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Liquid Crystals

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To cite this Article Kuebler, S. C. , Boeffel, C. and Spiess, H. W.(1995) 'Dynamics and structure of a flexible columnar liquid crystal based on tetrabenzocyclododecatetraene', Liquid Crystals, 18: 2, 309 — 318

To link to this Article: DOI: 10.1080/02678299508036627

URL: http://dx.doi.org/10.1080/02678299508036627

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LIQUID CRYSTALS, 1995, VOL. 18, NO. 2, 309–318

Dynamics and structure of a flexible columnar liquid crystal based on tetrabenzocyclododecatetraene

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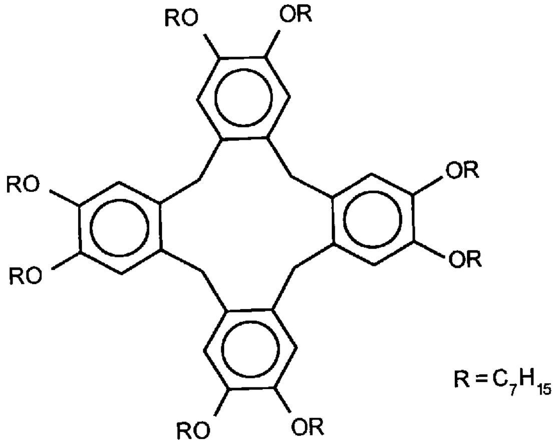
(*Received 20 April 1994; accepted 10 June*)

The dynamical and conformational behaviour of a flexible tetrabenzocyclododecatetraene derivative exhibiting a columnar mesophase has been studied by a combination of deuteron solid state NMR spectroscopy and molecular dynamics (MD) simulations. As shown by two-dimensional (2D) exchange NMR, the mesophase is characterized by slow axial reorientations ($\sim 10^{-3}$ s) of single molecular units where the phenylene rings exhibit a well-defined quasi-fourfold potential, while the 2D spectra of the core methylene sites are sensitive to the molecular conformation and reorientation mechanism. Motional narrowing of one-dimensional (1D) spectra reveals additional fast librations due to the internal flexibility of the mesogenic moiety. The various reorientation pathways comprising interconversions and pseudo-rotations between different energetically stable conformations are elucidated on a microscopic level by molecular dynamics simulations. The mesophase dynamics is ascribed to a complex axial motion involving rotational jumps combined with a pseudo-rotation between two symmetry related sofa forms. This is confirmed quantitatively by comparing the experimental 2D NMR spectra of the core methylene sites and the simulations which are based on the molecular geometries obtained by MD simulations. The lineshapes of one- and two-dimensional spectra of magnetically aligned samples specific to the orientation behaviour of the sofa conformer are discussed.

1. Introduction

Several non-planar mesogens exhibiting columnar mesophases have been described in the past few years. Among those are the substituted tribenzocyclononatrienes having a rigid core with a trigonal pyramidic shape [1, 2], as well as substituted orthocyclophanes [3–6] and metacyclophanes [7–9] consisting of flexible macrocyclic core. For the orthocyclophanes, various architectures are conceivable forming a columnar array. Different conformational states of the central mesogenic unit, namely sofa, boat and crown have already been discussed previously in terms of their stability [10, 11]. Therefore it is particularly interesting to investigate the conformational and dynamic characteristics accounting for the supramolecular organization of those macrocycles.

In the present work we describe experiments involving a member of the cyclotetraveratrylene (or tetrabenzocyclophane) series, namely octaheptyloxyorthocyclophane (I) in its mesomorphic state. Since one- and two-dimensional NMR techniques are highly sensitive to order and dynamics in condensed matter [12–14], it is possible to gain detailed information about the architecture and orientation of liquid crystalline compounds on a molecular level. By employing molecular dynamics calculations that are based on solving Newton's equations of motion numerically, further insight can be obtained on a microscopic level. Thus, energetically favourable conformations, as well as various internal degrees of freedom, are accessible [15] which are complementary to the experimental data available by NMR and X-ray diffraction [6]. For the system studied here, it is of particular interest



(I)

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to determine whether the high flexibility of the mesogenic core results in an averaged discotic arrangement with an effective fourfold symmetry or whether more complex structures are present in the liquid crystalline state.

2. Background

Solid state ^{2}H NMR spectra are dominated by the quadrupole coupling of a nucleus to the electric field gradient (EFG) at the nuclear site. To a good approximation, the interaction can be described by an axially symmetric field gradient tensor which leads to transition frequencies

$$(\omega_{\pm} = \omega_0 \pm \tfrac{1}{2}\delta \cdot (3\cos^2\vartheta - 1) \qquad (1)$$

where ω_0 denotes the Larmor frequency, $\delta = (3e^2qQ/4\hbar)$ with $e^2qQ/\hbar$ being the quadrupole coupling constant, and ϑ is the angle between the unique axis of the field gradient tensor (taken to be along the C–^{2}H bond) and the static magnetic field B_0. One-dimensional techniques allow the study of fast and intermediate motions [16], while two-dimensional exchange NMR [17] is employed to investigate slow dynamical processes [14]. A two-dimensional data set is generated as a function of two time variables t_1 and t_2. The spectrum obtained after double Fourier transformation can be interpreted as a two time distribution function, monitoring a molecular orientation before and after a mixing time t_m [18]. By varying the mixing time, the molecular dynamics can be followed in real time. For discrete jump motions the reorientational angle β can be directly determined from the characteristic elliptical exchange patterns [14, 19]. The reorientation angle β of a C–^{2}H bond is generally different from the rotation angle of ψ of the molecular rotation axis. For a conical distribution with χ being the angle between the central axis and the C–^{2}H tensors, both angles are related according to

$$\cos\beta = \cos^2\chi + \sin^2\chi\cos\psi. \qquad (2)$$

As can be seen immediately from this relation, the rotation and reorientation angle become identical when χ equals 90°.

3. Experimental

The synthesis of the compound deuteriated either at the aromatic sites or at the core methylene groups of the dodecatetraene ring has been described previously [5].

NMR spectra were recorded on Bruker CXP300 and ASX500 spectrometers operating at a magnetic field of 7 T and 11·7 T, respectively. Deuteron 1D spectra were recorded using the solid echo pulse sequence [20] with a 90° pulse length of ~ 3 μs. For the 2D experiments, about 50 data points were acquired for the t_1 dimension and 128 data points for the t_2 dimension with a spectral width between 312 and 416 kHz. Further experimental details are described in [21].

The differential scanning calorimetry diagram shows polymorphism in the crystalline phase with two transitions at 360 K (C_1) and 394 K (C_2) and a liquid crystalline phase transition at 410 K. The clearing temperature is at 435 K. Since our primary concern is the mesophase dynamics, the 2D exchange experiments were performed in the temperature range 410 K to 420 K, unless indicated otherwise.

The molecular dynamics simulation was carried out using the molecular mechanics and dynamics modules provided in the POLYGRAF molecular modelling package with the DREIDINGII force field [22, 23]. The calculations were performed in a NVT ensemble [24, 25] at 400 K with a total simulation length of 1350 ps, incremented in time steps of 0·001 ps.

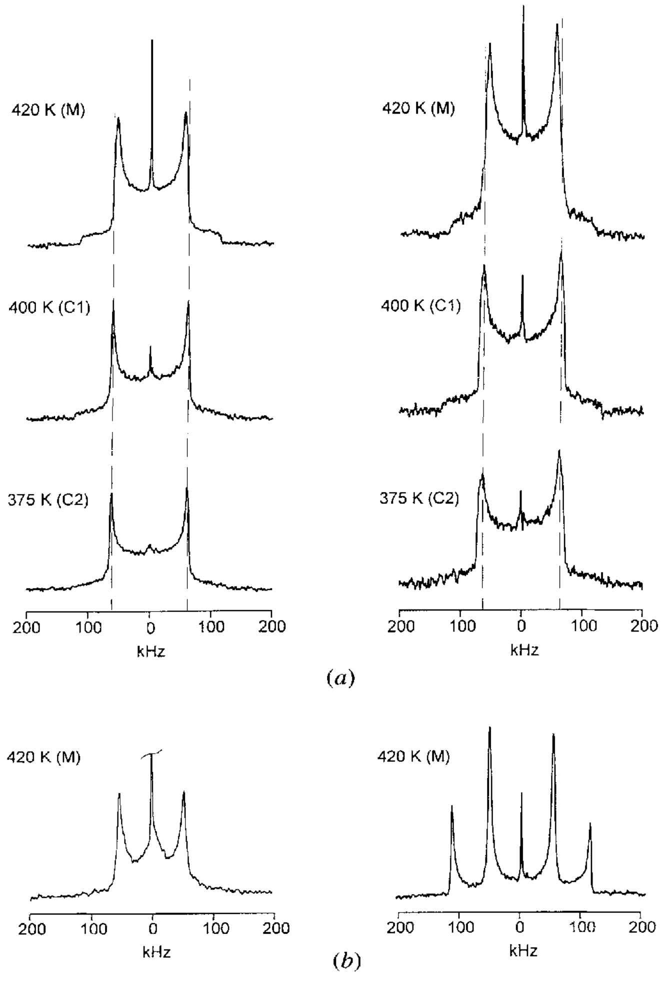


Figure 1. One-dimensional ^{2}H NMR spectra of tetrabenzocyclophane at the indicated temperatures and phases. (*a*) Non-oriented samples. Left: core methylene sites, right: aromatic sites. (*b*) Oriented samples. Left: core methylene sites, right: aromatic sites.

4. Results and discussion

4.1. *One-dimensional NMR spectra*

To obtain insight into the dynamics in the various phases, NMR spectra of the specifically labelled aromatic and core methylene sites were recorded. Typical spectra of each of the C_1, C_2 and M phases are shown in figure 1 (*a*). In the crystalline region, a powder spectrum is observed for the methylene deuteriated derivative (left column) with uniaxial quadrupole interaction ($\eta = 0$) and $\Delta\nu_q = 125$ kHz typical of rigid aliphatic deuterons, while $\Delta\nu_q$ is reduced to 110 kHz in the mesophase. Similarly, at the aromatic sites (right column), the quadrupole splitting of 126 kHz in C_1 and C_2 is reduced to 110 kHz in the mesophase with a small asymmetry parameter ($\eta = 0{\cdot}07$). These results indicate that no fast or intermediate motions ($\tau_c < 10^{-4}$ s) occur in the crystalline phases. Attributing the small reduction of the quadrupolar splitting in the mesophase to rapid librations of the C–^{2}H axis within a cone of semi-angle θ_c [26], librational amplitudes of approximately 20° (methylene sites) and 25° (aromatic sites) are obtained, reflecting the high internal flexibility of the mesogenic core. These observations differ from the behaviour usually obtained in other discotic systems where fast rotations occur around the columnar axis [2, 27], but they are typical for other members of the tetrabenzocyclophane series [4, 6]. Likewise, rapid rotational diffusion around the director axis was excluded for a member of the metacyclophane series via ^{2}H NMR [8].

Upon cooling from the isotropic phase into the mesophase region in the magnetic field, macroscopic alignment of discotic mesogens takes place resulting in a two-dimensional distribution of domains with the directors lying in a plane perpendicular to the external magnetic field [28]. The spectra of the aromatic sites thus obtained possess the characteristic features of a distribution of EFG tensors in a plane including the B_0 vector (see figure 1 (*b*), right). However, the parallel and perpendicular orientations of the C–^{2}H bonds are considerably more pronounced and the spectral intensities between the singularities are lower than would be expected for an orientation with transverse isotropy [12]—as it is indeed the case for triphenylenes [27], cf. also figure 11 (*b*). Notably, the oriented core methylene sample (see figure 1 (*b*), left) shows less pronounced changes in line-shape which consist of a reduced signal intensity at the outer edges, corresponding to orientations between 0° and 35°, as well as increased spectral intensity in the centre of the spectrum (ϑ between 50° and 60°), cf. equation (1).

4.2. *Two-dimensional NMR spectra*

To probe slow molecular reorientations, ^{2}H 2D exchange NMR was applied. Figure 2 (*a*) displays the experimental exchange spectrum of the aromatic sites in mesophase at a mixing time of 10 ms. The exchange pattern of the non-oriented sample displays straight exchange ridges perpendicular to the diagonal which are characteristic for a reorientation angle of 90° [19]. Presented in figure 3 is the simulated spectrum for a 90° jump ($\chi = 90°$) with a gaussian distribution of ± 5°. With a mixing time exceeding the correlation time of motion (complete exchange), the ratio of diagonal to exchange intensity I_d/I_e equals unity for a fourfold jump on a cone

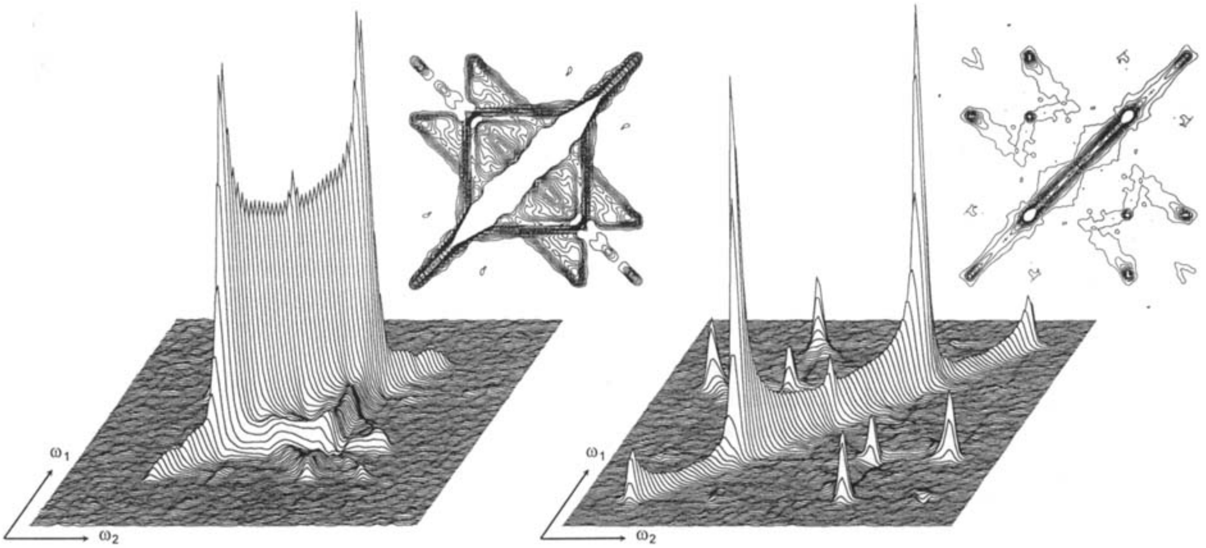


Figure 2. Experimental 2D spectra of tetrabenzocyclophane, labelled at the aromatic sites, at 420 K. (*a*) Non-oriented sample at a mixing time of 10 ms (spectral width 416 kHz, number of scans: 7360, total measuring time 43 h). (*b*) Oriented sample at a mixing time of 15 ms (spectral width 312 kHz, number of scans 4224, total measuring time 23 h). The contour plots are given as insets.

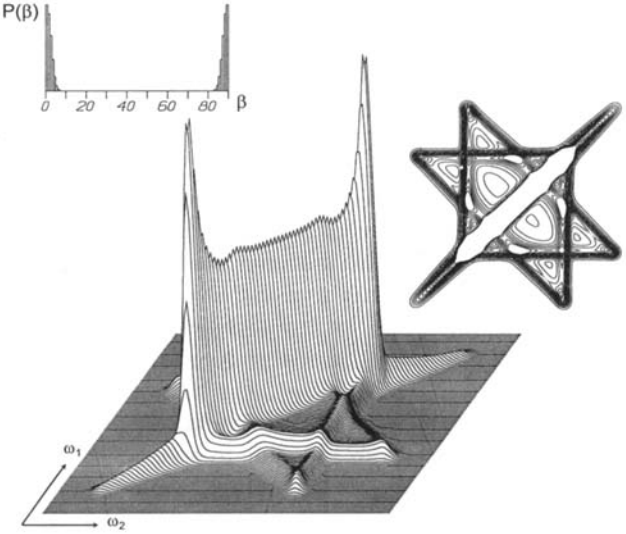


Figure 3. Simulated spectrum for complete exchange of the non-oriented aromatic sites for $\beta = 90°$ with a gaussian distribution of half width ± 5°. Also displayed above are the reorientation angle distribution RAD (left) and the contour plot (right).

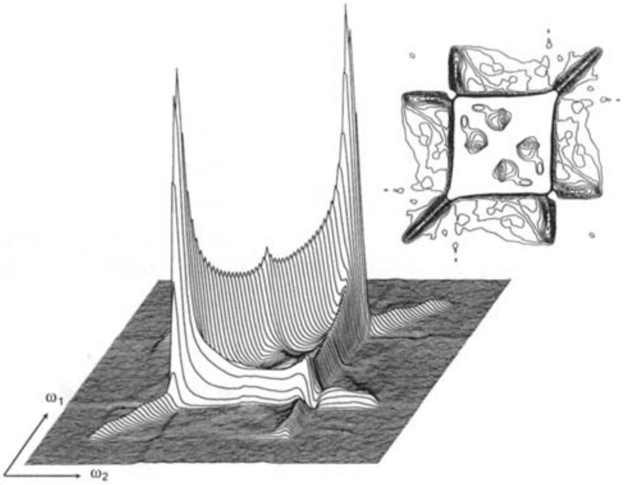


Figure 4. Experimental 2D spectrum of non-oriented tetrabenzocyclophane, labelled at the methylene sites, taken at 420 K and a mixing time of 15 ms (spectral width 312 kHz, number of scans 6976, measuring time 44 h).

with a semi-angle of 90° in which all positions are equally probable, since a jump around 180° contributes to the diagonal intensity. Comparison of experiment and simulation shows that the exchange pattern is characteristic of a distinct jump motion, while the correlation time is comparable to the mixing time. The reorientation angle of 90° is further confirmed by the 2D spectrum of the oriented compound (see figure 2 (*b*)), recorded under the same experimental conditions, which shows almost only exchange singularities between tensor orientations perpendicular and parallel to the magnetic field.

Likewise the 2D spectrum of the derivative deuteriated in the core methylene position (see figure 4 (*a*)) reveals a pronounced, but less obvious exchange intensity which reflects the complex geometry of the cyclophane ring. It should be noted, however, that this pattern is generated by a superposition of inequivalent EFG tensors and not by a molecular motion different from that monitored by the aromatic sites. From the contour plot, reorientational angles of 66° and 90° can be extracted, as well as a small angle value of 26° estimated. Since the methylene tensors are inclined at different angles with respect to the axis of motion (cf. equation (2)), a distinction between the various motional mechanisms and molecular conformations should be possible if the detailed geometry is accessible through structural data provided by computer models or X-ray diffraction measurements.

Whether the mesophase dynamics is predominated by motions of single mesogenic units or rather by columnar segments in a collective manner allows a further differentiation between different types of motion. Correlation times and activation energies can be determined from a series of mixing time dependent spectra at different temperatures. To this end, it proves to be sufficient to pursue the loss of correlation at a fixed value of t_1 (chosen to be 30 μs) by the deuteron spin alignment technique [29], instead of recording a full 2D spectrum. Assuming an Arrhenius behaviour, the activation energy for the mesophase dynamics was estimated to equal $62{\cdot}4 \pm 12\,\mathrm{kJ\,mol^{-1}}$ with a pre-exponential factor of about 3×10^{-11} s within a temperature range of 16 K.

This value is comparable to the activation energy of $65 \pm 7\,\mathrm{kJ\,mol^{-1}}$ obtained for the rotational dynamics of phthalocyanine units of a rod-like polysiloxane [30] which is characterized by a local motion. Slightly lower values are obtained for the tetrabenzocylophane derivatives for the sofa–sofa pseudo-rotation ($45{\cdot}6\,\mathrm{kJ\,mol^{-1}}$) [10] and the various reorientational processes of about $50\,\mathrm{kJ\,mol^{-1}}$ [11] in solution.

Additional 2D measurements for the crystalline phases C_1 and C_2 reveal that the large angle reorientation is frozen in at the phase transition liquid crystalline–solid, thus demonstrating that this type of motion is indeed characteristic of the mesophase.

4.3. *Molecular dynamics calculations*

To gain detailed information about the stable molecular geometries, as well as the various degrees of conformational freedom, molecular mechanics and molecular dynamics studies on a single molecule of tetrabenzocyclophane were performed. For the MD trajectory, a temperature of 400 K was chosen, corresponding to the mesophase and providing sufficient kinetic energy to

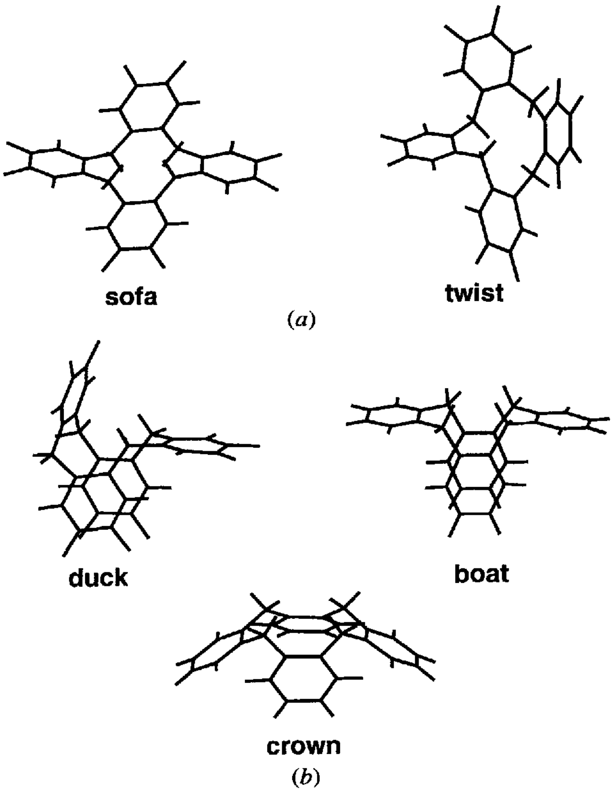


Figure 5. Various conformations of the cyclotetraveratrylene core: (*a*) Stable conformations obtained by MD and subsequent energy minimization. (*b*) Energetically unstable crown conformation.

Relative energies of the different conformers (in kJ mol^{-1}).

	Sofa	Boat	Duck	Twist	Crown
Core	5·9	0	23·4	55·2	894·5
Core–OC_7H_{15} (all *trans*-chain)	19·2	0	20·9	109·1	707·7

overcome conformational energy barriers of the mesogenic core. Figure 5 (*a*) shows the stable conformers obtained during the course of the simulation and by subsequent energy minimization. In addition to the sofa (C_{2h} symmetry) and boat conformers (C_{2v} symmetry) described previously [11], asymmetric twist and duck (C_s symmetry) conformers were found. The pyramidic analogue of the tribenzocyclophanes, the highly symmetric crown conformation (C_{4v} symmetry) displayed in figure 5 (*b*) was not observed during the simulation run. Molecular mechanics calculations demonstrate that the crown is energetically unstable and this was also suggested earlier by Maliniak *et al.* A comparison of the relative energies for the different conformers is listed in the table. The mesogenic core of the boat conformer is lowest in energy, with sofa slightly higher, while duck and twist are of still higher but comparable energy. The crown conformer is considerably higher and does not even correspond to a local minimum on the potential energy surface, which is mainly due to the van der Waals repulsion between the aromatic hydrogens.

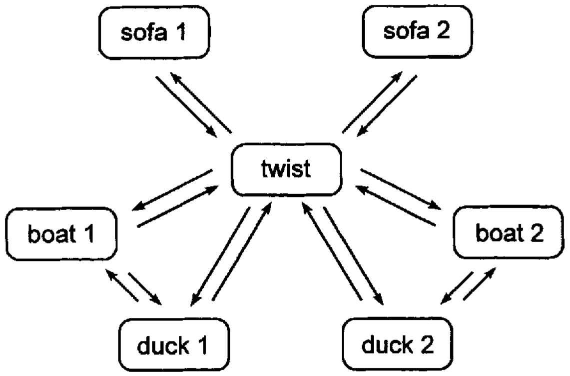


Figure 6. Reorientation pathways of the various conformers as traced by the molecular dynamics trajectory of 1350 ps, comprising interconversions (for example, sofa–boat) and pseudo-rotations (for example, sofa 1–sofa 2).

From the MD trajectory, the possible reorientation pathways can be extracted and are outlined schematically in figure 6. For symmetry reasons, different forms of the sofa, boat and duck conformers exist, each of them related by pseudo-rotation. As illustrated by the diagram, the stable twist conformation serves mainly as an intermediate between the various other conformers in the course of the trajectory. Moreover, twist and sofa are of closely related geometry, so that transitions between these two conformers, as well as the sofa–sofa pseudo-rotation are easily accomplished suggesting that the twist can also be regarded as an 'asymmetric sofa' molecule. Similarly, boat–duck interconversions are frequently observed. Sofa–boat interconversions occur either via twist or additionally via duck conformers, whereas a direct sofa–boat interconversion is not observed during the length of the simulation run. This is borne out by experimental results of proton high resolution exchange NMR in solution [11], for which the pseudo-rotation of the sofa exhibits the fastest exchange rate, while the corresponding boat–boat exchange rate is too slow to be measured.

4.5. *Discussion of various reorientation mechanisms*

In this section a detailed discussion of the mesophase dynamics in terms of molecular geometry is provided. Having a form-anisotropic core, sofa, twist and crown conformers are the only ones that can readily be stacked into columns. Among those, only the energetically unstable crown has a fourfold symmetry which can account immediately for a 90° jump. However, calculating the hypothetical 2D exchange spectrum of the methylene sites for the crown conformer yields broadened elliptical features centred at 70°. Thus it is indeed unlikely that the energetically unfavourable crown is present in the mesomorphic state. Therefore, to rationalize the dynamics in the mesophase, different possibilities have to be visualized. A quasi-fourfold potential can be induced either by the mesogen itself or by packing effects of surrounding molecules. Furthermore, several mechanisms may be considered for the jump motion which might occur around a molecular symmetry axis (or the column axis, if it is not coincident with the molecular axis), as well as reorientations around a molecular symmetry axis in combination with a conformational change. It must be borne in mind that the experimental activation energies favour the motion of single molecules rather than a collective process. Additionally, the pronounced jump motion accounts for a potential predominantly influenced by local effects. Therefore, any mechanisms involving co-operative reorientations are regarded as highly unlikely.

4.5.1. *Sofa conformation*

First the possibilities of the sofa conformer are outlined. As illustrated by the arrangement of the mesogenic cores in figure 7, the director *Z* does not coincide with the molecular S_2 axis. Reorientation around the columnar axis by 90° implies the motion of columnar segments, since a molecule does not fit into its original environment after the jump. Additionally, since a part of the aromatic C–^{2}H tensors lies on a cone with semi-angle different from 90°, significant deviations from the exchange pattern for the aromatic sites should be observed in the experimental spectrum, cf. equation (2).

Next, the case for which a quasi-fourfold symmetry of the sofa conformer is brought about by the molecule itself is discussed. As already mentioned, there exist two types of sofa conformers related by a pseudo-rotation (cf. figure 6) that are outlined schematically in figure 8 (*a*) and (*b*). The two non-equivalent planes of the phenyl rings are schematically depicted by the differently shaded areas. Shown as well are the relevant symmetry elements. A twofold rotation axis C_2 is formed by the intersection of the planes of the aromatic rings, while the inversion symmetry implies axes of symmetry S_2 and S_2', each perpendicular to the other axes. All aromatic C–^{2}H bonds lie either parallel or perpendicular to C_2 and S_2', while lying perpendicular to S_2. Subsequent rotation of 90° of the molecule in figure 8 (*b*) around S_2 leads to the arrangement in figure 8 (*c*) which is the exact symmetry analogue of figure 8 (*a*). Thus, a pseudo-rotation combined with a 90° jump can explain the inherent pseudo-fourfold molecular symmetry and readily accounts for the 90° reorientation angle of the phenyl deuterons. Following the trajectory of a given molecule, the pseudo-rotation involves the twist conformation as an intermediate as discussed above (cf. also figure 6), its form anisotropy closely related to the sofa. Accordingly, the sofa–twist interconversion can be easily accomplished without imposing substantial density fluctuations along the columnar axis. Overall, reorientation of single molecular units, which fit into their original environment again after the jump, is achieved.

The considerations above may be quantified by calculating the corresponding 2D exchange spectra using the MD results. Because of the very short time-scale accessible by molecular dynamics simulations, it is not feasible to calculate the reorientation angles by following the dynamics in real time. Instead, the calculation of the motional process above was performed indirectly, exploiting the molecular geometry of the sofa conformer. Using the symmetry properties of the conformer, the reorientational angles can be determined by calculating the angles between C–^{2}H bonds transforming into each other by the sofa–sofa pseudo-rotation. This is performed for each single sofa conformer and consequently in an internal molecular coordinate system. Thus it is possible to evaluate the reorientational angles of the core methylene, while confirming the results by calculating the exchange angles of the aromatic sites. In a molecular sense, this

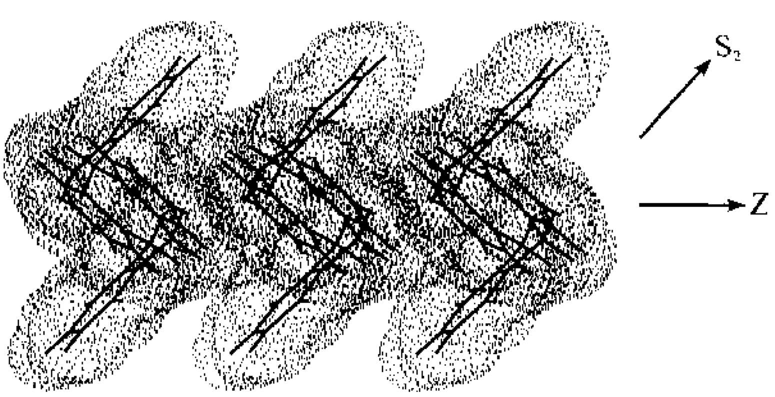
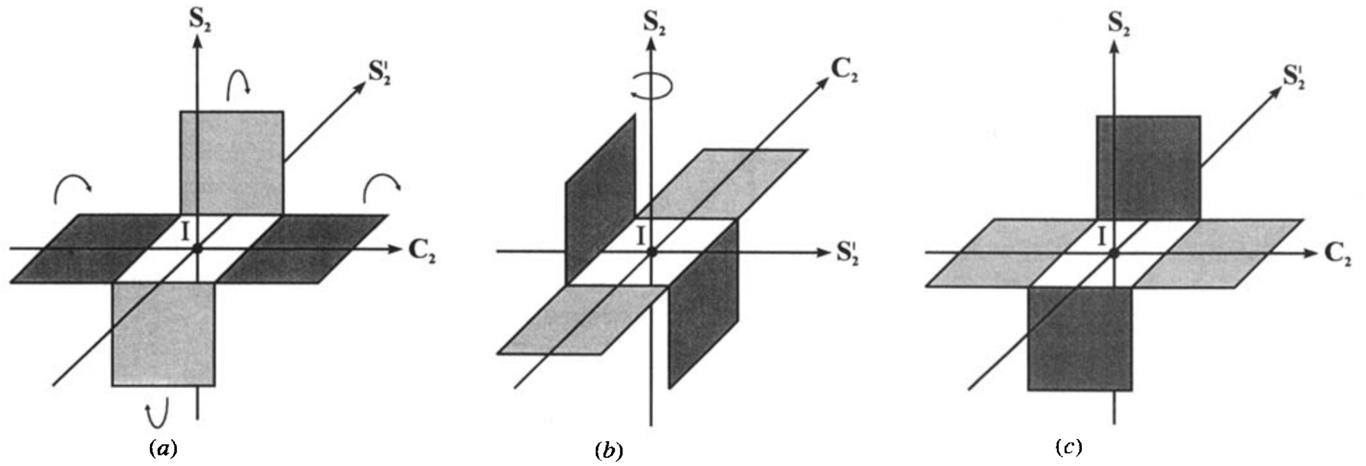


Figure 7. Columnar array of the mesogenic cores of the sofa conformer. Note that the columnar axis *Z* is different from the molecular symmetry axis S_2.



(*a*) (*b*) (*c*)

Figure 8. (*a*) Schematic view of the sofa conformer, The inequivalent phenyl rings are indicated by the differently shaded areas. S_2 and S'_2 denote the axes of symmetry implied by the centre of inversion I; C_2 is the twofold rotation axis. (*b*) After a sofa–sofa pseudo-rotation, the two subsets of phenyl rings are interchanged. (*c*) Subsequent rotation around S_2 leads to the exact symmetry analogue of (*a*).

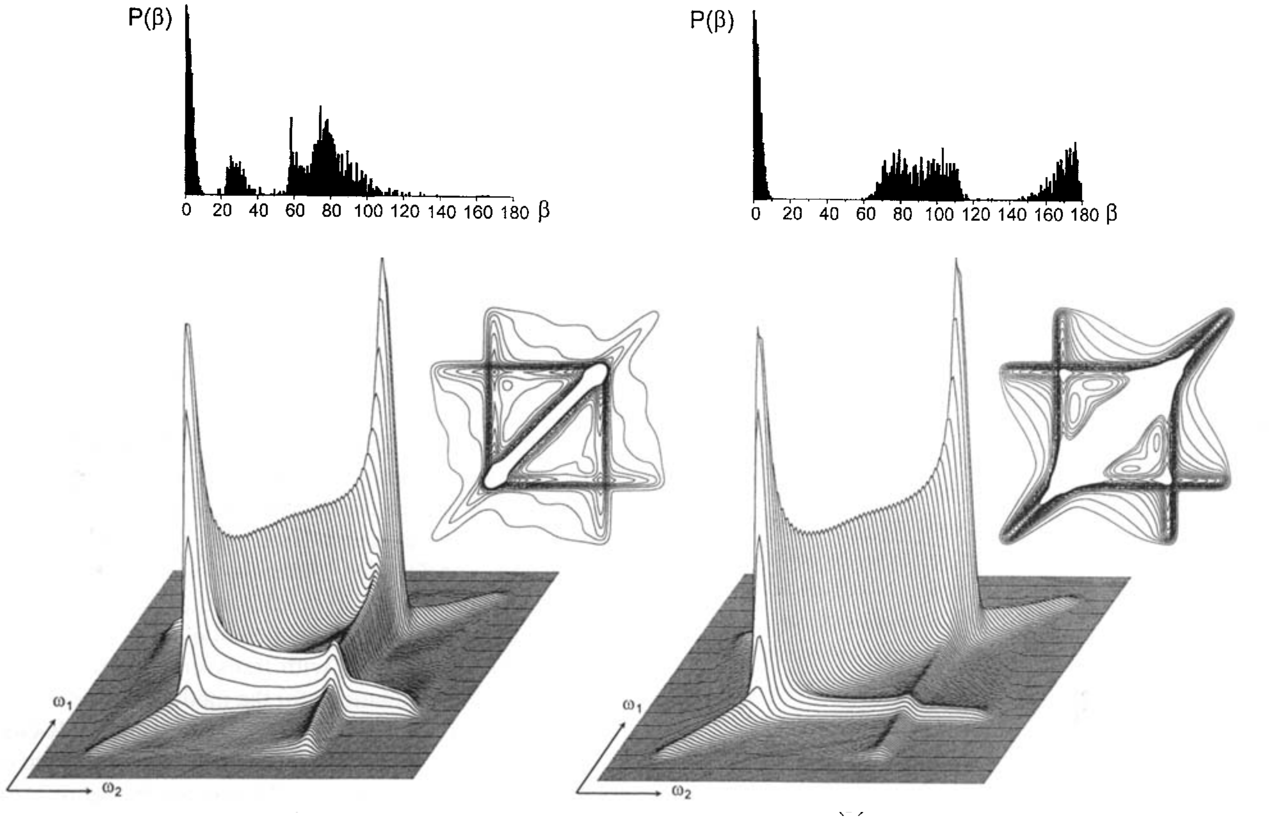


Figure 9. Calculated reorientational angle distribution of an ensemble of 110 sofa conformers for pseudo-rotation and twofold pseudo-rotation, as described in the text and weighted by a ratio of 2 : 1. The fraction of molecules that do not participate in reorientations are also accounted for by the gaussian distribution (half width of ± 5°) around 0°. (*a*) Simulated 2D spectrum of the methylene $C{-}^2H$ bonds. The corresponding RAD is shown on top. (*b*) Simulated 2D spectrum of the aromatic $C{-}^2H$ bonds as in (*a*).

model implies the conservation of the momentary local conformation, thus neglecting librational motions as well as fluctuations of the columnar axis. The calculation was performed with an ensemble of 110 energy-minimized sofa conformers extracted from the trajectory. This allows the determination of the distribution, as well as the average reorientational angles. The different types of motions that are observed on different NMR time-scales must also be

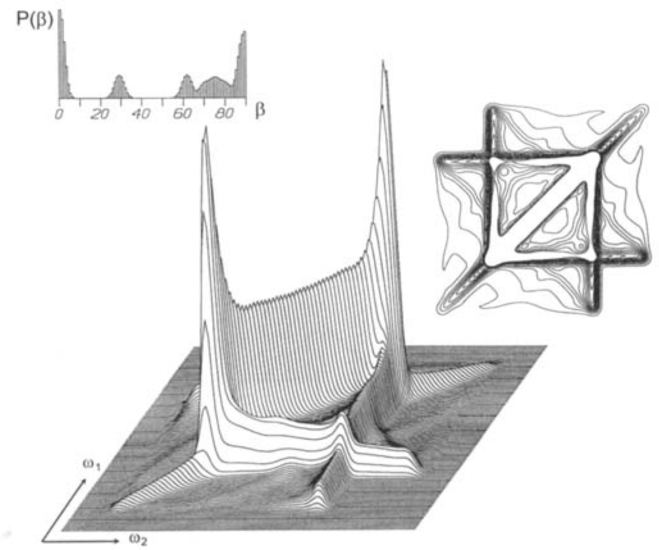


Figure 10. Reorientation angles of the methylene C–^{2}H bonds obtained by averaging over all conformers in figure 9 and subsequent gaussian broadening of ± 5°.

considered. Therefore, the distribution of reorientational angles resulting from the MD simulations represent the fast librational motions contributing to the 1D line-shape, i.e. the reduction of the quadrupolar splitting. 2D NMR, in particular, is sensitive to slow reorientations of the conformation already averaged by fast librations. Moreover, the flexibility of the mesogenic core will be reduced in the bulk phase compared to the isolated molecule. The reorientational angle distribution (RAD) obtained for all conformers is shown in figure 9 (*a*) and (*b*) for the core methylene and ring position, respectively. The probability of two subsequent pseudo-rotations has been weighted with a factor of $\frac{1}{2}$ with regard to the pseudo-rotation. Additionally, taking into account the molecules that do not alter their positions by a distribution of ± 5° around 0°, the RAD of the NMR experiment is represented directly. Figure 9 (*a*) shows a small angle reorientation between 20° and 40° and a broad unresolved distribution between 55° and 110°. Contraction to an interval between 0° and 90° leads to the 2D spectrum shown at the bottom of figure 9 (*b*). By comparison of the reorientation angle distribution of the simulated spectrum for the aromatic sites in figure 3 (*b*) with the experimental spectrum, it becomes evident that this broad distribution can indeed be attributed to fast librations. Evaluating the average reorientational angles for each aromatic C–^{2}H bond in the molecule yields values between 85° and 96° centred at 90° and about 180°, respectively for the one- and twofold pseudo-rotation. Figure 10 displays the 2D spectrum of the methylene sites obtained likewise by averaging the reorientational angles over all conformers and subsequent gaussian broadening of ± 5°, as estimated in figure 3. Angles of approximately 90° are found for the C–^{2}H bonds transforming by inversion, while those undergoing rotation are centred at 29° and 62°. A distribution between 70° and 81° results for the twofold pseudo-rotation.

Comparison between the experimental and simulated spectra (figures 4 (*a*) and 10) reveals good agreement in the exchange pattern. For both, the reorientation angle of 90° is present, while the ellipses of 26° and 66° in the experimental spectrum are slightly shifted with respect to the simulation.

4.5.2. *Oriented samples*

Further evidence for the presence of the sofa conformation in the mesomorphic state can be extracted from the oriented 1D spectra (see figure 1 (*b*)). Keeping in mind that the orientability is determined by the negative diamagnetic susceptibility of the phenylene rings, a preferential orientation shown in figure 11 (*a*) results. The phenylene rings are perpendicular to each other, but can stack in such a way that the bisector of their planes (C_2 axis defined in figure 8 (*a*)) orients along the magnetic field and is perpendicular to the reorientation axis S_2. The distribution of C–^{2}H EFG tensors can be described by a subset of two cones of semi-angles 0° and 90° with central axes lying parallel to B_0. This accounts for both the exceptionally pronounced features corresponding to the parallel and perpendicular orientation with respect to the magnetic field (see figure 1 (*b*)) and the 2D exchange pattern of the aligned sample (see figure 2 (*b*)) essentially consisting of singularities between those orientations. Likewise, the core methylene C–^{2}H tensors form cones parallel to B_0 with semi-angles of either about 60° (120°) and 80° (100°). Thus the significantly high intensity at the centre of the spectrum, as well as the decrease at the outer spectral part ($\vartheta < 35°$) can be rationalized. In figure 11 (*b*)–(*d*) the simulated spectra for different orientations (with a gaussian distribution of ± 10°) are presented. A planar distribution of directors perpendicular to the magnetic field as in figure 11 (*b*), with transverse isotropy, can be excluded. The simulations for the methylene and aromatic sites for the orientation of the sofa conformer as discussed above are shown in figure 11 (*c*) and (*d*), respectively. Comparing those with the 1D spectra in figure 1 (*b*), it becomes evident that more intensity between the singularities is present in the experimental spectra, the alignment thus being incomplete. This is attributed to the slow mesophase dynamics and the high viscosity of the samples.

4.5.3. *Other conformers and packing*

It is also conceivable that the mesophase structure could consist predominantly of the twist conformer. However, this is considered to be less likely for several reasons. First,

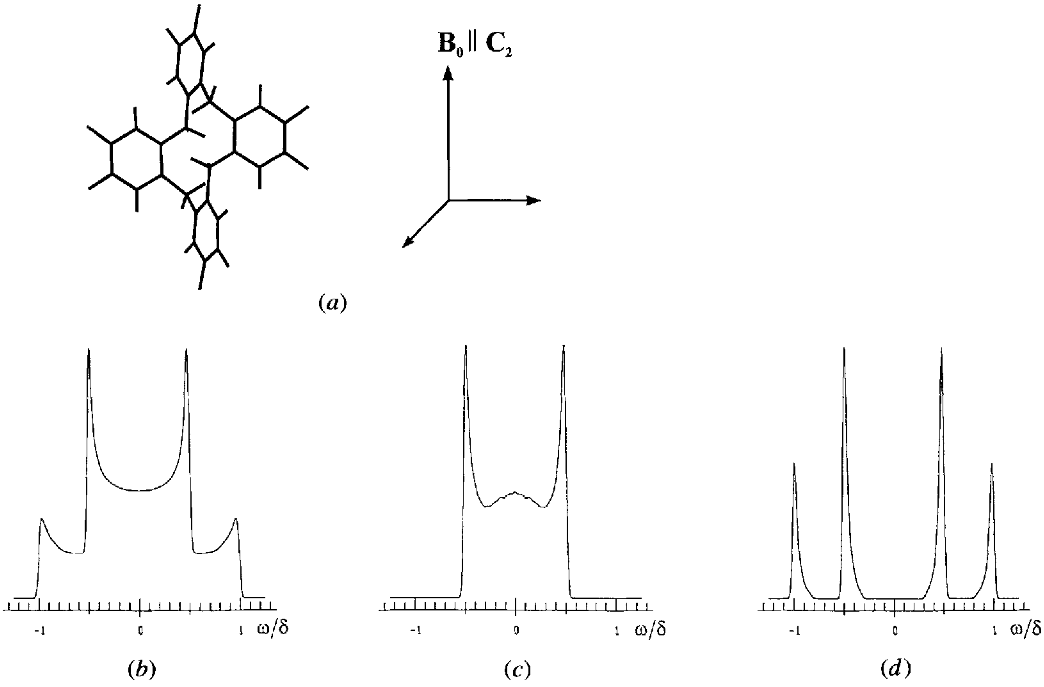


Figure 11. (*a*) Preferential orientation of the sofa conformer in the magnetic field. Simulated line-shapes: (*b*) Planar distribution of C–^{2}H tensors with transverse isotropy with the central axis perpendicular to the magnetic field on a cone with semi-angle of 90°. (*c*) Methylene sites with C–^{2}H tensors in a conical distribution parallel to B_0 with semi-angles of 60° and 80° (with a gaussian distribution of ± 10°) resulting from the orientation in (*a*). (*d*) Aromatic sites with C–^{2}H tensors in a conical distribution parallel to B_0 with semi-angles of 0° and 90° (with a gaussian distribution of ± 10°) resulting from the orientation in (*a*).

the 2D spectra of the aromatic sites show clear evidence for a well-defined potential. This suggests a highly ordered structure on the NMR time-scale, as also reflected in the oriented 1D and 2D spectra. Moreover, one would expect mesophase dynamics on the fast or intermediate time-scale if the mesogenic shape were essentially discotic, as it is for the twist conformation, or only a simple rotational process were present.

Additional structural information has been obtained previously from X-ray diffraction measurements [6] for the homologous series of alkanoyl substituted tetrabenzocyclophanes. For the heptyloxy substituted derivative studied here, a centred rectangular unit cell of c2 mm symmetry, containing two molecules, has been proposed. Apparently the molecules possess a local elliptical symmetry that is in agreement with the arrangement of the sofa conformer within a column. Additional evidence for the sofa to be the preferred conformer in the solid is given by single crystal X-ray analysis of the methoxy substituted cyclotetraveratylene core [11]. For the higher homologues of the orthocyclophanes, a phase transition from a rectangular to a hexagonal unit cell is observed in the mesophase on heating. Whether this change of the local molecular symmetry might be related to dynamical or conformational effects is still unresolved.

5. Summary

The combination of deuteron solid state NMR and MD simulations is able to yield highly specific information on dynamics and ordering of a complex structure like tetrabenzocyclophane in its liquid crystalline state. This macrocycle shows exceptionally slow mesophase dynamics compared to other discotic systems, despite its internal flexibility. The only motions observed in the 1D deuteron NMR spectra are small angle librations, while oriented samples exhibit an overall line-shape resembling discotic systems in which the director is oriented perpendicular to the magnetic field. The specific ordering can be explained by the local geometry of the sofa conformer for which the alignment is incomplete. 2D exchange NMR determined that the reorientation angles consist of discrete 90° jumps around the molecular axis in a quasi-fourfold potential monitored by the aromatic sites. Detailed information about the local geometry of the mesogenic core was extracted by the exchange spectrum of the methylene sites which are particularly sensitive to the conformational state.

In combination with molecular dynamics simulations, stable conformers, i.e. sofa, twist, boat and duck, were identified and the reorientation pathways elucidated. The main dynamical mechanisms are the sofa–sofa pseudo-rotation and the sofa–boat interconversion, both proceeding via the twist conformation as an intermediate. Since the activation energies observed favour a localized process rather than a collective behaviour, the quasi-fourfold potential must be evoked by the molecule itself. The natural conformations for a columnar staking being sofa and twist, this is accomplished by a combined mechanism which comprises 90° jumps and a sofa–sofa pseudo-rotation. This was confirmed by calculating the 2D exchange spectra using the averaged geometries obtained by MD simulation, which agree well with the experimental results. Further evidence for such a complex reorientation mechanism is given by the comparably slow reorientation rate.

Overall, the mesophase dynamics of the tetrabenzocylophane derivative can be described as a '90° jump with pseudo-rotation' in a quasi-fourfold potential brought about by the internal flexibility of the mesogenic core.

This work originates from a fruitful collaboration with Professor Zeev Luz, Rehovot, Israel. His advice about conformations and pseudo-rotation was extremely helpful and is gratefully acknowledged. We thank Dr R. Hentschke for his advice concerning the molecular dynamics simulations and Dr H. Long for a critical reading of the manuscript. Financial support from the Deutsche Forschungsgemeinschaft (SFB 262) is gratefully acknowledged.

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