

Conformational Analysis of Chain Molecules in Liquid Crystalline Phases by a Rotational Isomeric State Scheme with Maximum Entropy Method I. ^1H - ^1H Dipolar Couplings from *n*-Alkanes Dissolved in a Nematic Solvent

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ABSTRACT: For conformational analysis of chain molecules incorporated in nematic fields, a rotational isomeric state (RIS) scheme was revised for use with the maximum entropy method. Analysis thus based proceeds as follows. 1) All possible conformations are enumerated within the RIS approximation. 2) The principal axes of inertia, determined for each conformer, are considered molecular axes, and orientational order parameters are evaluated from dimensions of a rectangular parallelepiped closely fitted to the conformer. 3) Conformational statistical weight factors of first- and second-order interactions are adjusted and order parameters are scaled so as to reproduce experimental observation and maximize the information entropy regarding conformer populations. By this method, ^1H - ^1H dipolar couplings observed from *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane dissolved in a nematic liquid crystal Kodak EK11650 *p*-pentylphenyl-2-chloro(4-benzylbenzoyloxy)-benzoate [M. E. Rosen, S. P. Rucker, C. Schmidt, and A. Pines, *J. Phys. Chem.* **97**, 3858 (1993)] were analyzed. For all *n*-alkanes, good agreement between theory and experiment was attained. Anisotropic conformers were slightly more populated than in the free state. The present results were quantitatively comparable to those of analysis using the mean-field theory.

KEY WORDS *n*-Alkanes / Conformation / Liquid Crystal / ^1H - ^1H Dipolar Coupling / Rotational Isomeric State Scheme / Maximum Entropy Method /

In the free state, *n*-alkane chains are flexible and the C-C bonds prefer the *trans* to *gauche* state. Within the rotational isomeric state (RIS) approximation, the conformations and average shapes can be estimated using only two conformational energies E_σ and E_ω .¹ The former, due to first-order interaction (between CH_2 (or CH_3) groups separated by three bonds) is 0.5 kcal mol⁻¹, and the latter, due to second-order interaction (by four bonds) in the g^+g^- conformations, is 2.0–3.0 kcal mol⁻¹.² Alkyl chains are found in spacers and tails of thermotropic liquid crystals (LCs), main-chain and side-chain liquid crystalline polymers, surfactants and biological membranes. To understand the phase behavior of these LCs and estimate thermodynamic quantities related to phase transition, the conformations and orientations in the liquid crystalline phases should be clarified.

Nuclear magnetic resonance (NMR) data such as ^1H - ^1H dipolar couplings and ^2H quadrupolar splittings from alkyl chains in the liquid crystalline phases have been analyzed using theoretical models to investigate orientational ordering.^{3,4} The mean-field theory,⁵ based on statistical mechanics, has been used, and the partition function may be calculated from internal and external energies. The former depends only on conformation, and is given as a function of E_σ and E_ω . The latter depends on conformation and orientation. Orientational potential has often been approximated by second-order Legendre polynomials,^{6,7} and much effort has been directed to improvement of the potential function.^{8–11}

In previous studies^{12–14} the RIS scheme, developed mainly for polymeric chains, was extended to conforma-

tional analysis of chain molecules dissolved in nematic solvents. To reduce the number of adjustable parameters in the simulation, cylindrical-symmetry approximation and single-ordering-matrix approximation were assumed. In the former, biaxiality $S_{XX}-S_{YY}$ is neglected, and the latter means the orientational order parameter S_{ZZ} is identical for all the possible conformers. By this method, we analyzed ^2H NMR quadrupolar splittings¹⁵ observed from *n*-alkanes dissolved in nematic solvents as well as ^1H - ^1H dipolar couplings^{16,17} from *n*-hexane in a nematic LC.¹² Conformer populations thus evaluated are compatible with molecular rigidity predicted by thermodynamics studies,^{18,19} but have large discrepancy with those determined by mean-field approaches.²⁰

This study refines our simulation scheme. From shape anisotropy of the conformer, orientational order parameters S_{ZZ} and $S_{XX}-S_{YY}$ were determined for each conformer. The maximum entropy (MaxEnt) method^{21,22} was introduced into the fitting procedure to obtain the most probable results from limited number of experimental data. Even when the parameters outnumber the data, MaxEnt derives the most reliable conclusion.

In this study, using modified methodology, we analyzed (1) ^1H - ^1H dipolar couplings from *n*-alkanes dissolved in a nematic LC KODAK EK11650²⁰ (study I), (2) ^2H NMR quadrupolar splittings¹³ from dilute solutions of *n*-decane/4'-methoxybenzylidene-4-*n*-butylaniline (MBBA) and 1,6-dimethoxyhexane (1,6-DMH)/MBBA systems (study II),²³ and (3) deuterium quadrupolar splittings from lyotropic liquid crystalline phases of a ternary system of sodium octanoate, 1-decanol, and water.²⁴

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In this paper, the simulation scheme and results of study I are explained in detail. In the next paper,²³ as study II, conformational characteristics of 1,6-DMH are to be compared with those of *n*-decane, and the orientations of the solutes and solvent will be described as functions of temperature and concentration. The methodology proposed here is shown valid for conformational analysis of chain molecules incorporated in anisotropic fields.

MODEL

Rotational Isomeric State (RIS) Approximation

Conformations of chain molecules in the free state may be represented only in terms of short-range intramolecular interactions. The RIS scheme,¹ developed mostly for polymeric chains, is based on this hypothesis. The weights of all possible conformations may be evaluated from statistical weight matrixes, U_n s (n : bond number), assigned to skeletal bonds. When intramolecular interactions up to the second-order interactions are taken into account, relative weights of all conformations may be expressed as functions of only two parameters, σ and ω . Weights are defined as the Boltzmann factor of the corresponding conformational energy; e.g., $\sigma = \exp(-E_\sigma/RT)$, where R is the gas constant and T is the absolute temperature. U_n matrixes of *n*-alkanes are given by^{1,2}

$$U_2 = \begin{pmatrix} 1 & \sigma & \sigma \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (1)$$

and

$$U_n = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{pmatrix} (n \geq 3) \quad (2)$$

Here, the rows and columns of the matrixes are indexed to rotational states for the previous and current bonds. Fractional population $f_{\xi\eta\zeta\dots}$ of a conformation $\xi\eta\zeta\dots$ ($\xi, \eta, \zeta = t, g^+, \text{ or } g^-$) may be calculated as

$$f_{\xi\eta\zeta\dots} = \frac{\mathbf{J}^* [U_2(\xi)U_3(\xi\eta)U_4(\eta\zeta)\dots]\mathbf{J}}{\mathbf{J}^* \left[\prod_{n=2}^{N-1} U_n \right] \mathbf{J}} \quad (3)$$

where $\mathbf{J}^* = [100]$, \mathbf{J} is the 3×1 column matrix of which elements are unity, and N is the number of skeletal bonds. The $U_2(\xi)$ matrix may be obtained by filling the columns of the U_2 matrix other than that corresponding to the ξ state with zero, and the $U_3(\xi\eta)$ matrix by filling the elements of the U_3 matrix other than that corresponding to the $\xi\eta$ conformation with zero, etc.

If *n*-alkanes are placed in nematic fields, i.e., in a flexible cylindrical potential well, conformations must be perturbed from the free state. By minor revision, the RIS scheme may be applicable for evaluation of conformer populations of such perturbed molecules. The C-C bonds are expected to have different degrees of the rotational freedom. Thus, statistical weights of individual C-C bonds must be distinguished:

Table I. Geometrical parameters of *n*-alkanes^a

Bond length/Å	
C-H	1.087
C-C	1.529
Bond angle/degree	
∠HCH of methyl group	107.7
∠HCC of methyl group	111.2
∠HCC of methylene group	109.3
∠CCC	113.2
Dihedral angle for <i>gauche</i> state, degree	
bond 2	±112.2
bonds $n(\geq 3)$	±113.3
Van der Waals radius/Å	
H	1.20
C	1.70

^a Determined for *n*-hexane by geometrical optimization using *ab initio* molecular orbital calculations at the HF/6-31G* level.

$$U_2 = \begin{pmatrix} 1 & \sigma'_2 & \sigma'_2 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (4)$$

and

$$U_n = \begin{pmatrix} 1 & \sigma'_n & \sigma'_n \\ 1 & \sigma'_n & \sigma'_n \omega'_n \\ 1 & \sigma'_n \omega'_n & \sigma'_n \end{pmatrix} (n \geq 3) \quad (5)$$

where σ'_n and ω'_n represent statistical weights including effects of the nematic field. In this modified RIS scheme, all possible molecular symmetries are taken into account, and conformer populations can be calculated from eq 3 using a small number of parameters: σ'_n s and ω'_n s ($n=2,3,\dots,N-1$). No *a priori* assumptions on conformational (internal) energies or potential functions of the nematic field are required.

Orientalional Order Parameters

Orientalional order parameters were derived from molecular shape. The principal axes of inertia, determined for each conformer, are assumed coincident with those of the ordering matrix. The shape of the conformer k is approximated by a rectangular parallelepiped with dimensions of A_{X_k} , A_{Y_k} , and A_{Z_k} ($A_{Z_k} \geq A_{X_k} \geq A_{Y_k}$).²⁵ X , Y , and Z directions are parallel to the principal axes of inertia. The parallelepiped is set so as to just fit each conformer with a van der Waals volume (Table I).²⁶ For evaluation of order parameters, the 1980 model of Samulski²⁷ was modified and used. The order parameter S_{ZZ_k} of a conformer k is assumed to be

$$S_{ZZ_k} = C(T, c) \left(\frac{A_{Z_k}}{A_{X_k} + A_{Y_k}} - \frac{1}{2} \right) \quad (6)$$

where $C(T, c)$ is the measure of orientational ordering due to the nematic field and depends on solute-solvent interaction as well as temperature T and solute concentration c . Biaxiality is assumed to be given by

$$\frac{S_{XX_k} - S_{YY_k}}{S_{ZZ_k}} = \frac{A_{X_k} - A_{Y_k}}{A_{Z_k}} \quad (7)$$

In Samulski's original model,²⁷ the conformer was ap-

proximated as an ellipsoid. The orientational order parameters were defined using the ellipsoid semiaxes α_X , α_Y , and α_Z , instead of A_{X_k} , A_{Y_k} , and A_{Z_k} . Here α_X is estimated from the principal moments of inertia, I_{XX} , I_{YY} , and I_{ZZ} , according to $\alpha_X = [(I_{YY} + I_{ZZ} - I_{XX}) \frac{5}{2M}]$, where M is molecular weight. To clarify shape and anisotropy in real space, the parallelepiped approximation was adopted.

^1H - ^1H Dipolar Coupling

Observed dipole coupling D_{ij} between two protons i and j of the solute can be expressed as^{16,17,20}

$$D_{ij} = \sum_k^K f_k D_{ij,k} \quad (8)$$

where K is the number of conformers. The sum of f_k s is equal to unity: $\sum_k^K f_k = 1$. Dipolar coupling $D_{ij,k}$ of the conformer k is given as^{4,28}

$$D_{ij,k} = -\frac{\gamma_H^2 h^2}{8\pi r_{ij,k}^3} \left\{ S_{ZZ_k} (3\cos^2\theta_{Z,ij,k} - 1) + (S_{XX_k} - S_{YY_k}) \times (\cos^2\theta_{X,ij,k} - \cos^2\theta_{Y,ij,k}) \right\} \quad (9)$$

where γ_H is the gyromagnetic ratio of proton, h is the Planck constant, and, e.g., $\theta_{Z,ij,k}$ is the angle between the Z axis and internuclear vector $\mathbf{r}_{ij,k}$ of the conformer k .

Maximum Entropy Method

The MaxEnt method is useful to derive reliable results from a restricted number of data.^{21,22} Conformer probability of the solute must satisfy the reproducibility of the experimental observations. Agreement between theory and experiment may be monitored by

$$\chi^2 = \sum_{ij} \frac{(D_{ij,\text{calc}} - D_{ij,\text{obsd}})^2}{\varepsilon_{ij}^2} \quad (10)$$

where $D_{ij,\text{calc}}$ and $D_{ij,\text{obsd}}$ are, respectively, calculated and observed dipolar couplings, and ε_{ij} is the experimental error.

Entropy of the conformer probabilities is²⁹

$$S(f_k) = \sum_{k=1}^K (f_k - m_k - f_k \ln \frac{f_k}{m_k}) \quad (11)$$

where m_k is the initial model of f_k . In the MaxEnt method, the most probable solution of f_k s may maximize S . Accordingly, the solution may be found at maximum of

$$Q = \alpha S - \frac{\chi^2}{2} \quad (12)$$

where α is the regularization constant, which counterbalances the two requirements: maximizing of entropy and reproduction of experiment. Entropy S is convex and χ^2 is concave, and thus Q always reaches a unique maximum. MaxEnt simulation is carried out under the restriction of the RIS approximation.

The MaxEnt method has been incorporated into mean-field theories for anisotropic fields and applied to conformational analysis of flexible molecules dissolved in nematic solvents.³⁰⁻³² This method has been modified for simultaneous analysis of different types of experi-

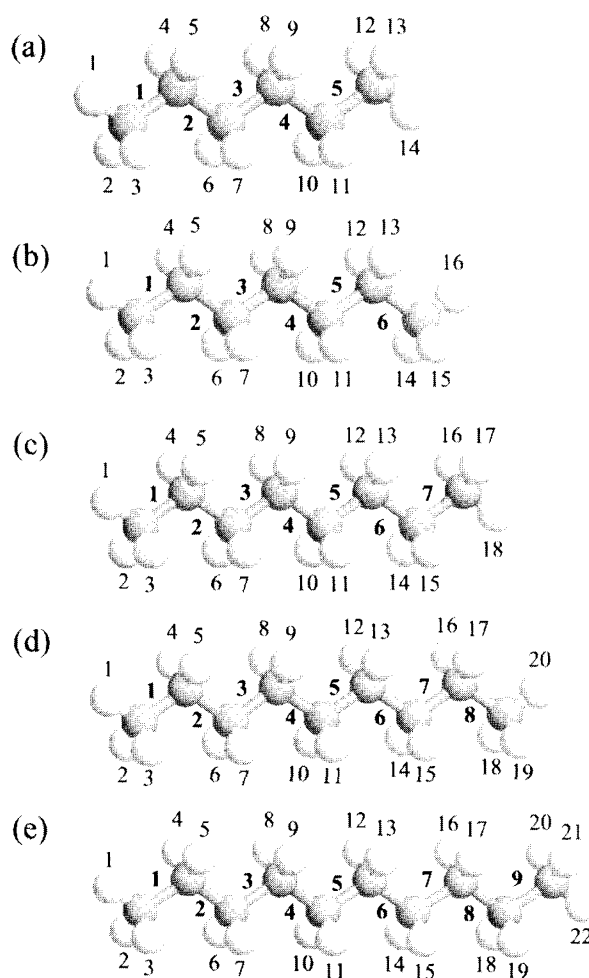


Figure 1. Schematic representation of n -alkanes in all-*trans* conformation: (a) n -hexane; (b) n -heptane; (c) n -octane; (d) n -nonane; (e) n -decane. Proton atoms and C-C bonds are numbered as indicated.

mental data from the flexible solutes.³³ However, our approach is based on the RIS scheme, and the MaxEnt method was adopted for parameter optimization to acquire the most probable solution from a restricted number of observations.

Procedure for Simulation

Based on the above, the simulation proceeds as follows: (Step 1) All possible conformations are enumerated within the framework of RIS approximation. Conformer fractions are calculated from eq 3 using a given set of statistical weight parameters σ'_n s and ω'_n s. Entropy S for conformer fractions is estimated according to eq 11 using a proper initial model m_k s. (Step 2) For each conformer, the principal axes of inertia are determined from geometrical parameters, and the dimensions A_{X_k} , A_{Y_k} , and A_{Z_k} of the conformer are evaluated. Orientational order parameters S_{ZZ_k} and $S_{XX_k} - S_{YY_k}$ are calculated from eqs 6 and 7. (Step 3) ^1H - ^1H dipolar couplings are calculated from eqs 8 and 9, and compared with experimental data to obtain χ^2 . Iterative computations of Steps 1 to 3 are carried out using a new set of variables σ'_n s, ω'_n s, and $C(T,c)$ determined so as to increase Q efficiently, until the Q function is maximized within a given allowance.

Table II. Calculated and observed values of dipolar couplings *n*-hexane

Proton pair ^a	<i>D</i> _{<i>ij</i>} /Hz	
	Calculated	Observed
<i>i</i> - <i>j</i>		
1-2	1557	1526
4-5	3202	3288
6-7	3744	3711
1-4	-275	-310
1-6	-841	-852
1-8	-515	-484
1-10	-260	-272
1-12	-163	-167
4-8	-1393	-1323
4-9	-895	-881
RMSE ^b /Hz	41	

^a For proton numbers *i* and *j*, see Figure 1. ^b Defined in eq 13.**Table III.** Calculated and observed values of dipolar couplings for *n*-heptane

Proton pair ^a	<i>D</i> _{<i>ij</i>} /Hz	
	Calculated	Observed
<i>i</i> - <i>j</i>		
1-2	1517	1489
4-5	3369	3461
6-7	3893	3897
8-9	4123	4093
1-4	-253	-226
1-6	-857	-916
1-8	-511	-520
1-10	-275	-290
1-12	-185	-192
1-14	-115	-127
4-8	-1436	-1453
4-9	-927	-924
6-10	-1538	-1575
6-11	-975	-975
RMSE ^b /Hz	34	

^a For proton numbers *i* and *j*, see Figure 1. ^b Defined in eq 13.

For simulation, the MemSys5 package³⁴ from the Maximum Entropy Data Consultants Ltd. was made to combine with the RIS scheme. Adjustment of the regulation constant α and calculations of *Q* and *S* are based on the original algorithm of MemSys5.³⁵

RESULTS AND DISCUSSION

Geometrical Parameters

Geometrical parameters determined from the *ab initio* molecular orbital (MO) calculations for *n*-hexane at the Hartree-Fock level of theory using the 6-31G* basis set (HF/6-31G*)^{36,37} were used for all *n*-alkanes here. The values are listed in Table I. The dihedral angle for the *trans* state was set equal to 0°. Dihedral angles for the *gauche* states of the bonds 2 and *n* (≥ 3) were based on those of the gtt and tgt conformers of *n*-hexane. The van der Waals radii of carbon and hydrogen atoms were taken from Bondi's table.²⁶

Analysis

The statistical weight parameter ω'_n represents the frequency of g^+g^- conformations at successive *n* - 1 and

Table IV. Calculated and observed values of dipolar couplings for *n*-octane

Proton pair ^a	<i>D</i> _{<i>ij</i>} /Hz	
	Calculated	Observed
<i>i</i> - <i>j</i>		
1-2	1656	1637
4-5	3479	3539
6-7	4050	4119
8-9	4363	4319
1-4	-292	-319
1-6	-912	-949
1-8	-510	-538
1-10	-288	-296
1-12	-205	-204
1-14	-135	-129
1-16	-89	-96
4-8	-1542	-1544
4-9	-961	-976
6-10	-1637	-1710
6-11	-1025	-1088
RMSE ^b /Hz	39	

^a For proton numbers *i* and *j*, see Figure 1. ^b Defined in eq 13.**Table V.** Calculated and observed values of dipolar couplings for *n*-nonane

Proton pair ^a	<i>D</i> _{<i>ij</i>} /Hz	
	Calculated	Observed
<i>i</i> - <i>j</i>		
1-2	1574	1546
4-5	3451	3570
6-7	3997	4104
8-9	4192	4420
10-11	4089	4220
1-4	-264	-265
1-6	-915	-958
1-8	-457	-539
1-10	-267	-300
1-12	-196	-206
1-14	-133	-138
1-16	-93	-93
1-18	-64	-73
4-8	-1580	-1554
4-9	-942	-977
6-10	-1640	-1721
6-11	-970	-1028
8-12	-1647	-1779
8-13	-960	-1097
RMSE ^b /Hz	90	

^a For proton numbers *i* and *j*, see Figure 1. ^b Defined in eq 13.

n bonds of the alkane chain. Even in the free state, these conformational sequences require as much as 3.0 kcal mol⁻¹ ($=2E_\sigma + E_w$) relative to the all-*trans* state.^{1,2} Since this must rarely occur in a uniaxial environment, ω'_n should be very small. To reduce the variables and facilitate simulation, all ω were assumed equal, *i.e.*, that the frequency of the chain folding does not depend on position. This hypothesis appears crude, because the central folding may more distort conformer shape and more disturb orientational orderings of solute and solvent than the terminal folding.

On the above assumption, parameters $C(T,c)$, σ'_n 's and ω' are treated as variables. All conformers within the framework of the RIS approximation were used: 27(*n*-hexane), 81(*n*-heptane), 243(*n*-octane), 729(*n*-

Table VI. Calculated and observed values of dipolar couplings for *n*-decane

Proton pair ^a	D_{ij}/Hz	
	Calculated	Observed
1-2	1712	1669
4-5	3608	3660
6-7	4218	4283
8-9	4559	4577
10-11	4689	4697
1-4	-315	-313
1-6	-931	-998
1-8	-490	-556
1-10	-280	-319
1-12	-198	-219
1-14	-142	-151
1-16	-102	-127
1-18	-76	-82
1-20	-54	-57
4-8	-1705	-1666
4-9	-967	-1020
6-10	-1856	-1863
6-11	-1062	-1062
8-12	-1885	-1970
8-13	-1078	-1140
RMSE ^b /Hz	43	

^a For proton numbers *i* and *j*, see Figure 1. ^b Defined in eq 13.

Table VII. Optimized parameters

	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane	<i>n</i> -Nonane	<i>n</i> -Decane
$C(T,c)$	0.431	0.406	0.409	0.373	0.392
σ'_2	0.355	0.295	0.231	0.193	0.189
σ'_3	0.453	0.365	0.324	0.226	0.201
σ'_4			0.412	0.374	0.311
σ'_5					0.393
ω'	0.000	0.000	0.000	0.000	0.000

Table VIII. Orientational order parameters of *n*-alkanes

	$\langle S_{ZZ} \rangle$	$\langle S_{XX} - S_{YY} \rangle$
<i>n</i> -Hexane	0.185	0.0106
<i>n</i> -Heptane	0.202	0.0127
<i>n</i> -Octane	0.229	0.0137
<i>n</i> -Nonane	0.231	0.0156
<i>n</i> -Decane	0.258	0.0205

nonane), and 2187 (*n*-decane). To investigate the dependence of the results on initial m_k , two sets of initial data were adopted: (1) uniform population, *i.e.*, $m_k = 1/K$ and (2) free state population, *i.e.*, the m_k value calculated from eqs 1–3 using $E_\sigma = 0.5$ and $E_\omega = 2.0 \text{ kcal mol}^{-1}$. Although the latter always gave more rapid convergence than the former, both data provided essentially the same results in all simulations.

In Tables II–VI, calculated ^1H – ^1H dipolar couplings of the *n*-alkanes are compared with the corresponding experimental data. Reproducibility may be given by the root-mean-square error (RMSE)

$$\text{RMSE} = \left[\sum_{ij}^L \frac{(D_{ij,\text{obsd}} - D_{ij,\text{calc}})^2}{L} \right]^{1/2} \quad (13)$$

where L is the number of experimental data. RMSEs for *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane were obtained as 41, 34, 39, 90, and 43 Hz, and the experimental error ε_{ij} was reported to be $\pm 25 \text{ Hz}$.²⁰ Except

Table IX. Conformer probabilities of *n*-alkanes

	Total no. of conformers	No. of <i>gache</i> bonds	No. of conformers	Probabilities	
				in LC	Free state ^a
<i>n</i> -Hexane	27	0	1	0.22	0.18
		1	6	0.51	0.49
		2	12	0.25	0.30
		3	8	0.02	0.03
<i>n</i> -Heptane	81	0	1	0.14	0.11
		1	8	0.44	0.38
		2	24	0.34	0.38
		3	32	0.07	0.12
		4	16	0.01	0.01
<i>n</i> -Octane	243	0	1	0.11	0.06
		1	10	0.37	0.28
		2	40	0.37	0.40
		3	80	0.13	0.22
		4	80	0.02	0.04
		5	32	0.00	0.00
<i>n</i> -Nonane	729	0	1	0.08	0.04
		1	12	0.32	0.20
		2	60	0.37	0.36
		3	160	0.17	0.29
		4	240	0.06	0.10
		5	192	0.00	0.01
		6	64	0.00	0.00
<i>n</i> -Decane	2187	0	1	0.06	0.02
		1	14	0.27	0.14
		2	84	0.36	0.31
		3	280	0.23	0.32
		4	560	0.07	0.17
		5	672	0.01	0.04
		6	448	0.00	0.00
		7	128	0.00	0.00

^a Calculated using conformational energies of $E_\sigma = 0.5$ and $E_\omega = 2.0 \text{ kcal mol}^{-1}$ for a reduced temperature $T^* = 0.875(T^* = T/T_{\text{NI}})$.

for *n*-nonane, agreement between theory and experiment is thus satisfactory.

In Table VII, optimized values of variables are listed. ω' was found to be null for all compounds, indicating even short chains such as *n*-hexane can hardly have $g^\pm g^\mp$ sequences in the nematic field. If *n*-alkanes had such folding, as chain length increases, the nematic order should be more disturbed by the defect. In other words, a longer *n*-alkane chain should not also have the conformational sequences. Consequently, the above simplification that all ω'_n s are set to the same value is justified.

Orientational Order, Conformation, and Shape of Solutes

In Table VIII, averaged orientational order parameters of the solutes are listed as calculated from

$$\langle S_{ZZ_k} \rangle = \sum_k^K S_{ZZ_k} f_k \quad (14)$$

and

$$\langle S_{XX} - S_{YY} \rangle = \sum_k^K (S_{XX_k} - S_{YY_k}) f_k \quad (15)$$

Since NMR measurements for all *n*-alkanes were performed at the same reduced temperature T/T_{NI} of

Table X. Averaged molecular dimensions of *n*-alkanes

	$\langle A_X \rangle / \text{\AA}$		$\langle A_Y \rangle / \text{\AA}$		$\langle A_Z \rangle / \text{\AA}$		$V^a / \text{\AA}^3$		$\langle r \rangle^b / \text{\AA}$	
	Nematic	Free state ^c	Nematic	Free state ^c	Nematic	Free state ^c	Nematic	Free state ^c	Nematic	Free state ^c
<i>n</i> -Hexane	5.56	5.61	5.00	5.04	9.69	9.64	269	273	5.70	5.62
<i>n</i> -Heptane	5.85	5.93	5.13	5.20	10.81	10.64	324	328	6.75	6.59
<i>n</i> -Octane	6.02	6.14	5.28	5.34	11.83	11.58	376	380	7.78	7.51
<i>n</i> -Nonane	6.31	6.49	5.38	5.47	12.88	12.49	437	443	8.82	8.40
<i>n</i> -Decane	6.64	6.82	5.46	5.58	13.82	13.35	501	508	9.78	9.26

^a $V = \langle A_X \rangle \langle A_Y \rangle \langle A_Z \rangle$. ^b Average distance between terminal methyl carbons. ^c Calculated using conformational energies of $E_\sigma = 0.5$ and $E_w = 2.0$ kcal mol⁻¹ for reduced temperature $T^* = 0.875$.

0.875,²⁰ we may compare order parameters among *n*-alkanes. $\langle S_{ZZ} \rangle$ increases with chain length.

In Table IX, conformer probabilities of *n*-alkanes are arranged according to the number of *gauche* bonds and compared with those for the free state. In LC, conformations with a small number of *gauche* states are more populated than in the free state. Fractions of the all-*trans* conformation were estimated as 22%(18%) for *n*-hexane, 14%(11%) for *n*-heptane, 11%(6%) for *n*-octane, 8%(4%) for *n*-nonane, and 6%(2%) for *n*-decane. The values in the parentheses are those for the free state.

From average dimensions of the rectangular parallelepiped, we may estimate the shape of a solute molecule. Ensemble averages, $\langle A_X \rangle$, $\langle A_Y \rangle$, and $\langle A_Z \rangle$, can be evaluated from, e.g.,

$$\langle A_X \rangle = \sum_k^K A_{Xk} f_k \quad (16)$$

The average distance between terminal methyl carbons was calculated and is shown in Table X. Differences in $\langle A_X \rangle$, $\langle A_Y \rangle$, and $\langle A_Z \rangle$ between in LC and in the free state are small, but indicate that nematic constraints somewhat enhance shape anisotropy. This can be seen from the end-to-end distance $\langle r \rangle$. Elongation relative to the free state was evaluated as 1.4% for *n*-hexane, 2.4% for *n*-heptane, 3.6% for *n*-octane, 5.0% for *n*-nonane, and 5.6% for *n*-decane. Relative elongation increases with chain length. Interestingly, average volume V of the rectangular parallelepiped was found to be virtually constant.

Comparison with Previous Studies

¹H-¹H dipolar couplings from *n*-hexane were analyzed according to the previous method using SOM approximation.¹² All conformers were assumed to have the same order parameters. In the simulation, adjustable parameters were S_{ZZ} , $S_{XX} - S_{YY}$, S_{XY} , S_{XZ} , S_{YZ} , σ_2 , and σ_3 , while ω_3 was fixed at zero.

RMSE was minimized to 28 Hz and thus comparable to the experimental error of 25 Hz. This simulation gave better agreement with experiment than the RIS-MaxEnt scheme (41 Hz), probably due to the difference in the number of variables. The fraction of all-*trans* conformation of the *n*-hexane was obtained as 0.34 (0.22), and those of conformers including one, two, and three *gauche* bonds are 0.50, 0.14, and 0.01 (0.51, 0.25, and 0.02), respectively. The values in the parentheses represent the corresponding fractions evaluated here. Our previous analysis suggested that the *n*-hexane molecule is considerably rigid. These results appear consistent with thermodynamic studies,^{18,19} which indicate that *n*-alkanes

behave like a chain composed of two complete rigid and additional semiflexible segments at infinite dilution. It should be noted that ¹H-¹H dipolar couplings were measured at a solute concentration of as high as 30 mol%. Thus, it seems reasonable to conclude that the SOM model overestimates populations of anisotropic conformers.

¹H-¹H dipolar couplings were analyzed using mean-field theories²⁰ based on the elastic continuum model (0.27),¹⁰ the biaxial-parallelepiped model (0.28),^{8,9} chord representation (0.20),¹¹ and Monte Carlo sampling (0.233).³⁸ Recently, the experimental data have also been treated by molecular dynamics simulations (0.21)³⁹ and the maximum entropy internal method (0.198).⁴⁰ Here, the values in parentheses represent the all-*trans* fraction of *n*-hexane, evaluated by the individual models. Conformer populations obtained here are quantitatively comparable to those reported in these studies. It is of interest and significance that our model gives essentially the same results as other theories.

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