

Enantiotopic Discrimination and Director Organization in the Twist-Bend Nematic Phase

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1. Structure and relative energy of conformers

According to the Rotational Isomeric State (RIS) approximation [1], the 8CB molecule is described in terms of a finite number of conformers. The dihedral angles that define the conformational degrees of freedom of 8CB-d₂ are shown in Figure S1. Conformers were selected based on a knowledge of the torsional potentials for the various dihedrals. The torsional potential for the biphenyl twist angle χ_0 exhibits four degenerate minima ($\chi_0 \sim \pm 35^\circ, \pm 145^\circ$) [2], whereas that for the χ_1 dihedral has two minima ($\chi_1 = \pm 90^\circ$) [3]. Each bond in the alkyl chain ($\chi_2 - \chi_7$) has three minima, corresponding to the so-called *trans* (*t*), *gauche+* (*g+*) and *gauche-* (*g-*) states.

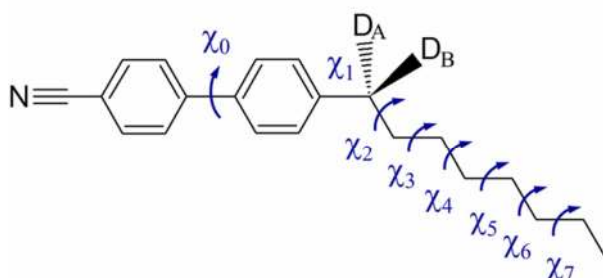


Figure S1. Molecular structure of 8CB-d₂ with labelling of the two prochiral deuterons and of the dihedral angles (the rotating dihedrals are indicated by arrows).

In our calculations we considered only conformers having no more than one *gauche* state in the alkyl chain. Two equivalent conformers of biphenyl were assumed ($\chi_0 \sim \pm 35^\circ$), together with a single state of the C_{ar}-CH₂ bond ($\chi_1 = 90^\circ$). Thus a total number of 26 conformers, listed in Table S1, was assumed. The structure of some of them is shown in Figure S2. Conformers are labeled by a six letter code: the first letter indicates the state of biphenyl (*P* and *M* for right- and left-handed twist, respectively) and the subsequent letters refer to the state of the CH₂-CH₂ bonds (*ttttt*, *g+tttt*, *g-tttt*, *tg+tttt*, *tg-tttt*, etc).

Table S1. Conformers of 8CB considered in our calculations.

1	<i>Mttttt</i>	10	<i>Mtg-tttt</i>	19	<i>Mttttg+t</i>
2	<i>Pttttt</i>	11	<i>Mttg+ttt</i>	20	<i>Pttttg-t</i>
3	<i>Mg+ttttt</i>	12	<i>Pttg-ttt</i>	21	<i>Pttttg+t</i>
4	<i>Pg-ttttt</i>	13	<i>Pttg+ttt</i>	22	<i>Mttttg-t</i>
5	<i>Pg+ttttt</i>	14	<i>Mttg-ttt</i>	23	<i>Mttttg+</i>
6	<i>Mg-ttttt</i>	15	<i>Mtttg+tt</i>	24	<i>Pttttg-</i>
7	<i>Mtg+tttt</i>	16	<i>Ptttg-tt</i>	25	<i>Pttttg+</i>
8	<i>Ptg-tttt</i>	17	<i>Ptttg+tt</i>	26	<i>Mttttg-</i>
9	<i>Ptg+tttt</i>	18	<i>Mtttg-tt</i>		

Assuming that the dihedral angles in the alkyl chain are uncorrelated, the conformational energy of the *J*-th conformer can be expressed as:

$$V^J = \sum_{i=2}^7 \Delta V_i \delta_{i,g}^J, \quad (\text{S1})$$

where the sum is over dihedral angles, ΔV_i is the *gauche-trans* energy difference for the *i*-th bond and $\delta_{i,g}^J$ is the Kronecker delta ($\delta_{i,g}^J=1$ if the *i*-th bond is in the *g+* or *g-* state, otherwise $\delta_{i,g}^J=0$). Energy differences were evaluated at the quantum chemical level, by DFT with M06-2X functional and 6-31+G** basis set [4]. For χ_2 the value $\Delta V_2 = -1.1$ kJ/mol was obtained, in agreement with the literature [5]. For all the other chain dihedrals $\Delta V_i = 2.2$ kJ/mol was found, a value in agreement with the results of high-level *ab initio* calculations [6].

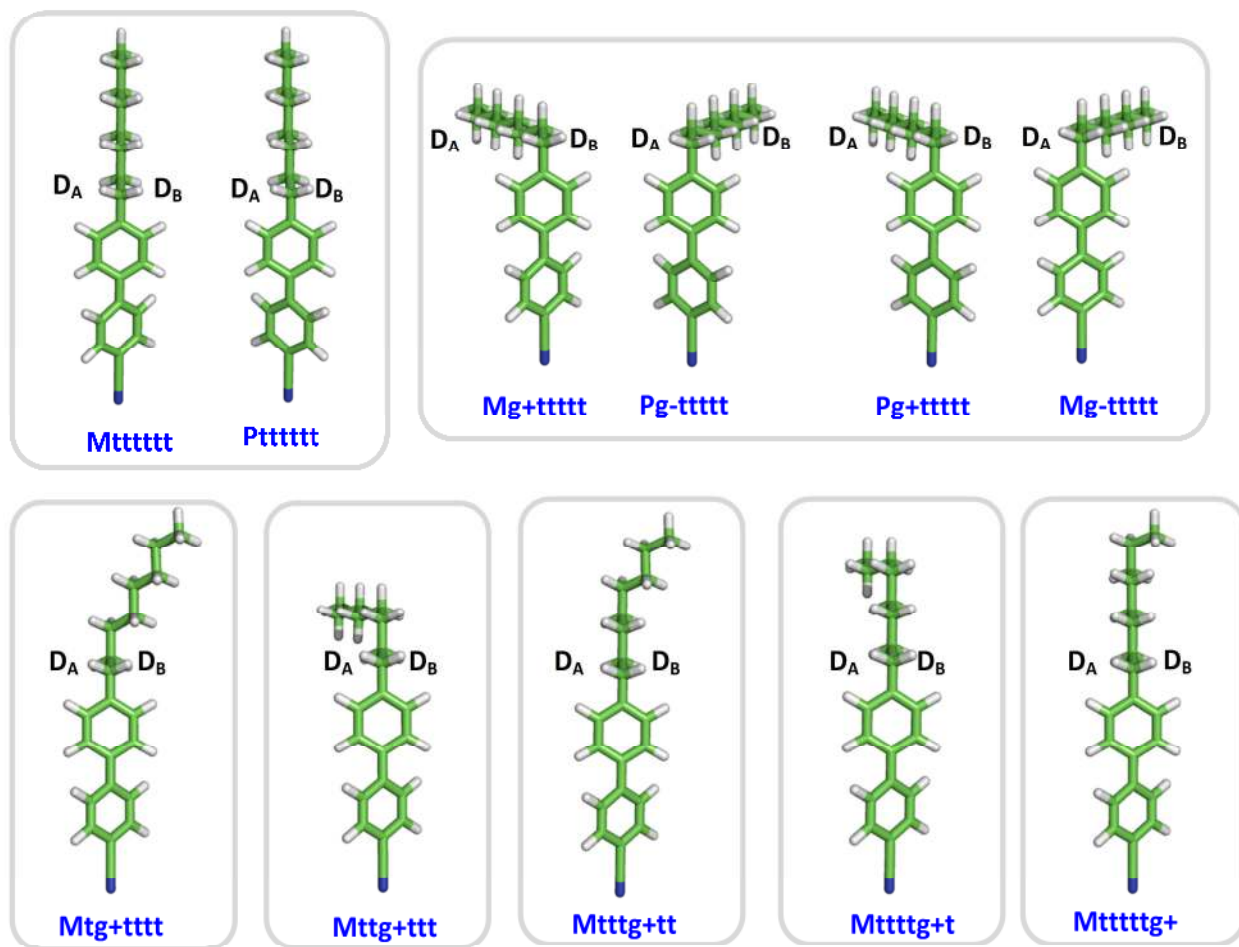


Figure S2. Some of the conformers of 8CB-d₂ employed for the calculations of the quadrupolar splittings.

2. Details on calculation of S_{CD} order parameters

According to eq. (5) in the main text, calculation of the S_{CD} order parameters requires the sum of quantities evaluated for single conformers. The partition function Q_I and the average $\langle \cos^2 \beta_{CD} \rangle_I$ are computed for each conformer by integrating over the (α, β, γ) angles that define the molecular orientation in the LAB frame, with its Z axis parallel to the helix axis (see Figure S3).

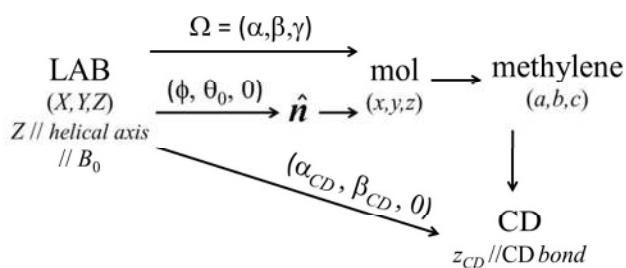


Figure S3. Reference frames and the transformations between them.

For each orientation the potential of mean torque $U(\Omega)$, eq. (4) in the main text, is calculated as the sum of contributions from discrete elements of the molecular surface. The contribution to the potential of mean torque of a given tessera is calculated as:

$$P_2(\hat{n} \cdot \hat{s}) = \frac{3}{2} \left[\sin^2 \theta_0 (s_x^2 \cos^2 \phi + s_y^2 \sin^2 \phi + s_x s_y \sin 2\phi) + s_z^2 \cos^2 \theta_0 + s_x s_z \sin 2\theta_0 \cos \phi + s_y s_z \sin 2\theta_0 \sin \phi \right] - \frac{1}{2} \quad (\text{S1})$$

where s_x (s_y , s_z) are components of the unit vector \hat{s} normal to the tessera, expressed in the LAB frame and ϕ is the azimuthal angle, defined as $\phi = 2\pi Z/p$, with p being the helical pitch.

A tessellation into triangles of the molecular surface was used, as defined by the algorithm reported in ref. [7] and implemented in the program MSMS. The following parameters were used: rolling sphere radius equal to 0.3 nm, surface density of vertices equal to 500 nm⁻² [8], together with the van der Waals radii $r_H = 0.1$ nm, $r_N = 0.15$ nm and $r_C = 0.185$ nm [9].

3. S_{CD} order parameters of single conformers

Figure S4 shows the effect of the chain conformation on the quadrupolar splittings calculated in the nematic phase, $\Delta v = \Delta v_{DA} = \Delta v_{DB}$, for a range of ϵ -values. The curve labeled as *ttttt* was obtained by averaging the results computed for the *Pttttt* and *Mttttt* conformers of 8CB-d₂ (see Figure S2), that differ in the biphenyl twist angle. The curve labeled as *gtttt* reports the splittings calculated by averaging over the four conformers: *Pg+tttt*, *Mg+tttt*, *Pg-tttt*, *Mg-tttt* (see Figure S2). Analogous considerations hold for the other curves. We can see in the figure that at low orienting strength the largest splittings were obtained for the *ttttt* set of conformers, and splittings are predicted to decrease monotonically as the *gauche* state is moved from the tail towards the first position of the alkyl chain (*gtttt* set), but at higher ϵ -values odd-even effects appear.

Figure S5 shows the mean and the difference of the quadrupolar splittings, calculated as a function of the orienting strength ϵ for 8CB-d₂ in the N_{TB} phase, with $\theta_0 = 30^\circ$ and $p = 50$ Å. For both quantities, the largest values are obtained for the *ttttt* set of conformers and an odd-even effect can be detected.

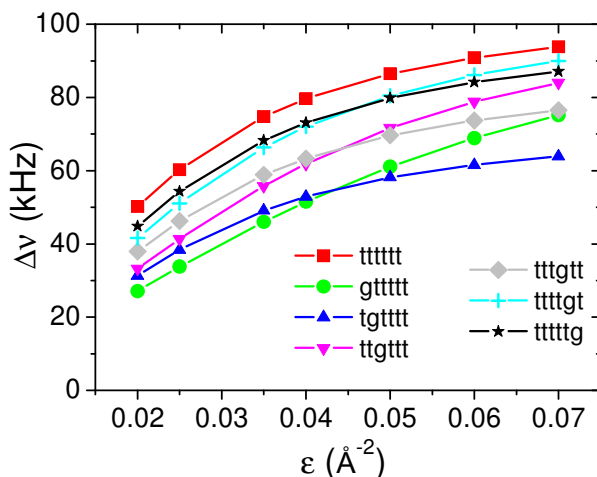


Figure S4. Quadrupolar splittings, $\Delta\nu$, calculated for conformers of 8CB- d_2 in the nematic phase, as a function of the orienting strength, ϵ .

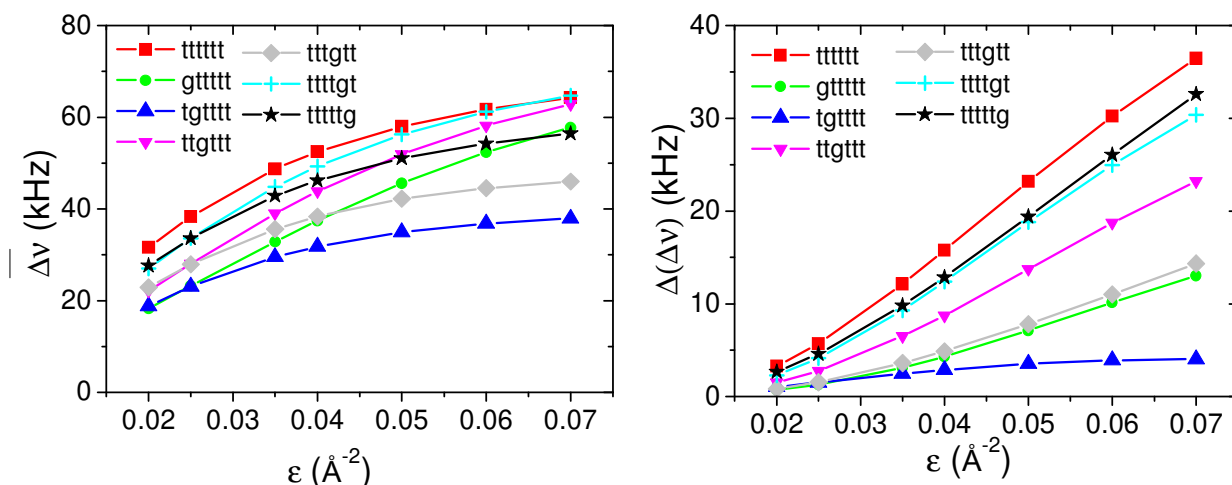


Figure S5. Mean (left) and difference (right) of the quadrupolar splittings, $\Delta\nu$, calculated for conformers of 8CB- d_2 in the N_{TB} phase, as a function of the orienting strength, ϵ . The conical angle $\theta_0=30^\circ$ and the helix pitch $p=50 \text{ \AA}$ were assumed.

3 Conformational distribution

Figure S6 shows the conformational distribution, calculated using Eq. (6) of the main text, in the isotropic phase, in the nematic phase close to the N_{TB} -N transition ($\epsilon=0.023 \text{ \AA}^{-2}$) and in the N_{TB} phase ($\theta_0^*=35^\circ$, $p = 50 \text{ \AA}$, $\epsilon = 0.075 \text{ \AA}^{-2}$). A temperature of 376 K, comparable to the experimental N_{TB} -N transition temperature of the CB7CB liquid crystal host [10], was assumed in the Boltzmann exponent. The conformer probability in the isotropic phase is determined solely by the torsional potential, thus it reflects the *trans/gauche* energy difference. Since the absolute minimum of $V(\chi_2)$ corresponds to a *gauche* state, conformers having a *gauche* in the first $\text{CH}_2\text{-CH}_2$ bond have the highest probability. The next most probable conformers are those with an all-*trans* chain; finally there are the conformers having a *gauche* state in a $\text{CH}_2\text{-CH}_2$ bond different from the first one,

which all have the same probability. In the liquid crystal phases the interaction with the environment is superimposed on the torsional potential, and gives a different stabilization of the conformers, depending on how well they are accommodated. All-*trans* conformers, which are the most elongated, become the most stable, and some difference is introduced between conformers having a *gauche* in even (χ_2, χ_4, χ_6) or odd (χ_3, χ_5, χ_7) positions along the chain, the first less elongated than the last. This is an example of the odd-even effect. The changes observed on moving from the isotropic to the N phase are magnified when the N_{TB} phase is considered, but this is only due to the higher ordering (larger ϵ -value in the calculations). There is a further effect that is peculiar to the chiral N_{TB} phase, that is the different probability of enantiomeric conformers (such as *Mttttt* and *Pttttt*). Again the largest differences are for the all-*trans* and for conformers with a *gauche* state in odd positions along the chain. However, these differences are very small, and clearly scarcely significant if compared to the large effect of the chiral N_{TB} environment on the quadrupolar splittings, which has been demonstrated in the main text.

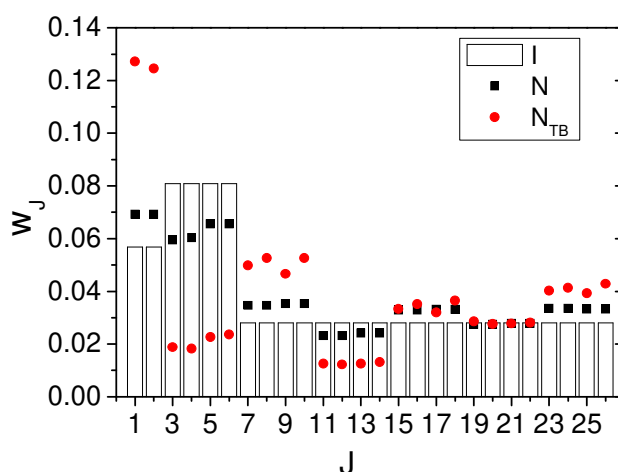


Figure S6. Conformer distribution calculated for 8CB in the isotropic ($\epsilon = 0$, bars), in the nematic ($\epsilon = 0.023 \text{ \AA}^{-2}$, black squares) and in the N_{TB} phase ($\epsilon = 0.075 \text{ \AA}^{-2}$, red circles).

4 Quadrupolar splittings for a fictitious achiral conformer

Figure S7 shows the quadrupolar splittings calculated for a single, fictitious achiral conformer of 8CB- d_2 having an all-*trans* chain and perpendicular rings in the biphenyl moiety; this structure has C_s point symmetry. The results reported in the Figure are intended only to highlight the role of molecular chirality and should not be compared with the experimental data. They were obtained assuming for each ϵ value the same p and θ_0 values used for the calculations shown in Figure 3(b) of the main manuscript, which had been estimated for the set of physically meaningful conformers of 8CB.

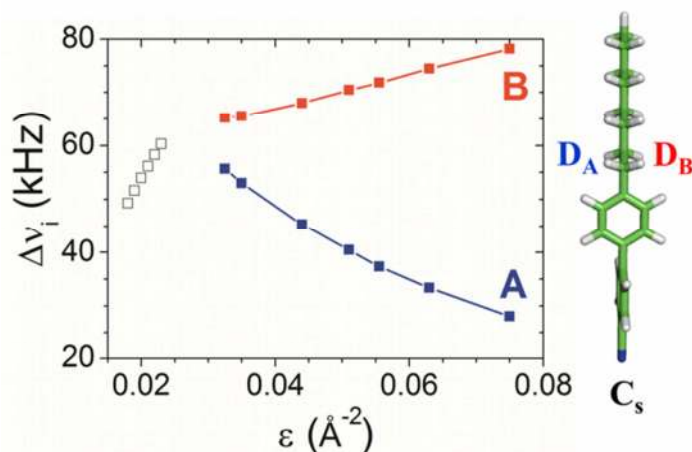


Figure S7. Quadrupolar splittings calculated for the achiral conformation of 8CB-d₂ shown on the right, in the nematic phase (open symbols) and in the N_{TB} phase along a path of constant helical pitch, $p=50$ Å (closed symbols).

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