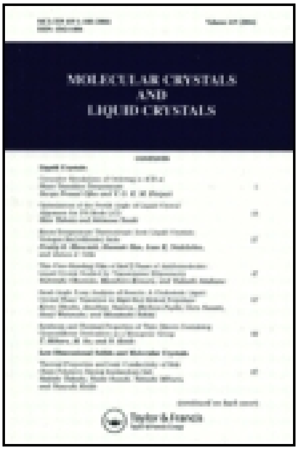

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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To cite this article: Andrei V. Komolkin & Yuri V. Molchanov (1990): Molecular Structure of Rod-Like Nematics. The Simple Simulation Accounting Intermolecular Interactions, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 192:1, 173-177

To link to this article: http://dx.doi.org/10.1080/00268949008035626

Mol. Cryst. Liq. Cryst. 1990, Vol. 192, pp. 173–177
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Printed in the United States of America

MOLECULAR STRUCTURE OF ROD-LIKE NEMATICS. THE SIMPLE SIMULATION ACCOUNTING INTERMOLECULAR INTERACTIONS

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Abstract The model accounting steric factors and intra- and intermolecular van der Waals interactions is presented. The molecular structure of 5CB is discussed.

INTRODUCTION

Many attempts to study the molecular structure of liquid crystals by numerical calculation accounting intermolecular interactions have been made recently. Volino et al[1] simulated the averaged conformation of TBBA butyl chain using mean field potential. Samulski et al[2,3] took into consideration the influence of the liquid crystal environment by introducing a hypothetical cylinder, which restricted the molecular aliphatic chain mobility. The authors of Refs.|4,5| examined the behaviour of the "rigid" molecular fragments in mean torque field. In the works[2-5] probabilities of alkyl chain conformers were obtained using the DMR data for verification. Simulating liquid crystals structure by means of atom-atom potentials[6] yields conformation and arrangement of the molecules, but the computational difficulties limit abilities of this method.

Here we carry out the simple calculation of the molecular structure of nematic 4-n-pentyl-4'-cyanobiphenyl (5CB). The results are tested using the PMR and DMR data.

THE METHOD

The probability of the existence of the molecular conformer is given by Boltzmann factor exp(-E/kT). For each conformer the energy is considered as a sum

$$E = E^{intra} + E^{inter}. \qquad (1)$$

Intramolecular term E^{intra} is determined following the Ref. | 6 | (the case of an isolated molecule) as a sum of the energy of the van der Waals interactions between the atoms, the torsional energy, and the energy of the deviation of bond angles from its equilibrium values.

Calculating the intermolecular energy, we assume that the liquid crystal environment restricts the free volume for a molecule. Nematic molecule rapidly rotates around the long molecular axis. It allows us to consider this volume as a cylinder with the axis coincident with the long molecular axis. The conformational mobility and the rotation of the entire molecule are independent, and the time of the existence of a conformer is shorter than the correlation time of the rotational diffusion. So when the molecule changes its conformation, the long molecular axis does not reorient in the laboratory frame, but the positions of some molecular fragments are being moved relatively to the axis. For the each conformer this axis is the principal axis of the molecular inertia tensor. The cylinder radius does not depend on the conformational state and this is the only parameter describing the influence of the environment on the molecule. Being the molecule inside the cylinder it suffers the influence of the environment molecules. The main part of the influence is the van der Waals interactions between atoms. For the full calculation of these interactions one ought to sum the interactions of each atom of the studied molecule with the atoms of the environment. In the first approximation accounting short range of the van der Waals forces we are limited in consideration of the only atoms of the environment placed on the cylinder wall in the nearest point to the each atom of the molecule. The environment atom is believed to be the hydrogen atom. In this case the intramolecular energy is calculated using the standard Lennard-Jones 6-12 potential with the MCMS parameters[7]

$$E^{inter} = \sum_i^N (A_{iH}/r_{iH}^{12} - B_{iH}/r_{iH}^{6}), \quad (2)$$

where r_{iH} is the distance between atom i and the cylinder surface (Fig.1).

SIMULATION OF 5CB

The molecular structure of 5CB is shown in Figure 1.

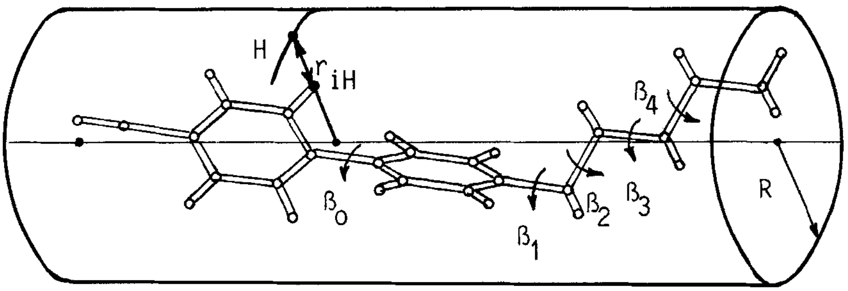

FIGURE 1 The molecule of 5CB in hypothetical cylinder.

The distributions of probabilities $p(\beta_0)$ for angle β_0 between the two planes of the rings in biphenyl is given in Figure 2.

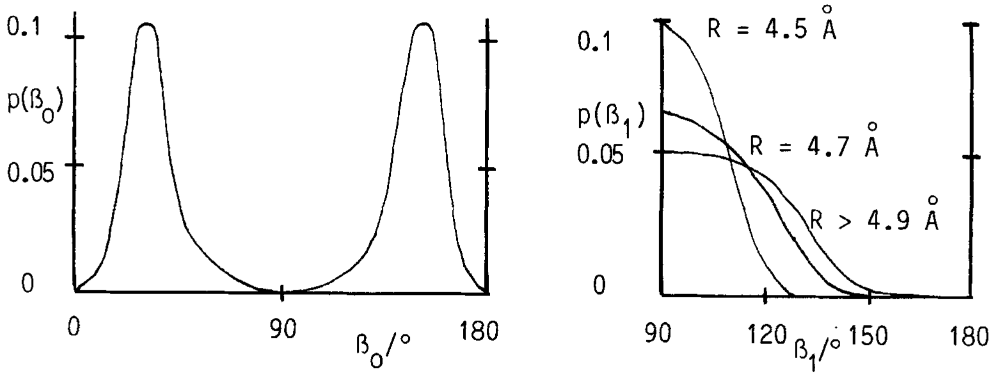

FIGURE 2 The probability of angles β_0 and β_1 in the conformers of 5CB.

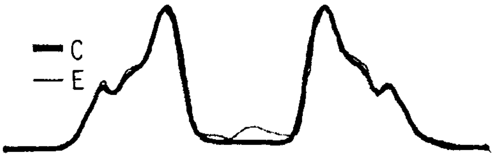

FIGURE 3 Calculated (C) and experimental (E) PMR spectra of 5CB-d_{11}.

The profile is practically independent of the alkyl chain conformation and the cylinder radius R. It has its maximum at 30°. The good agreement of the computated and the experimental proton NMR spectra of the biphenyl unit of 5CB is obtained for $\beta_0 = 31°$ (Figure 3)[8]. This result is practically coincident with the results of other methods.

The most probable value of the first dihedral angle β_1 in the alkyl chain at the junction of the aromatic ring is equal to 90°. Variation of radius R gives only changes in maximum height of the probability profile (Figure 2).

The alkyl chain of 5CB was simulated within the rotational isomeric state limit. We admitted the angle values in trans (Tr) state 180° and in gauche (G$\pm$) states as 60° and 68°. In the computations we fixed $\beta_0 = 31°$ and $\beta_1 = 90°$. The resulting sets of possible conformers for some values of R including $R = \infty$ (the isolated molecule) are presented in Table 1. In the last column of the Table the conformer probabilities of the pentyl chain

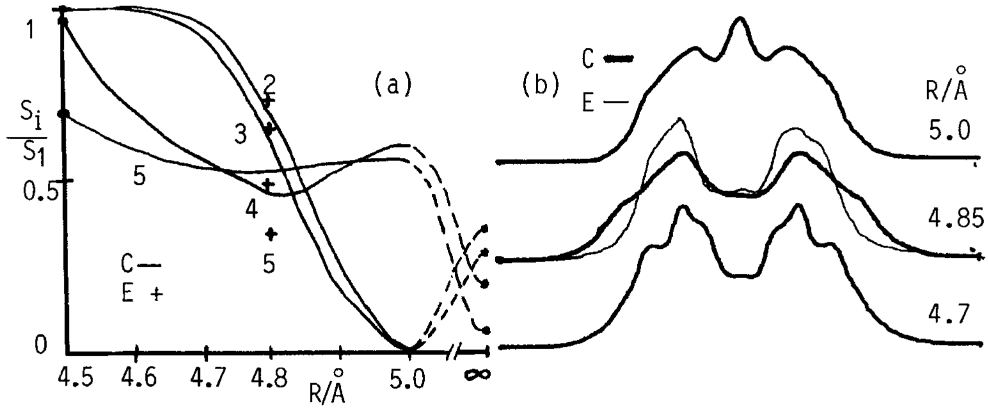

FIGURE 4 Calculated (C) and experimental (E) DMR splittings for 5CB-d_{11} (a) and PMR spectra of 5CB (b).

TABLE 1 Conformer probabilities of 5CB (%).

Angles			Cylinder radii R/Å						
β_2	β_3	β_4	4.70	4.80	4.85	4.90	5.00	∞	Ch,∞
Tr,	Tr,	Tr	44.7	32.5	25.7	19.5	12.1	5.4	15.2
Tr,	Tr,	G±	0	0.1	0.4	1.3	3.5	2.8	7.9
Tr,	G±,	Tr	15.4	11.9	9.7	7.6	5.0	2.9	7.9
Tr,	G±,	G±	11.0	13.4	12.2	10.1	6.8	2.4	4.1
G±,	Tr,	Tr	0	0	0	0	0	15.8	7.9
G±,	Tr,	G±	0	0	0	0	0	8.1	4.1
G∓,	Tr,	G±	0	1.8	5.9	11.7	20.1	6.7	4.1
G±,	G±,	Tr	0	0	0	0	0	5.9	4.1
G±,	G±,	G±	1.2	6.5	8.9	9.6	8.6	2.5	2.2

non-interacting with biphenyl unit are given for R = ∞ .

The influence of this interaction on conformational structure is obvious. It leeds to growth of the probability of G$^{\pm}$TrTr conformers and redistribution of others.

For the deuteriated pentyl chain of 5CB, the best agreement of the DMR splitting observations[9,2] and the calculations is obtained when R is equal 4.8 Å (Figure 4a). The best agreement of the PMR spectra of 5CB is observed with R = 4.85 Å (Figure 4b).

The PMR and DMR spectra are caused by the different mechanisms of interactions. The offered model gives the same molecular structure of 5CB for the both PMR and DMR data. It means that the model can be successfully employed for the conformational analysis.

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