g^{\mp}$ sequence(s) is included in a conformer, the dihedral angles may be shifted from the above values. For the $g^{+}g^{-}ttttt$, $tg^{+}g^{-}tttt$, and $ttg^{+}g^{-}ttt$ states, therefore, the geometrical optimization was attempted. Owing to a severe steric conflict between C^1H_3 and C^5H_2 groups, the $g^{+}g^{-}ttttt$ state was led to $tg^{-}ttttt$ by the geometrical optimization. Thus the $g^{+}g^{-}ttttt$ conformer is considered absent here. The dihedral angles determined for two other conformers are also listed in Table II. These values were used for the conformers including the $g^{\pm}g^{\mp}$ sequence(s).

In Table III the free energies and statistical weights of the seven conformers are given. From these free energies the intramolecular interaction energies were evaluated as follows: $E_{\rho} = 1.29$, $E_{\sigma 1} = -0.46$, $E_{\sigma 2} = 0.67$, $E_{\sigma 3} = 0.58$, $E_{\omega 1} = 0.20$, and $E_{\omega 2} = 1.39$ kcal mol^{-1} The $E_{\sigma 1}$ value was found to be negative. Other energy parameters were obtained as positive.
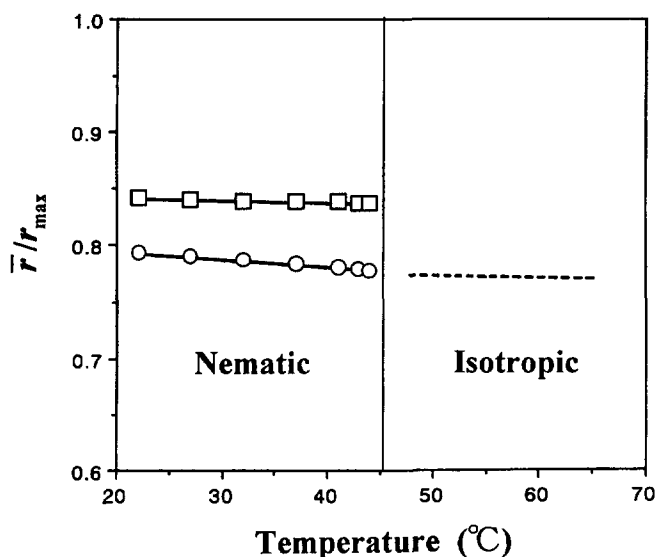
Fig. 2. — Average chain extension $\bar{r}/r_{max}$ of 1,6-DMH (0.505 mol%) in 4'-methoxybenzylidene-4-*n*-butylaniline (MBBA) as a function of temperature: (○), the P-S-T model; (□), the SOM model [1]. The dotted line represents the $\bar{r}/r_{max}$ value for the isotropic phase. $\bar{r}$ is the average distance between the terminal methyl carbons, and r_{max} is the end-to-end distance of the all-trans form.

In contrast to 1,2-DME and 1,2-DMP, whose $(C-H)\cdots O$ interactions were found to be attractive $(E_{\omega 1} = -1.0$ to -1.9 kcal mol$^{-1})$, the 1,6-DMH molecule has a positive $E_{\omega 1}$ value of 0.2 kcal mol^{-1}. The gauche stability of the C–C bond of 1,2-DME and 1,2-DMP was shown to be ascribed to the second-order $(C-H)\cdots O$ attraction, while that of 1,6-DMH is suggested to be due to the first-order interaction σ_1. However, this problem is not discussed here.

Using the U_j matrices of equations (1–7) and the geometrical parameters, the simulations for ^{2}H-NMR quadrupolar splittings from 1,6-DMH (0.505 mol%) in MBBA at 27 °C were carried out. In the P-S-T simulation the intramolecular interaction energies obtained as above were used in the calculations of the $E(n)$ values.

For the SOM simulation, only slight differences could be found between the present and previous [1] results. This is partly because the SOM analysis does not require the intramolecular interaction energies of the free state, partly because the conformers with the $g^{\pm}g^{\mp}$ sequence(s) are excluded from the ensemble. The small differences may be due to changes in the geometrical parameters employed. Thus the previous SOM simulations can be considered still valid. The discussion stated below is based on the previous data.

In Table IV the results of the P-S-T simulations are compared with those obtained in the previous study [1]. Although the R values were not fully reduced, the present simulation shows an improvement; D_{DD_5} was estimated to be larger than D_{DD_4}, which agrees with the experiment. The two-parameter $(\tilde{w}_0(C-C)$ and $\tilde{w}_1(C-C,C-C))$ simulation yielded too small D_{DD_i} values, while the single-parameter $(\tilde{w}_0(C-C))$ fitting reproduced the experiment well. We may discuss the characteristic features of the P-S-T model from the results of the single-parameter simulation.

Figure 2 shows the temperature dependence of the reduced average end-to-end distance $\bar{r}/r_{max}$ of 1,6-DMH (0.505 mol%) in MBBA. In the $\bar{r}/r_{max}$ value of the P-S-T simulation,

Table IV. — *Results of simulations for 1,6-DMH by the P-S-T model.*

Parameter	$|\Delta\nu_4|$ (kHz) ($DD_{DD,}$, Hz) Calcd Present study Single parameter	Two parameters	Previous study [a] Single parameter	Two parameters	Obsd [b]	Bond no.	f_{tj} Present study Single parameter	Two parameters	Free state
Atom no. 1	15.31	10.60	11.57	7.86	8.60	2	0.885	0.874	0.879
3	21.49	19.51	24.24	22.59	21.48	3	0.228	0.288	0.212
4	26.76 (57.6)	27.51 (18.9)	27.24 (57)	27.76 (39)	28.31 (61)	4	0.711	0.709	0.679
5	27.49 (59.3)	31.08 (20.1)	27.02 (53)	29.51 (36)	29.67 (65)	5	0.662	0.709	0.658
R (%)	15.35	6.88	5.6	1.7					
$\tilde{w}_0$(C–C) (kcal mol^{-1})	0.161	-0.458	0.178	-0.145					
$\tilde{w}_1$(C–C,C–C) (kcal mol^{-1})		0.747	0.213	0.435					
S_{chain}	0.197	0.291	0.213	0.279					

[a] The following values of intramolecular interaction energies were employed:
$E_\rho = 1.0$, $E_{\sigma1} = -0.2$, $E_{\sigma2} = 0.3$, $E_{\sigma3} = 0.5$, $E_{\omega1} = 0.47$, and $E_{\omega2} = 2.0$ kcal mol^{-1} Reference [1].
[b] Observed at 27 °C. The 1,6-DMH concentration was 0.505 mol%.

Table V. — *Results of simulations: comparison between the P-S-T and SOM models.*

Conformer	Multiplicity	r [a]	n_{kink}	n_{crank}	n_{jog}	Fraction (%)		
						P-S-T [b]	SOM	Free State
tg^+tttg^-t	2	9.90	0	0	1	3.87	2.64	3.38
tg^+tttg^+t	2	9.55	0	0	0	3.58	2.64	3.38
tg^+ttttt	4	10.18	0	0	0	2.00	2.32	1.56
$tg^+tg^-tg^+t$	2	9.90	2	0	0	1.46	1.07	1.28
$tg^+tg^+tg^-t$	4	9.57	1	1	0	1.34	1.07	1.28
$tg^+tg^+tg^+t$	2	9.53	0	2	0	1.32	1.07	1.28
$ttttttt$	1	11.02	0	0	0	1.23	2.03	0.72
$\bar{n}_{kink}$[c]						0.274	0.279	0.267
$\bar{n}_{crank}$[c]						0.253	0.279	0.267
$\bar{n}_{jog}$[c]						0.099	0.106	0.090

[a] The distance between carbons 1 and 10.

[b] The single-parameter simulation.

[c] Weight-average values of numbers n_{kink}, n_{crank}, and n_{jog} of kink ($g^{\pm}tg^{\mp}$), crankshaft ($g^{\pm}tg^{\pm}$), and jog ($g^{\pm}tttg^{\mp}$) configurations included in a conformer.

no particular change can be observed between before and after nematic-to-isotropic (N-I) transition. As seen from Table IV, the trans fractions f_{tj} are comparable with those in the free state. These tendencies were found in the simulation for n-decane [1]. Thus the P-S-T model indicates that the chain molecules in the nematic field have almost the same degree of flexibility as in their free state. In Table V the fractions of highly populated conformers are listed. The bonds 3 and 7 of 1,6-DMH have the intrinsic gauche preference ($E_{\sigma 1} = -0.46$ kcal mol^{-1}). Thus the most populated conformations in the free state are tg^+tttg^+t and tg^+tttg^-t (3.38%). The P-S-T model, in which the long-range correlation between bond orientations is incorporated by the alignment of the *chords*, can distinguish between tg^+tttg^+t (3.58%) and tg^+tttg^-t (3.87%). The latter ($r = 9.90$ Å), including the so-called jog configuration $g^{\pm}tttg^{\mp}$, is more extended than the former (9.55 Å). In the SOM model, however, the statistical weight parameters are determined independently of each other, and hence no explicit long-range correlation of the bond orientation is included; the SOM analysis gave the same fraction (2.64%) to the four conformations. The P-S-T simulation also suggests enhancement of populations of anisotropic conformers having the so-called kink ($g^{\pm}tg^{\mp}$) and crankshaft ($g^{\pm}tg^{\pm}$) configurations: for example, $tg^+tg^-tg^+t$ (1.28% in the free state → 1.46% in the liquid crystal), $tg^+tg^+tg^-t$ (1.28% → 1.34%), and $tg^+tg^+tg^+t$ (1.28% → 1.32%). The anisotropic conformers are suggested to be more populated.

In the SOM model, each conformer is treated as an ellipsoid of inertia, and assumed to conform itself to the nematic field by aligning the *longest* principal-axis of inertia with the nematic director. Consequently, the solute becomes rigid and extended; the trans fractions of the *skeletal* bonds are enhanced. The population of the all-trans conformer was evaluated to be 2.03%, while the P-S-T simulation yielded a value of 1.23% (*cf.* 0.72% in the free state).

In the SOM simulation ω_1 and ω_2 were set equal to zero; the conformers with the $g^{\pm}g^{\mp}$ sequence(s) were assumed to be absent in the nematic field. However, the $E_{\omega 1}$ value of the free chain was calculated to be 0.20 kcal mol^{-1} Thus the assumption is crude, although the four variables, ρ and σ_is ($i = 1 - 3$), may compensate this simplication. It is, in principle, possible to add ω_1 to the SOM simulation as an additional variable. However, then the number of adjustable parameters ($\rho, \sigma_1, \sigma_2, \sigma_3$, and ω_1) exceeds that of the experimental data ($\Delta\nu_1, \Delta\nu_3, \Delta\nu_4$, and $\Delta\nu_5$); no unique solution would be obtained. To settle this problem, an improvement in the fitting technique is necessary and will be a subject of future work.

Both SOM [2, 20] and P-S-T [21] models were shown to succeed in reproducing 16 proton-proton dipolar couplings observed from n-hexane in a nematic liquid crystal EK11650. The SOM model indicates that the n-hexane molecule is rigid and extended compared with that in the isotropic phase, wheares the P-S-T model shows that the n-alkyl chain keeps its flexibility even in the liquid crystalline solvent. As stated above, the two simulation models give quite different images of the solutes. Although thermodynamic studies [22, 23] have suggested that n-alkane molecules behave a chain composed of two complete rigid and some additional semiflexible segments in nematic fields, direct and quantitative measurements of bond conformations of the solutes are strongly required. Researchers having such experimental techniques are expected to join this study.

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