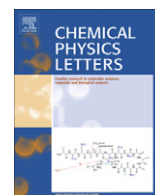




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The butane condensed matter conformational problem

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ABSTRACT

From the dipolar couplings of orientationally ordered *n*-butane obtained by NMR spectroscopy we have calculated conformer probabilities using the modified Chord (Cd) and Size-and-Shape (CI) models to estimate the conformational dependence of the order matrix. All calculation methods make use of GAUSSIAN 03 structures for the *gauche* and *trans* conformers. Calculations were performed for both the Rotational Isomeric State (RIS) approximation, as well as a continuous gas-phase potential for the dihedral angle rotation. Conformational probability distribution functions for butane as a solute in the ordered liquid–crystal solvent are obtained.

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Comprehension of the conformational statistics of chain molecules is essential to an understanding of the properties of these ubiquitous compounds. For example, the facility with which cyclic structures are formed in a chemical reaction from acyclic chains is related to the statistical distribution of the two ends of the chain relative to one another and so depends on their conformational characteristics. Constitutive properties of a chain molecule, which are dependent upon its conformation, include the mean-square dipole moments, the optical anisotropy and the spectral dichroism of the molecule. The behaviour of flexible hydrocarbons in condensed phases is particularly important in the field of liquid crystals as they are an essential component of mesogens that form partially ordered phases [1]. Butane (Fig. 1) is the simplest flexible alkane with only one conformational degree of freedom and is well suited to the study of the effect of the condensed phase on the conformational behaviour of non-rigid molecules.

Flory suggested that the intramolecular potential which gives rise to hydrocarbon conformers should closely resemble that in the gas phase with the conformational space populated according to the Boltzmann distribution over conformations as a function of intramolecular energy with intermolecular effects being ignored [2]. This view was later challenged by Chandler et al. whose rigorous theory of hydrocarbons predicted an increase in the *gauche* population resulting from short-range packing in the liquid phase [3,4]. Experiments have given credence to the latter view with gas-phase studies typically reporting the *trans*–*gauche* energy, E_{tg} , to be 788–884 cal/mol [5–9] while studies of *n*-butane, both as a

liquid and dissolved in other isotropic liquid solvents, consistently report a lower range of 502–597 cal/mol [10–12].

Proton dipolar couplings from the NMR spectra of molecules in partially ordered phases are an excellent means to obtain conformational information as they are very accurate and highly sensitive to the relative distances between hydrogens on a given solute molecule [1]. Obtaining these values for spin systems with more than eight spins is difficult because of the multitude of lines that are characteristic of such spectra, and the normal approach is to use selective deuteration and/or multiple quantum techniques to solve the congested spectra. Recent applications of sophisticated Evolutionary Algorithm analysis have reduced this task to a much more routine exercise [13].

In order to say something useful on the subject of condensed-phase effects on conformational statistics it would be good to extract a probability distribution function to compare with that of the gas phase. A problem in this respect arises when extracting conformational information from dipolar couplings since the probability of a conformer, p^n , appears multiplied by its order matrix, $S_{\alpha\beta}^n$,

$$D_{ij} = \frac{2}{3} \sum_n p^n \sum_{\alpha\beta} S_{\alpha\beta}^n D_{ij,\alpha\beta}^n \quad (1)$$

and there is no straightforward way to determine each separately [14] ($D_{ij,\alpha\beta}^n$ is defined later in Eq. (4)). One way around this is to use mean-field models (that describe the orientational potential which gives rise to $S_{\alpha\beta}^n$) in order to estimate how the order parameters change with conformation. One such orientational model describes the interaction between solute and liquid crystal as arising from the size and shape anisotropy of the solute; a particularly successful variant of this treatment is the Circumference Integral (CI) model [15]. Another model is specially tailored to chain molecules, called the modified Chord (Cd) model, and treats the C–C bond ori-

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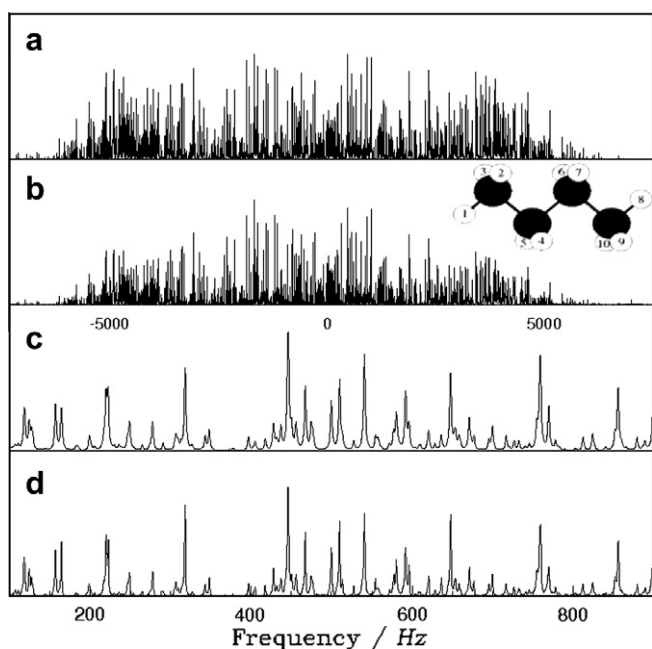


Fig. 1. Calculated (a) and experimental (b) NMR spectrum of *n*-butane in 1132 at 298.5 K. (c and d) An expanded region of the calculated and experimental spectra.

entation relative to the director and correlations between orientations of neighbouring C–C bonds as key factors in molecular ordering [16].

Another important aspect of this problem is how we think of the different accessible conformations that can be populated and what their relative importance and properties are. Since there is no axis system for butane dissolved in a liquid–crystal solvent that would allow the separation of internal and reorientational motion [14], one is forced to make assumptions in order to determine p^n and $S_{\alpha\beta}^n$. One way of addressing these issues is by using the three-state rotational isomeric state (RIS) model [2] to describe the accessible conformational states of each C–C bond of the molecule. Another way is to allow all dihedral angles to be populated assuming a continuous rotational potential and commensurate Boltzmann statistics. One can also allow each member of this continuum to have its own order matrix, or alternatively one can restrict all conformers to have the order matrix of the *trans* or *gauche* conformers according to the well in the potential in which they are found.

Various orientational potentials were used in conjunction with the RIS approximation in fits to the dipolar couplings of *n*-butane dissolved in a so-called ‘magic mixture’ (MM) liquid crystal and it was found that the Chord model gave the best fits although the full accuracy of the experimental dipolar couplings was not exploited [17]. Since solving these spectra has become routine with our Covariance Matrix Adaptation Evolution Strategy (CMA-ES) [18], we now revisit this general problem with more experiments and improved methods of accounting for the potentials used previously [17] with the hope of better understanding the contributions of the gas and condensed phases as well as orientational ordering on the conformational problem.

n-Butane (see Fig. 1 for structure) and 1,3,5-trichlorobenzene (tcb, added as an orientational reference for potential comparison of orientational order with samples from other studies) were co-dissolved in the four different liquid crystals *p*-ethoxybenzylidene-*p*'-*n*-butylaniline (EBBA), Merck ZLI-1132 (1132), 4-*n*-pentyl-4'-cyanobiphenyl (5CB) and a MM of 55 wt% 1132 and 45 wt% EBBA (data taken from [17]). Since *n*-butane is

a gas at room temperature and ambient pressure it was allowed to flow into a vacuum and then condensed into the 5 mm o.d. standard NMR tube which was submerged in liquid nitrogen. Enough solute was added to obtain roughly 5.0 mol% and 0.50 mol% for *n*-butane and tcb. After each sample was sealed and mixed thoroughly in the isotropic phase it was placed into a Bruker Avance 400 MHz NMR spectrometer magnet. With the temperature controlled by the Bruker air-flow system proton NMR spectra were acquired at 300.5 K in EBBA, 298.5 K in 1132 and 298.5 K in 5CB. Each liquid crystal is in the nematic phase at these respective temperatures and its director will be aligned with the magnetic field direction.

The spectral parameters (dipolar couplings (D_{ij}), indirect couplings (J_{ij}) and chemical shifts differences ($\delta_1 - \delta_4$)) of *n*-butane in each liquid crystal were then obtained automatically with the use of CMA-ES [13,18–21]. Since the algorithm iterates on both frequencies and intensities, the broad liquid–crystal background is removed prior to the fitting with a cubic-base spline. An excellent fit to the experimental spectrum is obtained as shown for 1132 in Fig. 1. The NMR parameter values are shown in Table 1. The dipolar couplings and chemical shift differences are significantly different between liquid–crystal solvents, whereas the indirect couplings are constant within experimental error as expected.

All computational chemical calculations were carried out using GAUSSIAN 03 [22] and the structural parameters obtained can be found in the supplementary materials [23]. Möller–Plesset 2nd-order perturbation theory [24] was employed using Dunning's cc-pvdz basis set [25]. The designated minima were confirmed to be minima by using analytical 1st and 2nd energy derivatives as is routine with MP2.

The dipolar coupling between protons i and j in an orientationally ordered molecule is given by

$$D_{ij} = -\frac{\gamma^2 \hbar \mu_0}{8\pi^2} \left\langle \frac{\frac{3}{2} \cos^2(\theta_{ij}^z) - \frac{1}{2}}{r_{ij}^3} \right\rangle \quad (2)$$

where r_{ij} is the internuclear distance and θ_{ij}^z is the angle between the internuclear vector and the static magnetic field. A pragmatic way of analyzing dipolar couplings of partially oriented flexible molecules is to assume that the molecule exists in several discrete conformations each having its own Saupe order matrix S_{ij}^n . This assumption is necessary since the *trans* and *gauche* conformers are not related by symmetry [14]. An important model used for approximating the conformations of hydrocarbon chains is Flory's

Table 1
Spectral parameters (Hz).

Parameter	EBBA (300.5 K)	1132 (298.5 K)	5CB (298.5 K)	MM ^a (301.4 K)
D_{12}	924.55(7)	1142.45(4)	662.79(4)	817.63(3)
D_{14}	-243.66(6)	-272.42(4)	-157.56(3)	-199.57(5)
D_{16}	-407.90(5)	-553.43(3)	-324.40(3)	-388.84(2)
D_{18}	-205.34(5)	-277.85(3)	-162.92(3)	-196.14(2)
D_{45}	1812.29(12)	2196.44(8)	1313.25(7)	1601.09(4)
D_{46}	80.57(19)	94.37(12)	50.44(11)	65.61(8)
D_{47}	34.30(19)	63.55(12)	24.26(11)	33.98(8)
$\delta_1 - \delta_4$	-258.04(18)	-289.87(11)	-228.14(10)	-309.40(7)
J_{45}	-13.5 ^b	-13.5(4)	-12.3(5)	-14.9(1.5)
J_{14}	7.29(12)	7.40(8)	7.47(6)	7.37(5)
J_{16}	-0.23(10)	-0.22(6)	-0.28(6)	-0.19(2)
J_{46}	8.85(34)	8.73(23)	8.74(19)	8.83(2)
J_{47}	5.84(34)	6.02(23)	6.26(20)	6.04(2)
D_{tcb}	156.50(25)	225.46(47)	147.03(11)	173.03(2)

^a Taken from Ref. [17] which used a 500 MHz NMR spectrometer.

^b Was fixed to the average of the other three spectra since an error could not be calculated.

RIS model [2] in which each C–C bond is assumed to exist in three different orientations with respect to an adjacent C–C bond, *trans* and \pm *gauche*, with dihedral angles of 0° and $\pm\phi_g$ corresponding to the angles at the minima of the rotational potential.

The order matrix of the n th conformer in Eq. (1) can be written as

$$S_{\alpha\beta}^n = \left\langle \frac{3}{2} \cos(\theta_{\alpha,Z}^n) \cos(\theta_{\beta,Z}^n) - \frac{1}{2} \delta_{\alpha\beta} \right\rangle \quad (3)$$

where $\theta_{\alpha,Z}^n$ is the angle between the α -molecular axis of the n th conformer and the nematic director which, in these experiments, is aligned with the magnetic field along the Z axis. The $D_{ij,\alpha\beta}^n$ tensor elements are then defined by

$$D_{ij,\alpha\beta}^n = -\frac{\mu_0 \gamma^2 \hbar}{8\pi^2 r_{ij}^3} \left(\frac{3}{2} \cos(\theta_{\alpha,Z}^{ij,n}) \cos(\theta_{\beta,Z}^{ij,n}) - \frac{1}{2} \delta_{\alpha\beta} \right) \quad (4)$$

where $\theta_{\alpha,Z}^{ij,n}$ is the angle between the ij and the molecule-fixed α directions. Assuming a mean-field ordering potential one can write the order matrices as follows:

$$S_{\alpha\beta}^n = \frac{\int \left(\frac{3}{2} \cos(\theta_{\alpha,Z}^n) \cos(\theta_{\beta,Z}^n) - \frac{1}{2} \delta_{\alpha\beta} \right) \exp(-U_n^{\text{aniso}}(\Omega)/kT) d\Omega}{\int \exp(-U_n^{\text{aniso}}(\Omega)/kT) d\Omega} \quad (5)$$

where U_n^{aniso} is the anisotropic nematic ordering potential of the n th conformer. The conformer probability is a function of both the isotropic (U_n^{iso}) and anisotropic (U_n^{aniso}) parts of the intermolecular potential and can be written

$$p^n = \frac{G^n \exp(-U_n^{\text{iso}}/kT) \int \exp(-U_n^{\text{aniso}}(\Omega)/kT) d\Omega}{\sum_n G^n \exp(-U_n^{\text{iso}}/kT) \int \exp(-U_n^{\text{aniso}}(\Omega)/kT) d\Omega} \quad (6)$$

where $G^n = \sqrt{I_{xx}^n I_{yy}^n I_{zz}^n}$ is a rotational kinetic energy factor which is dependent on the principal values of the moment of inertia tensor for each conformer. The isotropic part of the intermolecular potential, U_n^{iso} , is composed of an intramolecular component, $U_{\text{int},n}^{\text{iso}}$, and an intermolecular part, $U_{\text{ext},n}^{\text{iso}}$. The *trans-gauche* energy difference, E_{tg} , is

$$E_{\text{tg}} = U_{\text{gauche}}^{\text{iso}} - U_{\text{trans}}^{\text{iso}} = E_{\text{tg}}^{\text{int}} + E_{\text{tg}}^{\text{ext}} \quad (7)$$

where $E_{\text{tg}}^{\text{int}} \equiv E_{\text{tg}}^{\text{gas}} = 651 \text{ cal mol}^{-1}$ is taken as the energy difference as calculated by GAUSSIAN 03. As discussed above, since the conformer probabilities and molecular order parameters appear as products, they cannot be determined independently and so one must use a model for U_n^{aniso} in order to proceed. In the current study we shall focus on two different models, namely the Cd and CI models. When these two models are employed without the RIS approximation we will employ a gas-phase rotational potential which is a function of dihedral angle, is calculated with GAUSSIAN 03, and is shown as the points in Fig. 2.

The size-and-shape potential

$$U_n^{\text{CI}}(\Omega) = \frac{1}{2} k(C_n(\Omega))^2 - \frac{1}{2} k_s \int_{Z_{\text{min},n}}^{Z_{\text{max},n}} C_n(Z, \Omega) dZ \quad (8)$$

involves two terms, the first of which involves a Hooke's law restoring force [26] where $C_n(\Omega)$ is the minimum circumference traced out by the projection of the solute onto a plane perpendicular to the nematic director; the second term represents an anisotropic surface potential where the area of the infinitesimally thin ribbon $C_n(Z, \Omega) dZ$ is summed over its projection onto the plane parallel to the nematic director [27]. Note that $U_n^{\text{CI}}(\Omega)$ is comprised of both isotropic and anisotropic components; therefore, in the calculations we use

$$U_n^{\text{CI,aniso}}(\Omega) = U_n^{\text{CI}}(\Omega) - \langle U_n^{\text{CI}} \rangle \quad (9)$$

where $\langle U_n^{\text{CI}} \rangle$ is the isotropic average over all angles.

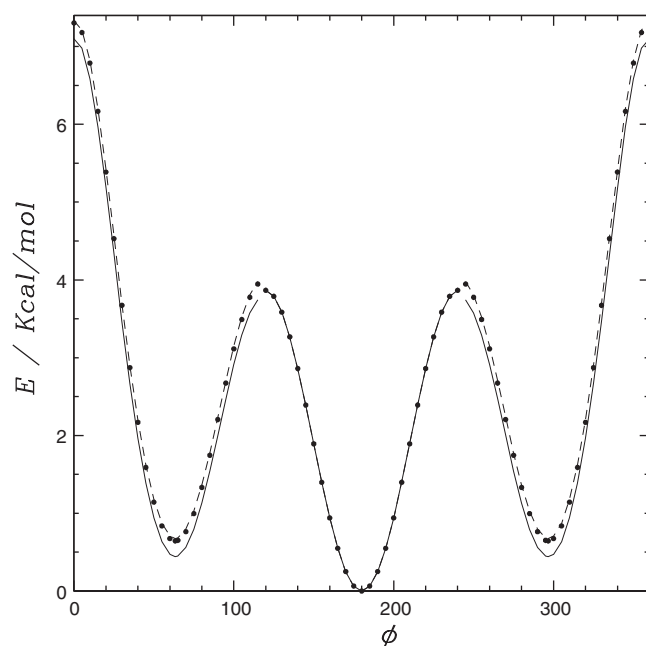


Fig. 2. Energies, calculated from GAUSSIAN 03 for *n*-butane as a function of dihedral angle ϕ . The points are for *n*-butane in the gas phase. The dashed line for the *gauche* conformer is shifted due to the isotropic part of the intermolecular potential in the condensed phase when the orientational order is described by the CI (2k) model. The solid line for the *gauche* conformer is shifted downward and obtained when describing the orientational order with the CCd model. Both the CCd and CI (2k) traces were obtained while varying the CCH angle and the $E_{\text{tg}}^{\text{gas}}$ calculated by GAUSSIAN 03 is 651 cal mol^{-1} .

The Cd model is especially tailored for the orientational order of molecules comprised of repeating identical units in a uniaxial phase [16,28], and is derived from a rigorous expansion of the mean-field interaction potential in which only the leading terms are retained

$$U_n^{\text{Cd,aniso}}(\Omega) = - \sum_{i=1} [\tilde{w}_0 P_2(s^i, s^i) + \tilde{w}_1 P_2(s^i, s^{i+1})] \quad (10)$$

where

$$\tilde{w}_i = \frac{3}{2} S w_i \quad (11)$$

are effective coupling constants, and w_i are coupling constants that describe the strength of the various interaction terms which are scaled by the liquid-crystal order parameter S in the mean-field potential. The s^i is a unit vector describing the orientation of the i th C–C bond of the hydrocarbon chain and the sum is over all bonds in the chain. The factors $P_2(s^i, s^{i+m})$ are given by

$$P_2(s^i, s^{i+m}) = \frac{3}{2} \cos(\theta_z^i) \cos(\theta_z^{i+m}) - \frac{1}{2} s^i \cdot s^{i+m} \quad (12)$$

where θ_z^i is the angle between the i th bond and the nematic director. The first term in Eq. (10) corresponds to the independent alignment of separate C–C bonds. The second term incorporates correlations between adjacent bond orientations, and therefore distinguishes between conformations that may have equal numbers of *trans* and *gauche* bonds, but significantly different shapes and so accounts for shape-dependent excluded-volume interactions. It should be realized that values given for \tilde{w}_0 and \tilde{w}_1 in the literature do not always conform to the definition of Eq. (10).

In Table 2 the results of seven different calculations are shown. In addition to the RIS approximation we employ a modified version, RIS (± 20), which includes the original dihedral angle calculated by GAUSSIAN 03 for both *trans* and *gauche* conformers

Table 2
Fitting parameters for simultaneous fits to all four sets of dipolar couplings. The CCH angle was varied in the top set of calculations and held constant in the bottom set.

Model	CCd/CCd'	DCd	RIS	RIS (± 20)	CI (2k)	CI (k)
E_{lg} (cal mol ⁻¹)	442(3)/471(3)	441(3)	476(3)	481(3)	676(8)	697(8)
$\bar{w}_0^{ebba}/k_s^{ebba}$	197.8(1.0)/209.2(1.2)	197.4(1.0)	191.6(1.3)	195.9(1.0)	1.0(5)	2.195(10)
$\bar{w}_0^{132}/k_s^{132}$	212.3(8)/211.3(8)	211.7(8)	205.0(1.0)	210.3(7)	3.8(2)	2.696(9)
\bar{w}_0^{MM}/k_s^{MM}	161.7(5)/163.3(4)	161.5(5)	156.2(7)	159.9(5)	2.7(2)	1.976(6)
$\bar{w}_0^{5CB}/k_s^{5CB}$	126.6(6)/129.0(6)	126.4(6)	122.5(7)	125.3(6)	2.5(2)	1.605(6)
$\bar{w}_1^{ebba}/k_s^{ebba}$	117.7(1.6)/109.1(1.2)	118.4(1.6)	121.4(2.1)	119.4(1.5)	67.4(6.0)	
$\bar{w}_1^{132}/k_s^{132}$	193.8(1.1)/193.5(8)	194.6(1.1)	198.3(1.4)	195.4(1.0)	49.5(3.0)	
\bar{w}_1^{MM}/k_s^{MM}	135.0(8)/133.6(6)	135.6(9)	138.6(1.1)	136.6(8)	38.3(1.9)	
$\bar{w}_1^{5CB}/k_s^{5CB}$	119.5(9)/117.1(7)	119.9(1.0)	122.0(1.2)	120.6(9)	27.1(2.7)	
$(\bar{w}'_0/\bar{w}_0)^{ebba}$	0.950(3)					
$(\bar{w}'_0/\bar{w}_0)^{132}$	0.988(3)					
$(\bar{w}'_0/\bar{w}_0)^{MM}$	0.977(3)					
$(\bar{w}'_0/\bar{w}_0)^{5CB}$	0.972(3)					
CCH angle decrease (deg)	1.05(5)/0.88(4)	1.00(6)	0.90(5)	1.00(5)	1.43(11)	1.52(13)
RMS (Hz)	3.5/2.2	3.6	4.6	3.3	7.8	9.0
Model	CCd	DCd	RIS	RIS (± 20)	CI (2k)	CI (k)
E_{lg} (cal mol ⁻¹)	417(5)	417(4)	456(4)	458(4)	618(8)	641(5)
$\bar{w}_0^{ebba}/k_s^{ebba}$	196.1(1.8)	196.0(1.7)	190.2(1.8)	194.2(1.7)	1.4(1)	2.228(12)
$\bar{w}_0^{132}/k_s^{132}$	208.7(1.3)	208.5(1.3)	202.0(1.3)	207.0(1.2)	4.0(5)	2.734(9)
\bar{w}_0^{MM}/k_s^{MM}	158.5(9)	158.5(9)	153.5(9)	156.8(8)	2.9(2)	2.004(6)
$\bar{w}_0^{5CB}/k_s^{5CB}$	125.6(1.0)	125.7(1.0)	121.7(1.0)	124.4(1.0)	2.7(2)	1.628(7)
$\bar{w}_1^{ebba}/k_s^{ebba}$	123.6(2.8)	123.8(2.7)	126.4(2.9)	64.2(2.6)	85.2(2)	
$\bar{w}_1^{132}/k_s^{132}$	202.8(1.7)	203.0(1.6)	206.1(1.7)	47.8(1.6)	86.4(6.0)	
\bar{w}_1^{MM}/k_s^{MM}	143.3(1.3)	143.4(1.2)	145.8(1.3)	35.9(1.2)	54.8(3.1)	
$\bar{w}_1^{5CB}/k_s^{5CB}$	123.5(1.6)	123.5(1.6)	125.4(1.7)	25.1(1.5)	2.4(1.9)	
RMS (Hz)	6.1	5.9	6.3	5.8	10.9	12.2

The \bar{w}'_n and k^l/k_s^l are in units of cal mol⁻¹ and N m⁻¹. $E_{lg}^{int} \equiv E_{lg}^{gas} = 651$ cal mol⁻¹ as calculated by GAUSSIAN 03 [22]. The CCd' result is shown only for when the CCH angle is varied.

(weighted 50%) and the original dihedral angle $\pm 20^\circ$ (each weighted 25%). These RIS calculations were performed with the Cd model for orientational order. The Cd model was also applied with a continuum of conformers. In this case three different variants were calculated. The continuous chord model, CCd, allows each conformer to have its own order matrix while the discontinuous chord model, DCd, restricts all conformers to have the order matrix of the *trans* or *gauche* conformer (calculated at the well minimum) according to in which potential well a given conformer is found. An additional calculation CCd' with the CCd model incorporates possible end effects in the chord model, whereby the values of \bar{w}_0 and \bar{w}_1 for the end segments of a hydrocarbon chain might differ from those for the inner segments. From a theoretical analysis of data for hexane, heptane and octane \bar{w}_0 values for the

end C–C bonds were found to be of order $1.1 \times \bar{w}_0$, with that for nonane being 0.96 and for decane 1.0 [29]. For butane, there is then a \bar{w}'_0 for the two end bonds, a \bar{w}_0 for the inner bond and a single \bar{w}_1 . Values of \bar{w}'_0/\bar{w}_0 obtained for butane vary between 0.95 and 0.99, with little change in other parameters. The CI model was employed in a manner similar to the CCd calculation where the two parameters in the orientational potential were varied independently (CI (2k)) but was also performed restricting the ratio of these two parameters (CI (k)) to the value found in a study of 46 solutes in the MM [27].

All of these calculations are divided into those where we varied the methyl CCH bond angle and those where we did not. Detailed studies of methyl groups in methyl fluoride, methyl iodide and ethane have shown that vibration–reorientation interaction effects are

Table 3
Experimental and calculated dipolar couplings (Hz) for the CI (2k), CCd and CCd' calculations where the CCH bond angle was varied.

Liquid crystal	Calculation	D_{12}	D_{14}	D_{16}	D_{18}	D_{45}	D_{46}	D_{47}
EBBA	Experimental	924.55	-243.66	-407.90	-205.34	1812.29	80.57	34.30
	CI (2k)	902.91	-227.79	-424.16	-222.40	1817.74	61.23	35.05
	CCd	932.86	-246.63	-409.48	-209.16	1791.64	76.44	64.99
	CCd'	924.41	-242.45	-407.47	-205.30	1813.62	68.82	53.95
1132	Experimental	1142.45	-272.42	-553.43	-277.85	2196.44	94.37	63.55
	CI (2k)	1146.87	-286.76	-542.73	-278.57	2197.47	94.01	82.91
	CCd	1140.52	-273.50	-552.83	-279.28	2199.75	88.40	76.18
	CCd'	1142.09	-271.60	-554.13	-276.08	2197.66	89.31	77.81
MM	Experimental	817.63	-199.57	-388.84	-196.14	1601.09	65.61	33.98
	CI (2k)	817.00	-204.28	-386.46	-201.15	1601.03	61.59	45.59
	CCd	819.14	-201.06	-387.60	-199.50	1599.02	60.15	46.68
	CCd'	817.31	-198.49	-388.28	-197.07	1601.55	58.76	45.00
5CB	Experimental	662.79	-157.56	-324.40	-162.92	1313.25	50.44	24.26
	CI (2k)	667.96	-167.04	-316.02	-164.03	1308.46	50.95	37.57
	CCd	664.49	-158.27	-322.97	-167.13	1309.05	45.97	33.30
	CCd'	663.28	-156.71	-322.98	-164.70	1313.77	44.62	31.57

Table 4
RIS chord.

Parameter	Old ^a	New
E_{tg} (cal mol ⁻¹)	518(9)	468(9)
\tilde{w}_0 (cal mol ⁻¹)	143.2(3)	151.6(3)
RMS (Hz)	6.7	6.5

^a Taken from [17]. The parameters \tilde{w}_0 and \tilde{w}_1 reported here correspond to the original definitions in [28]. Hence, the \tilde{w}_0 of [17] is multiplied by the factor $\sqrt{2/3}$ to be consistent with [28].

transferable among methyl groups in different molecules and lead to an apparent increase in HCH angle when neglected [30–33]. The variation of the CCH angle is intended to account, in a crude way, for the vibration–reorientation effects on the methyl protons. As found for an earlier study of pentane [18] this crude vibration–reorientation correction obtained by adjusting the CCH angle gives a significant improvement for all fits.

We show in Table 3 the experimental and recalculated dipolar couplings for the CI (2k), CCd and CCd' model calculations. The worst relative disagreement is found for the intermethylene couplings D_{46} and D_{47} . These couplings are particularly sensitive to conformational aspects of the problem. These differences could form the starting point for the testing of new ideas for the anisotropic intermolecular potential.

The fits can also be carried out on a single liquid crystal at a time (*i.e.* a separate E_{tg} for each). It is found that the fitting parameters do not change substantially and a lower RMS (around 2–3 Hz) is obtained. However, even if one does not vary the CCH methyl angle we have a slightly better fit than in [17] as can be seen in Table 4 where we compare the chord model with the RIS assumption for the previous and present studies. This repeated calculation is performed with the single parameter chord model ($\tilde{w}_0 = \tilde{w}_1$) and the RIS (± 20) approximation. The difference in the parameters obtained is likely due to the use of a rough geometry ($\phi_g = 116.0^\circ$)

in the old calculations and high-quality GAUSSIAN 03 geometries [23] ($\phi_g = 116.6756^\circ$) for the present study.

For the CCd and DCd calculations we used a continuous gas-phase potential barrier calculated with GAUSSIAN 03 at 5° intervals over the entire rotation. The $E_{\text{tg}}^{\text{ext}}$ in these instances is the shift due to the condensed phase (see Fig. 2) of all points in a *gauche* well relative to those in the *trans*. We also apply the same idea with the CI (2k) and CI (k) calculations. It is interesting to note that the shift from the calculated GAUSSIAN 03 value (651 cal mol⁻¹) is upward in the case of the CI models when the CCH angle is varied and roughly the same when the CCH angle is constant. On the other hand the shift is markedly downward in the case of the CCd and DCd models.

There seems to be no significant benefit to assuming a continuous order matrix over a discontinuous one as the goodness of fits in the CCd and DCd calculations is roughly equal. The RIS (± 20) approximation seems to give the best fit but only slightly better than the other Cd model calculations. There were only two distinct probability distributions as a function of dihedral angle that emerged from the different calculations, and these are presented in Fig. 3. The Cd model probability distribution favours the *gauche* conformer more than does the CI model regardless of which liquid crystal is used for the condensed-phase environment, how we treat the available conformers, what rotational potential is used or whether or not we vary the CCH angle to correct for vibrational–reorientational effects.

We find the effect of the condensed phase on the conformational statistics obtained is determined not by the particular liquid crystal or assumptions with regards to the available butane conformations and order matrices. Instead, the effect appears dependent only on the model chosen to describe the orientational potential. In order to better understand this observation the calculated order parameters of the *trans* and *gauche* conformers are shown in Table 5. The order parameters are calculated from dipolar couplings taken from oriented butane in the MM at 301.4 K where comparisons with the CI model are most appropriate. The angles required to diagonalize the order matrices are the same for a given conformer in the two calculations indicating both models identify the same principal ordering axis. While the asymmetries of the order matrices, η^n , are fairly similar for both models concerning the *trans* conformer, they differ significantly for the *gauche*. To assess the extent of orientational ordering of a conformer we define its 'average orientational ordering' to be

$$\sqrt{\langle S^2 \rangle}^n = \sqrt{S_{xx}^2 + S_{yy}^2 + S_{zz}^2} \quad (13)$$

Table 5

Calculated conformer order parameters using the RIS approximation for the Cd and CI (2k) models. The calculated order parameters shown are from fits to *n*-butane dipolar couplings when dissolved in the MM and while varying the CCH bond angle.

Model	Cd	CI
$\sqrt{\langle S^2 \rangle}^t$	0.130	0.118
S_{zz}^t	0.184	0.164
η^t	0.097	0.144
θ^t	42.3	43.5
$\sqrt{\langle S^2 \rangle}^g$	0.071	0.077
S_{zz}^g	0.093	0.108
η^g	-0.802	-0.428
θ^g	22.9	23.4

θ is the angle needed to diagonalize the order matrix, and is the angle between the C–C bond (original *z*) and new *z* directions; S_{zz}^n is the principal value of the diagonalized order matrix; the asymmetry of the diagonalized order matrix is $\eta^n = \frac{S_{xx} - S_{yy}}{S_{zz}}$, where *y* is the C₂ symmetry axis for both conformers. See [23] for original *xyz* coordinates.

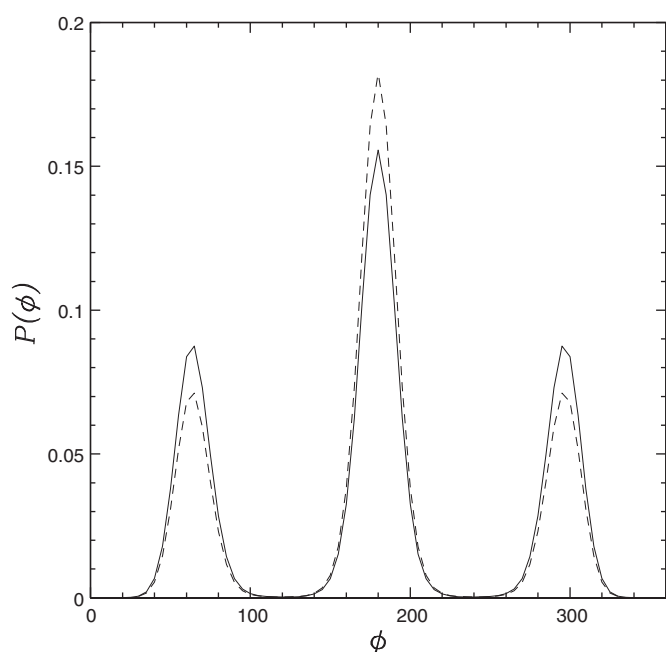


Fig. 3. The probability $P(\phi)$ of finding *n*-butane at dihedral angle ϕ for the CCd model (solid line) and the CI (2k) model (dashed line) in the MM at 301.4 K.

It can be seen that the mean-square orientational ordering, $\sqrt{\langle S^2 \rangle^t}$, of the *trans* conformer calculated by the Cd model is significantly larger than that calculated by the CI model whereas the $\sqrt{\langle S^2 \rangle^g}$ for the *gauche* conformer is lower when calculated by the Cd model. This explains why the Cd model favours the *gauche* conformation since the order matrix multiplies the conformer probability function in Eq. (1) and both calculations are fitting to the same dipolar couplings.

In summary, we find that the effects of a liquid–crystal condensed phase on the conformational statistics of butane are largely dependent on the model chosen to describe the orientational potential. In particular, the value obtained for E_{tg}^{ext} (which from Eq. (7) is $E_{tg} - E_{tg}^{int}$, where $E_{tg}^{int} = 651 \text{ cal mol}^{-1}$ from GAUSSIAN 03) is the main difference between models. Thus for the chord models, E_{tg}^{ext} is of order $-200 \text{ cal mol}^{-1}$, while for the CI model it is of order 0. This number represents the different influences of the isotropic part of the intermolecular potential on the conformers of butane in the condensed phase. The fact that this number is model dependent indicates the need for further investigation to determine which (if either) model is in any way related to the actual intermolecular potential of butane in these condensed phases. The precise description of the ordering potential is of course a fundamental and recurring question in chemistry and physics. Perhaps changing the Boltzmann factor *via* the temperature could help sort things out. Clearly further investigation is warranted and is in progress [34].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cpllett.2010.07.014.

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