Supplemental Information

for

Influence of Electrostatic Interactions on the Properties of Cyanobiphenyl Liquid Crystals Predicted from Atomistic Molecular Dynamics Simulations

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Figure S1. Local coordinate system used to define molecular polarizability in x, y and z direction in ab initio calculations and force field fitting procedure.

Order parameter evolution from simulations using the as-fit (original) force field

Figure S2a shows the order parameter evolution for POL force field at all temperatures investigated. Figure S2b shows the instantaneous order parameter for the NP version of the as-fit force field. For this force field at 340K the system became completely isotropic after about 60ns. At 335K the NP system showed a faster rate of decay of ordering, achieved similar S value as the NP 330K system after about 150ns, but after that the system began fluctuating between 0.3 and 0.6 indicating that this system is right near the transition between nematic and isotropic phases. Overall, we estimate T_{NI} from NP force field to be between 330K and 335K, which is still rather unsatisfactory compared to experimental value of 307K.

Figure S2. Instantaneous order parameter obtained from simulations using (a) POL version of the as-fit force field and (b) using the NP force field at all temperatures investigated.

Order parameter time evolution from simulations using the refined force field of *modT* and *modD*

The changes in biphenyl dihedral potential parameters (*modT* force field) have noticeably decreased the T_{NI} , from 330-340K, predicted by the original force field, down to 308-320K. Specifically as shown in Figure S3a, at 308K the system displayed very stable nematic phase for over 200ns and showed no signs of NI phase change. However, the 313K system with nematic initial ordering gradually transitioned to isotropic phase, reaching an S value of ~ 0.25 at around 113ns, and then went back to the nematic phase, indicating that this system could be right near the transition between nematic and isotropic phases. At 320K, the system spent first 80ns fluctuating around S value of 0.5, then finally transitioned to isotropic phase. Lastly, for 340K, the system showed quite stable isotropic phase.

The SI also provides plots of the order parameter evolutions for simulations using *modD* force fields (Figure S3c and d). An interesting behavior for the *modD*_POL force field system at 325K can be observed. In this system, the nematic order parameter shows fluctuations/transitions between highly ordered nematic phase and almost disordered isotropic phase. The observed multiple switches between two phases over a relatively short time scale of 230ns indicates that this behavior is likely caused by close proximity of this temperature to the innate T_{NI} .

Figure S3. Order parameter evolution obtained from simulations using *modT*_POL (a), *modT*_NP (b) and *modD*_POL (c), *modD*_NP (d) force fields.

Order parameter time evolution from simulations using combined *modTD* force field

Simulations using combined *modTD* force field showed that we can achieve even better description of T_{NI} compared to experiment. These simulations showed that at temperatures equal or above 313K the 5CB bulk clearly transitions to isotropic phase, while at 303 K is stable in the nematic. Therefore, we estimate the transition temperature for this force field to be around 310 K.

Figure S4. Evolution of the order parameter in simulations using combined *modTD* force field.

Force fields parameters

Figure S5. 5CB molecule with numbering schemes for each atomic interaction site.

The nonbonded interaction potential $U^{NB}(r)$ is comprised of repulsion and dispersion $U^{RD}(r)$, fixed charges coulombic $U^{coul}(r)$, and polarization energy $U^{pol}(r)$ from induced dipole-dipole and induced dipole-induced dipole interactions,

$$U^{NB}(r) = U^{RD}(r) + U^{coul}(r) + U^{pol}(r) = \sum_{i>j} (A_{\alpha\beta} \exp(-B_{\alpha\beta} r_{ij}) - C_{\alpha\beta} r_{ij}^{-6} + D \left(\frac{12}{B_{\alpha\beta} r_{ij}} \right)^{12}) + \sum_{i>j} \left(\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right) - \frac{1}{2} \sum_i \vec{\mu}_i \vec{E}_i^0$$

(SI 1)

where $\vec{\mu}_i = \alpha_i \vec{E}_i^{tot}$ is an induced dipole at force center i , α_i is the isotropic atomic polarizability, $\vec{E}_i^{tot}$ is the total electrostatic field at the atomic site i due to permanent charges q_i and induced dipole $\vec{\mu}_j$, ϵ_0 is the permittivity of free space. $A_{\alpha\beta}$ and $B_{\alpha\beta}$ serve to specify the repulsive core of the potential, and $C_{\alpha\beta}$ is the dispersion parameter for interaction between atoms i and j with atom types α and β , the specific values for $A_{\alpha\beta}$, $B_{\alpha\beta}$ and $C_{\alpha\beta}$ are shown in Table S1. The term $D(12/B_{\alpha\beta} r_{ij})^{12}$, with $D = 5 \times 10^{-5}$ kcal/mol for all pair interactions, is essentially zero at typical nonbonded atomic separations, but becomes the dominant term at $r_{ij} < 1$ Å, ensuring that the repulsive interaction at close approaches remains monotonic in nature. Nonbonded interactions are included for atoms separated by three or more covalent bonds.

Table S1. Parameters for the nonbonded potential of 5CB.

Nonbonded parameters	$A_{\alpha\beta}$ (kcal/mol)	$B_{\alpha\beta}$ ($\text{\AA}^{-1}$)	$C_{\alpha\beta}$ (kcal $\text{\AA}^6/\text{mol}$)	Induced polarizability ($\text{\AA}^3$)	Mass (g/mol)
N1	23599.4	3.2432	744.06	1.52	14.007
C2	19530.6	3.4783	404.69	1.2	12.011
C3, 4, 6, 9, 11, 14, 16, 18, 19, 21	97431	3.6222	519.87	1.4	12.011
H	5352.3	4.3646	22.59	0.35	1.008
C8, 13	97431	3.6222	519.87	0	12.011
C23, 26, 29, 32	97431	3.6222	519.87	0.9	12.011
C35	108283	3.6405	560.53	0.9	12.011

Nonbonded parameters (cross terms)	$A_{\alpha\beta}$ (kcal/mol)	$B_{\alpha\beta}$ ($\text{\AA}^{-1}$)	$C_{\alpha\beta}$ (kcal $\text{\AA}^6/\text{mol}$)
N1 - C2	21004.2	3.34647	548.74
N1 - C3, 4, 6, 9, 11, 14, 16, 18, 19, 21	45430.98	3.39676	621.94
N1 - H	7893.52	3.54719	129.65
N1 - C8, 13	45430.98	3.39676	621.94
N1 - C23, 26, 29, 32	45430.98	3.39676	621.94
N1 - C35	47658.32	3.40253	645.81
C2 - C3, 4, 6, 9, 11, 14, 16, 18, 19, 21	43301.47	3.54516	458.68
C2 - H	8239.03	3.75864	95.61
C2 - C8, 13	43301.47	3.54516	458.68
C2 - C23, 26, 29, 32	43301.47	3.54516	458.68
C2 - C35	45560.74	3.55295	476.28
C3, 4, 6, 9, 11, 14, 16, 18, 19, 21 - H	19676.84	3.87866	108.37
C3, 4, 6, 9, 11, 14, 16, 18, 19, 21 - C8, 13	97431	3.6222	519.87
C3, 4, 6, 9, 11, 14, 16, 18, 19, 21 - C23, 26, 29, 32	97431	3.6222	519.87
C3, 4, 6, 9, 11, 14, 16, 18, 19, 21 - C35	102702.04	3.63127	539.82
H - C8, 13	19676.84	3.87866	108.37
H - C23, 26, 29, 32	19676.84	3.87866	108.37
H - C35	20901.72	3.89336	112.53
C8, 13 - C23, 26, 29, 32	97431	3.6222	519.87
C8, 13 - C35	102702.04	3.63127	539.82
C23, 26, 29, 32 - C35	102702.04	3.63127	539.82

The total potential energy $U_{\text{tot}}(r)$ for each interaction site (r) in the system is defined as

$$U^{\text{tot}}(r) = U^{\text{NB}}(r) + \sum_{\text{bonds}} U^{\text{bond}}(r_{ij}) + \sum_{\text{bends}} U^{\text{bend}}(\theta_{ijk}) + \sum_{\text{dihedrals}} U^{\text{dihedral}}(\varphi_{ijkl}) + \sum_{\text{impropers}} U^{\text{improper}}(\varphi_{ijkl}^{\text{imp}}) \quad (\text{SI } 2)$$

where the sums are over all bonds, bends, dihedrals, and improper dihedrals in the system. The potential energy from bonds, bends, dihedrals, and out-of- plane improper dihedrals are defined as

$$U^{\text{bond}}(r_{ij}) = \frac{1}{2} k_{ij}^{\text{bond}} (r_{ij} - r_{ij}^0)^2 \quad (\text{SI } 3)$$

$$U^{\text{bend}}(\theta_{ijk}) = \frac{1}{2} k_{\alpha\beta\gamma}^{\text{bend}} (\theta_{ijk} - \theta_{ijk}^0)^2 \quad (\text{SI } 4)$$

$$U^{dihedral}(\varphi_{ijkl}) = \sum_n \frac{1}{2} k_{\alpha\beta\gamma\delta,n}^{dihedral} [1 - \cos(n\varphi_{ijkl})] \quad (\text{SI } 5)$$

$$U^{improper}(\varphi_{ijkl}^{imp}) = \frac{1}{2} k_{\alpha\beta\gamma\delta}^{imp} (\varphi_{ijkl}^{imp})^2 \quad (\text{SI } 6)$$

where θ_{ijk} and θ_{ijk}^0 are the instantaneous and equilibrium bending angles formed by atoms i, j and k, φ_{ijkl} is the dihedral angle of atoms i, j, k, and l, and φ_{ijkl}^{imp} is the out of plane improper dihedral angle for an sp² orbital at site j, $k_{\alpha\beta\gamma}^{bend}$, $k_{\alpha\beta\gamma\delta,n}^{dihedral}$ and $k_{\alpha\beta\gamma\delta}^{imp}$ are the force constants, and α , β , γ , and δ are the atom type correspond to site i, j, k, and l, respectively. The values for all the bonded interaction parameters are shown in Table S2.

Table S2. Parameters for the bonded potential of 5CB.

Bonds	K_{bond} (kcal/mol/Å ²)	r_{ij}^0 (Å)	r_{ij}^0 (constrained) (Å)
C2 - N1	1300	1.16	1.16
C2 - C3	618	1.42	1.42
C3 - C4	618	1.4	1.4
H - C4	655	1.083	1.083
C4 - C6	618	1.4	1.4
H - C6	655	1.083	1.083
C6 - C8	618	1.41	1.41
C8 - C13	618	1.41	1.41
C16 - C18	618	1.4	1.4
C18 - C23	618	1.48	1.5
H - C23	655	1.089	1.089
C23 - C26	618	1.53	1.53
H - C26	655	1.1	1.1
C26 - C29	618	1.53	1.53
C32 - C35	618	1.53	1.53
H - C35	655	1.1	1.1

Bends	K_{bend} (kcal/mol/rad)	ϕ_{ijk} (deg)
C3-C2-N1	0	179.2
C4-C3-C2	140	127.6
C6-C4-C3	144	120
H5-C4-C3	77	120
C4-C6-C8	144	120
H7-C6-C8	77	120
C6-C8-C9	144	119
C6-C8-C13	144	120
C16-C18-C23	140	120
H24-C23-C18	86	107.3
C18-C23-C26	140	112
H24-C23-H25	77	108.2
H24-C23-C26	86	110
C23-C26-C29	108	112
C26-C29-C32	108	112
C29-C32-C35	108	112

H33-C32-C35	86	110.5
H36-C35-C32	86	110.5
H35-C35-H37	77	107.7

Torsions	$K1$ (kcal/mol)	$K2$ (kcal/mol)	$K3$ (kcal/mol)	$K4$ (kcal/mol)
C6-C4-C3-C11	0	5.347		
C8-C6-C4-C3	0	25		
H7-C6-C4-H5	0	1.575		
C4-C6-C8-C13	0	25		
C6-C8-C13-C14	0(31.510) ^a	2.138 (1.763) ^a	0(-0.295) ^a	-0.24 (-0.026) ^a
H24-C23-C18-C16	0	0	-0.3	
C26-C23-C18-C16	0	0.15		
H27-C26-C23-C18	0	0	-0.3	
C29-C26-C23-C18	0	0.15		
H27-C26-C23-H24	0	0	-0.3	
H30-C29-C26-C23	0	0	-0.3	
C32-C29-C26-C23	-0.271	0.152	-0.187	-0.5
C35-C32-C29-C26	-0.271	0.152	-0.187	-0.5
H30-C29-C32-C35	0	0	-0.3	
H36-C35-C32-C29	0	0	-0.3	
H36-C35-C32-H33	0	0	-0.3	

^aTorsional parameters in parenthesis are used in *modTD* force field

Improper	K^{imp} (kcal/mol)
C4-C3-C2-C11	36.5
C4-C6-C8-H7	41.8
C16-C18-C23-C19	10