Computer simulation of a real liquid crystal

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We carried out a computer simulation study of a liquid crystal using semi-empirical atom–atom potentials (the Lennard-Jones 6-12 modification) with nematic 4-ethoxybenzylidene-4-n-butylaniline as an example. The two stages of the calculations were (1) simulation of the structure of an isolated molecule and (2) Monte Carlo simulation of liquid crystal phase. The energy of the system was calculated as the sum over all atomic pair interactions. The molecular structure preferred in the nematic phase is discussed.

1. Introduction

The interpretation of N.M.R. spectra and the study of the molecular structure of liquid crystals by N.M.R. spectroscopy is confronted with the difficulty of obtaining a stable and unambiguous solution. This difficulty is caused by the large number of parameters which have to be determined resulting from the low molecular symmetry and flexibility. One way to solve this problem is to simulate the molecular structure of liquid crystals. In [1, 2] the influence of the conformations of the semi-flexible alkyl chains of mesogenic molecules were modelled. The influence of the liquid crystal environment was introduced by restricting the trans-gauche isomerization of the chains to those occuring within a hypothetical cylinder defined by the central molecular fragment. In [3, 4] a more accurate model of the butyl chains for TBBA molecule was developed. However, with taking the molecular environment into account, the authors had to allow a sub-stantial simplification of the intermolecular potential by introducing a set of adjust-able parameters.

As distinct from [1–4], where the liquid crystal environment is considered as an energy or molecular field with empirical characteristics, we suggest a simultaneous simulation of the molecular and phase structure. Our approach has the following features:

(1) the use of atom–atom potentials to compute the conformational energy of an isolated molecule;

(2) using the Monte-Carlo technique of computer simulation with atom–atom potentials to the molecular structures prefered by the liquid-crystalline phase; this makes the use of adjustable parameters unnecessary;

(3) obtaining a full set of data on the liquid crystal molecular structure, the intra- and intermolecular mobility, and the orientational order parameters.

The nematogen 4-ethoxybenzylidene-4'-n-butylaniline (EBBA) ($T_{CN} = 310 \, K$, $T_{NI} = 353 \, K$) at $T = 312 \, K$ and atmospheric pressure has been chosen as an example with which to illustrate this approach.

2. Simulation of an isolated molecule

To simplify the computations, a precalculation of the conformational energies of an EBBA molecule (see figure 1) in a vacuum was performed following the method described in [5]. For each conformational state the energy is calculated as

$$E = E_{vW} + E_{rot} + E_{val}. \tag{1}$$

The first term in equation (1) is the energy of the van der Waals interactions between the atoms. It is calculated using the standard Lennard-Jones 6-12 potential

$$E_{vW} = \sum_{i<j} (A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6}), \tag{2}$$

where r_{ij} is the distance between atoms i and j,

$$A_{ij} = \left(\frac{r_{0i} + r_{0j}}{2}\right)^6 \frac{B_{ij}}{2}, \quad B_{ij} = \frac{1520\,\alpha_i\alpha_j}{(\alpha_i/N_i^{ef})^{1/2} + (\alpha_j/N_j^{ef})^{1/2}},$$

α_k is polarizability, N_k^{ef} is the effective number of electrons on the valence shell, and r_{0k} is the van der Waals radius of atom k. The torsional energy is calculated using

$$E_{rot} = \sum_{b} \frac{V_{0b}}{2} (1 \pm \cos(n_b\tau_b - \delta_b)). \tag{3}$$

Here τ_b is the dihedral angle between two planes defined by the four atoms surrounding the bond b (see figure 2) and V_{0b} is the torsional barrier around the bond b. The parameters n_b and δ_b are defined by the valency of the bonded atoms. The third term in equation (1) corresponds to the energy produced by the deviation of the bond angle φ_k from its equilibrium value φ_{0k}:

$$E_{val} = \tfrac{1}{2} \sum_{k} C_k(\varphi_k - \varphi_{0k})^2, \tag{4}$$
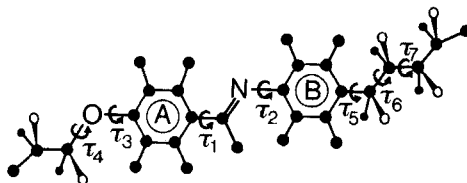
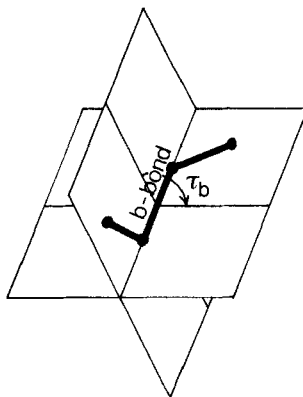Figure 1.   A molecule of EBBA. The notation for the main dihedral angles is shown.

Figure 2.   Definition of the dihedral angles τ_b. The value of the angle represents its deviation from the cis position. The positive direction is clockwise.

Table 1.   The interaction parameters describing the atoms in EBBA.

Atom	α	N^{ef}	$r_0/\text{Å}$	$C/\text{kJ mol}^{-1}$	$\varphi_0/°$
C_I, aliphatic	0·93	5·2	3·4	170	112
C_{II}, aromatic	0·93	5·2	3·4	210	120
C_{III}, double bonded	1·51	5·2	3·4	210	120
O	0·59	7·0	3·4	250	118
N	0·7	6·1	3·1	250	120
H_I, aliphatic	0·42	0·85	2·4	–	–
H_{II}, aromatic and near double bond	0·42	0·85	2·4	–	–

Table 2.   The parameters describing the chemical bonds in EBBA.

Bond	$V_0/\text{kJ mol}^{-1}$	n	$\delta/°$	Length/Å
C_I–C_I	12·6	3	0	1·53
C_I–C_{II}	42	3	0	1·52
C_I–O	11·3	3	0	1·43
C_{II}–C_{II}	–	–	–	1·39
C_{II}–C_{III}	19·7	2	180	1·50
C_{II}–O	14·7	2	180	1·37
C_{II}–N	8·4	2	180	1·43
C_{III}–N	84	2	180	1·26
C_I–H_I	–	–	–	1·1
C_{II}–H_{II}	–	–	–	1·0
C_{III}–H_{II}	–	–	–	1·05

where the values of C_k determine the strength of the bond-angle potential. Electrostatic interactions were taken to be insignificant.

The values of the bond lengths and angles used in the simulations result from the mean values observed by X-ray diffraction in the crystal [6, 7]. We suppose the bond lengths and angles do not change their values when the crystal melts to form the nematic state. The values of the atom and bond parameters required to calculate the intramolecular energy were taken from [5]. These values are listed in tables 1 and 2. Possible conformations of an EBBA molecule were found by variation of the dihedral angles τ_b ($b = 1 \ldots 7$) (see figure 1). It was established that changes in the angles τ_1 and τ_2 are independent of each other. The corresponding energy profiles, shown in figure 3, are similar to those obtained in [8]. The most probable conformers have the dihedral angle τ_1 fluctuating in the interval $-9° \ldots 9°$. The angle τ_2 is equal to $+45°$
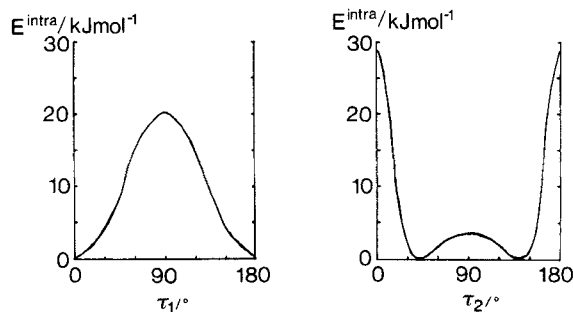
Figure 3.   The conformational energy profiles for rotation on the angles τ_1 and τ_2.

or $-45°$. The benzene rings, A and B, rotate by 180° jumps. The values obtained for τ_1 and τ_2 are within the normal range. The angle τ_1 is equal or is close to 0° not only for EBBA but also for a great number of benzylideneanilines [6, 7, 9, 10]. The angle τ_2 for EBBA in the solid phase, according to X-ray data, is 57·6° [6]. When the crystal melts to give the nematic phase the angle τ_2, decreases to 43° as shown by N.M.R., [11]. We note that the value of τ_2 more clearly than for τ_1 depends not only on the phase but also on the type of groups substituted in the benzylideneaniline core. Thus for nematic 4-methoxybenzylidene-4'-*n*-butylaniline τ_2 is equal to 47° [12], and for other mesogenic benzylideneanilines τ_2 varies over a rather wide interval [9, 10, 13].
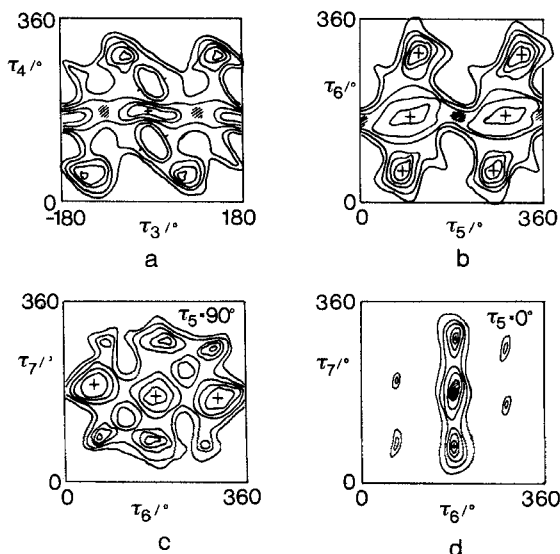

Figure 4.   Conformational energy maps for an EBBA molecule. The distance between the energy levels is equal to $4·2\,kJ\,mol^{-1}$. The definition of the angles is shown on figure 1. Plus sign indicates the energy minima of an isolated molecule; cross hatching indicates the minima for the nematic state.

The ethoxy group of the isolated molecule tends to be located in the plane of ring A (see figure 4(a)). The butyl chain is perpendicular to ring B (see figure 4(b)). This chain retains considerable freedom of its trans-gauche isomerization and has 18 possible conformers (see figure 4(c)). The freedom of the τ_6 angle rotation is distorted only for the flat arrangement of ring B and the butyl chain (see figure 4(d)). However the probability of such conformations for an isolated molecule is low (see figure 4(b)). The calculated structure of the butyl chain differs sharply from its structure in the crystal, where it possesses a complete trans conformation and lies in the plane of ring B [6]. Thus, in a vacuum we have found that an EBBA molecule has 72 conformations with an approximately identical energy of about $935\,kJ\,mol^{-1}$. The conformers are characterized by dihedral angles: $\tau_1 = 0°$; $\tau_2 = \pm45°$; $\tau_3 = 0°$, 180°; $\tau_4 = 180°$; $\tau_5 = \pm90°$; τ_6 and $\tau_7 = 180°$, $\pm60°$.

3.   Simulation of liquid crystal

We assume that the strong influence of the nematogenic environment on the molecular structure leads to the appearance of unstable conformers. Therefore we

Table 3. The values of the dihedral angles τ_b described for the conformers.

b	Angles/°		
1		0	
2		± 45	
3		0, ± 90, 180	
4		180	
5	± 90		0, 180
6	± 60, 180		180
7	± 60, 180		± 60, 180

took into consideration some conformers with an energy greater than the minimum energy found in a vacuum. To the 72 stable conformers we added the 120 conformers which are unstable in a vacuum and have energies of less than $1000 \, \text{kJ} \, \text{mol}^{-1}$. All of the 192 conformers considered are defined by the values of dihedral angles τ_b and are given in table 3.

The total energy of the liquid crystal was calculated as the sum of inter- and intramolecular energies. The value of intramolecular energy was taken from calculations for a vacuum. The intermolecular energy was calculated as the sum of the energies from each pair of atoms belonging to different molecules including the hydrogen atoms. Equation (2) was used, where now i and j are atoms in different molecules. The number of force centres in this interaction model was equal to the number of molecules in the system multiplied by the number of atoms in one molecule. To reduce the computer time for the simulation we have considered a small number of molecules in a cubic cell with periodic boundary conditions. An isothermal–isobaric ensemble consisting of 60 EBBA molecules (2640 force centres) was examined in a cell with side $\sim 27 \, \text{Å}$. The number of molecules and the size of the cell were selected such that the density in the model system was close to the density of real EBBA namely $\sim 1 \cdot 02 \, \text{g} \cdot \text{cm}^{-3}$ at 40°C [14].

Simulation of the liquid-crystalline phase was carried out by the Monte-Carlo procedure using Metropolis sampling. The variables in this procedure were

the coordinates of the molecular centres of gravity (x_i, y_i, z_i);
the Euler angles defining the molecular orientation in the cell $(\varphi_i, \theta_i, \psi_i)$;
the length of cell side (L);
the conformation of each molecule.

The change in the variable for one step of the procedure amounted to $\Delta x_i \leqslant 0 \cdot 1 \, \text{Å}$, $\Delta y_i \leqslant 0 \cdot 1 \, \text{Å}$, $\Delta z_i \leqslant 0 \cdot 2 \, \text{Å}$, $\Delta \varphi_i \leqslant 5°$, $\Delta \theta_i \leqslant 3°$, $\Delta \psi_i \leqslant 5°$ and $\Delta L \leqslant 0 \cdot 025 \, \text{Å}$. The configurations were accepted or rejected in accordance with the Boltzmann factor $\exp(-\Delta E / kT)$. ΔE was determined by

$$\Delta E = E^{\text{inter}} - E_0^{\text{inter}} + E^{\text{intra}} - E_0^{\text{intra}} + p(V - V_0) - NkT \ln(V/V_0), \quad (5)$$

where E_0^{inter} and E^{inter} are the energies of intermolecular interactions in the system before and after the move, E_0^{intra} and E^{intra} are the intramolecular conformational energies, V_0 and V are the corresponding volumes of the base cell, p is pressure, and N is the number of molecules in the system. The E^{intra} values were taken from the vacuum calculation using equation (1), and the E^{inter} values were obtained from equation (2). To reduce the computer time for calculating E^{inter} the maximum radius of interaction between atoms i and j was taken to be equal to $7 \, \text{Å}$. To check the simulation results some of the computations were repeated with interaction radii of $10 \, \text{Å}$ and $12 \, \text{Å}$.

The main problems in the computer simulation were caused by the high energy of the system. As a result we had either to go through a large number of configurations or construct several parallel Markov chains with different initial characteristics. Complete equilibration of the system required about 10^3 moves per molecule. The averaging of the desired parameters was done on 1–2 M configurations. The generation of the new conformations was achieved by either successive or simultaneous variation of the parameters; this did not have any effect on the equilibration rate.

The initial set of parameters characterizing the system was random, except for the angle θ_i between the long molecular axes and the Z axis of the base cell. The latter was chosen as the director. The values of θ_i were from $0°$ to $45°$. The long (z) axis and the short (x and y) axes of each conformer were taken to coincide with the principal axes of the inertia tensor. Because of possible correlation of intra and intermolecular mobility the accumulation of the orientational ordering matrix components was performed separately for each of the conformers. These components were averaged taking into account the statistical weight of each conformer. As a result we obtained the two independent principal order parameters

$$S_{zz} = (1/2)\langle 3\cos^2\theta - 1\rangle$$

and

$$S_{xx} - S_{yy} = (3/2)\langle \sin^2\theta\cos\psi\rangle,$$

which describe the ordering of the molecules in the nematic phase. The initial value of order parameter S_{zz} for the system was ~ 0.3 and it changed rapidly to its equilibrium value of about 0.8. This value turns out to be close to the experimental value $S_{zz} = 0.68$, reported in [11]. The calculated value $S_{xx} - S_{yy}$ was approximately 0.03; this value corresponds rather well to those observed in experiments on various nematics [15, 16]. However, since this value is comparable to the computational error, we cannot seriously consider it as reflecting the biaxial ordering.

In our simulation the length of the side of the cell changed insignificantly from its initial value of 27 Å. Thus the resulting density differed little from the original density.

A set of the most probable molecular structures for the liquid crystal phase was also obtained. It must be noted that these structures do not coincide with the set found in a vacuum. The variation of the angle τ_1 observed in an isolated EBBA molecule remained the same in the liquid crystal. The angle τ_2 retained its value of $\pm 45°$. However, in the simulated system the molecules can have only one sign, either positive or negative. This indicates that the liquid-crystalline state of EBBA leads to a cooperative behaviour of the intramolecular τ_2 rotation in each of the nematic domains. Unlike the isolated molecule the probability of conformers with the flexible butyl chain perpendicular to ring B was below 3 per cent. In contrast, ring B and the first three carbon atoms of the chain lay in the same plane. The angle τ_5 was equal to $0°$. Rotation around the τ_6 angle was not observed. The freedom of the τ_7 rotation was preserved. The rigidity of the butyl chain of the EBBA molecule in the nematic phase is confirmed by Raman scattering experiments [17]. The ethoxy fragment of EBBA tended to take a position normal to ring A which is not typical of an isolated molecule. In this case the τ_3 angle turns out to be equal to $+90°$ when $\tau_2 = +45°$ and $-90°$ when $\tau_2 = -45°$.

Thus the molecular structure of EBBA in its nematic phase proved remarkably different from that in a vacuum. Simulation of the liquid crystal yields an almost rigid molecule. Rotation around the τ_4, τ_5 and τ_6 angles is frozen and the rotation on the

angles τ_2 and τ_3 tended to be cooperative. Except for the free rotation of the methyl groups and 180° jumps of the benzene rings only trans-gauche isomerization on angle τ_7 was observed. As a result, more than 74 per cent of all the molecular conformers can be reduced to two practically indistinguishable structures with $\tau_2 = -45°$ and $+45°$.

4. Conclusions

Simulating liquid crystal structure by means of atom–atom potentials yields a set of molecular conformations for an isolated molecule. Combining this with the Monte Carlo method enables us to investigate the influence of the liquid crystal environment on the molecular conformation. The results obtained for EBBA have demonstrated that this influence can be significant. It is clear that the computational difficulties limit the number of molecules which can be studied. However, results obtained from the EBBA simulation correspond rather well to known experimental data. The full set of liquid crystal characteristics obtained as a result of such computer simulations can be useful for interpreting N.M.R. spectra and for evaluating various liquid crystal properties. This work is now in progress.

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