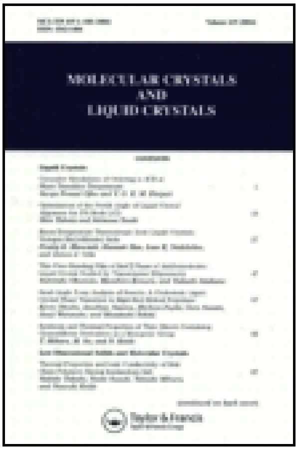

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Dynamic Nmr Studies of a New Series of Pyramidic Liquid Crystals

Zeev Luz [a], Raphy Poupko [a], Ellen J. Wachtel [a], Herbert Zimmermann [b] & Victoria Bader [b]

[a] The Weizmann Institute of Science, Rehovot, 76100, Israel

[b] Max-Planck-Institut für Medizinische Forschung, Heidelberg, 69120, Germany

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DYNAMIC NMR STUDIES OF A NEW SERIES OF PYRAMIDIC LIQUID CRYSTALS

Zeev Luz, Raphy Poupko, and Ellen J. Wachtel
The Weizmann Institute of Science, Rehovot 76100, Israel

Herbert Zimmermann and Victoria Bader
Max-Planck-Institut für Medizinische Forschung,
Heidelberg 69120, Germany

A new homologous series of compounds, nonaalkanoyloxy tribenzocyclononene (TBCN-n, where n is the number of carbons per side chain) with n = 2 to 14 was synthesized. The compounds exist in two isomeric forms, crown and saddle. For sufficiently long side chains (n ≥ 4 for the saddle and n ≥ 5 for the crown) the homologues of both series are mesogenic, exhibiting columnar hexagonal mesophases. The mesomorphic properties of the compounds were studied by differential scanning calorimetry, optical polarizing microscopy, X-ray diffraction and carbon-13 solid state NMR spectroscopy. No interconversion between the crown and saddle isomers is observed in the solid and mesophases (except very slow saddle to crown transformation, close to the clearing points of the mesophase), but isomerization is fast in the melt. This leads to peculiar phase diagrams which are discussed in the text. Analysis of the carbon-13 NMR spectra indicates that in the crown mesophases there is rapid reorientation of the molecules about the columnar axes, while no such motion is found in the mesophases of the saddle isomers. The latter appear, however, to undergo thermally activated high-amplitude librations, which freeze out on cooling to room temperature and below.

Keywords: discotic liquid crystals; pyramidic liquid crystals; dynamic carbon-13 MAS NMR; molecular reorientation; tribenzocyclononene; saddle-crown isomerization

INTRODUCTION

Discotic liquid crystals were discovered 25 years ago by Chandrasekhar *et.al.* [1] who used optical and X-ray methods to study the mesophase structure. Soon afterwards, Billard *et.al.* [2] reported optical observations of similar mesomorphic behavior in another discotic system. The first discotic mesogens were based on small rigid and flat cores, such as benzene, triphenylene or truxene. As the research of these phases developed the core size gradually increased reaching areas ten to twenty times larger than the original ones. This is well demonstrated by the hexabenzocoronene [3] and areno-condensed annulenes [4] cores. At the same time cores were discovered which are not flat and even not rigid. Amongst these are included the derivatives of tribenzo-cyclononene [5–9] and tetrabenzo-cyclododecatetraene [10–12] (see Figs. 1b and 1c). Both these cores are obtained by cyclization of veratryl alcohol (Fig. 1a) under suitable conditions [13]. The shape and flexibility (or rigidity) of these cores affect the ordering and dynamic properties of the resulting liquid crystals.

In the present work we study these properties on a new homologous series derived from the tribenzo-cyclononene (TBCN) core. The most stable structure of the TBCN core is the crown conformation. When hexasubstituted with sufficiently long side chains the compounds are mesogenic, exhibiting columnar mesophases, which because of their special

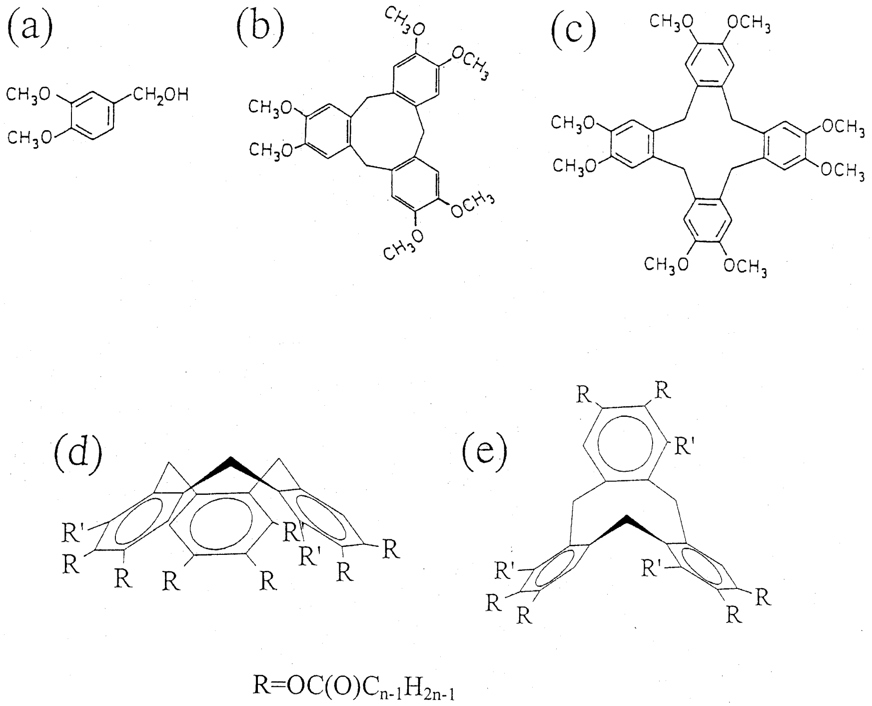

FIGURE 1 Structural formulae and conformations. (a) Veratryl alcohol. (b) Hexamethoxy-tribenzocyclononene (cyclotriveratrylene). (c) Octamethoxy-tetrabenzo-cyclododecatetraene (cyclotetraveratrylene). (d) and (e) The crown (left) and saddle (right) isomers of nonaalkanoyloxy-tribenzocyclononene (TBCN).

packing modes have been termed pyramidic liquid crystals [5,6]. When the TBCN core is clockwise (or anticlockwise) nonasubstituted the crown structure is destabilized and equilibrium is established between the crown and the saddle conformations (see Figs. 1d and 1e). We have found that when the substituents (R groups) are alkanoyloxy chains with more than 3 or 4 carbons per chain, both the saddle and the crown forms are mesogenic exhibiting columnar hexagonal mesophases [14]. The equilibration rate between the crown and saddle conformations in the solid and in the mesophase is extremely slow, even at high temperatures. However, in the melt and in solution, depending on the temperature, the equilibration may be fast. It is of the order of a day at 60°C and becomes faster (slower) on heating (cooling). This has important consequences concerning the investigation of these compounds. First, because at room temperature the crown-saddle interconversion is slow, the two isomers can be separated and their mesomorphic properties studied separately. Second, since in the melt the equilibration is fast there results a coupling between the isomerization and mesomorphism of the two isomers, leading to peculiar thermal behavior.

In the following we first describe the thermal behavior of TBCN mesophases, as studied by differential scanning calorimetry (DSC), optical polarizing microscopy (OM) and X-ray diffraction. We then present a carbon-13 MAS NMR study of their dynamic properties. It will be shown that the dynamic properties of the mesophases of corresponding isomers is quite different, reflecting the different shapes of the core.

RESULTS AND DISCUSSION

1. Thermal Properties of the Mesophases

We have synthesized and studied the saddle and crown isomers of the first thirteen ($n = 2$ to 14.) members of the TBCN-n series. The crown isomers are mesogenic for $n \geq 5$, while the saddle for $n \geq 4$. The mesophases of all mesogenic homologues are columnar hexagonal, with lattice parameters ranging from 18Å to 30Å (for $n = 4$ to 14) and being similar for corresponding crown and saddle isomers. The clearing temperatures, and for the crown also the melting points, are summarized in Table 1. No clear melting transitions were observed for the mesogenic saddle homologues. As synthesized these compounds acquire a pasty texture, suggesting that they are formed in a supercooled mesomorphic state.

It may be noted that for all homologues the clearing transition of the crown isomer is higher by some 25°C to 30°C relative to that for the saddle form, while within each series the clearing temperatures are fairly constant (about 160°C for the crown and 130°C for the saddle). These relations

TABLE 1 Clearing Temperatures (c.p.) of the Crown (C) and Saddle (S) Mesogenic Homologues of the TBCN-n Series. For the Crown Isomers also the Melting Transitions (m.p.) are Given. All Entries are in Degrees Celsius

n		4	5	6	7	8	9	10	11	12	13	14
C	m.p.	–	–[a]	25	19	45	39	43	44	60	65	71
C	c.p.	–	164	162	170	164	160	160	164	159	160	156
S[a]	c.p.	148	135	135	127	137	115	125	128	126	126	126

[a] Solid to mesophase transition not observed.

result in peculiar DSC thermograms, as demonstrated in Figure 2 for the isomers of the TBCN-8 homologue.

These DSC thermograms were studied in parallel with OM and during the heating cycle samples were removed, quenched to room temperature

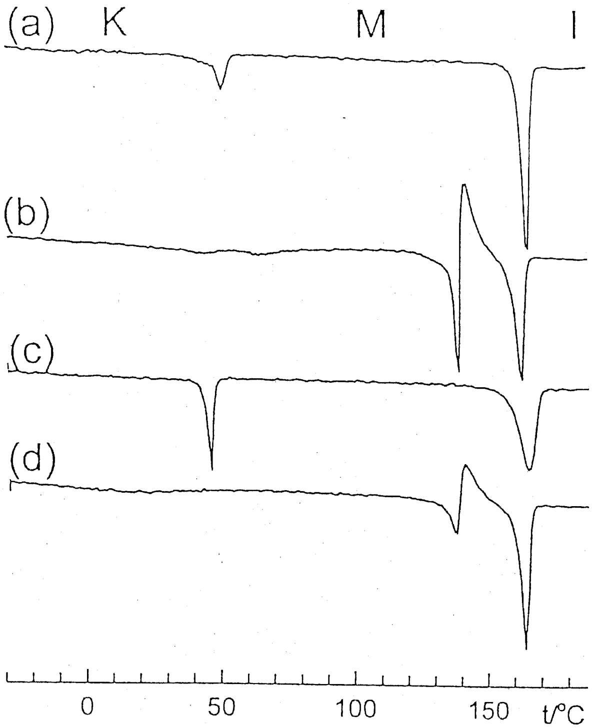

FIGURE 2 Differential scanning calorimetry (DSC) thermograms of TBCN-8 samples. All thermograms correspond to heating (10 K/min). (a) As-synthesized pure crown isomer. (b) As-synthesized pure saddle isomer. (c) Sample obtained by slow cooling from the melt. (d) Sample obtained by rapid cooling from the melt. The symbols K, M and I correspond to solid, mesophase and isotropic melt, respectively.

and their composition determined by high-resolution ^{1}H NMR. Trace a in Figure 2 corresponds to a regular melting (45°C) and clearing (164°C) sequence of the crown isomer. The sample retains its crown conformation throughout the heating process, but in the melt a saddle-crown equilibrium is established, dominated by the saddle form ($K = [\text{saddle}]/[\text{crown}] = 2.7$).

The behavior of the as-synthesized saddle isomer is quite different (see trace b of Fig. 2). No melting transition is observed (or at most a very broad one around 50°C), but at 137°C there is a clearing transition, followed immediately by an exothermic peak. Under OM the clearing transition is manifested by the appearance of an isotropic liquid, which, however, immediately transforms to a birefringent non-fluid phase. NMR measurements of this birefringent material shows that it is pure crown. Further heating yields at 164°C a second endothermic transition which corresponds to the clearing point of the crown. This experiment confirms that in the solid and mesophase the isomers retain their conformation, while in the melt rapid equilibration takes place. Thus, above the clearing point of the saddle isomer some crown is formed in the melt which rapidly "crystallizes" into the crown mesophase. The equilibrium in the melt immediately shifts until all the saddle is transformed into the crown. Further heating leads to clearing of the crown, a melt is obtained which consists predominantly of the saddle. We thus have the following sequence of events on heating the (supercooled) saddle isomer: mesophase (saddle)→liquid (saddle) →mesophase (crown) →liquid (predominantly saddle).

When the melt is slowly cooled it "crystallizes" to the pure crown mesophase at 164°C, as is confirmed by NMR measurements and by the DSC of trace c in Figure 2. However, if the melt is rapidly quenched to room temperature the high-temperature equilibrium ratio of the melt is retained in the resulting (supercooled) mesophase and the DSC thermogram of the quenched material (trace d) is similar to that of pure saddle (trace b). Essentially the same thermal behavior is observed for all mesogenic homologues of the series.

2. Dynamic Properties of the Mesophases

The dynamic properties of the mesophases of the TBCN-n series were studied by carbon-13 MAS NMR. As a representative example we discuss again the TBCN-8 homologue. In Figure 3 (left) are shown such spectra for the crown isomer in the mesophase region. Only the low-field part of the spectrum, corresponding to the aromatic and carboxylic carbons, is shown.

In the low-temperature region of the mesophase the spectrum consists of six peaks (in the range 123 ppm to 143 ppm) which can be identified with the six types of non-equivalent aromatic carbons of the TBCN core, and three carboxylic peaks (around 170 ppm) due to the three

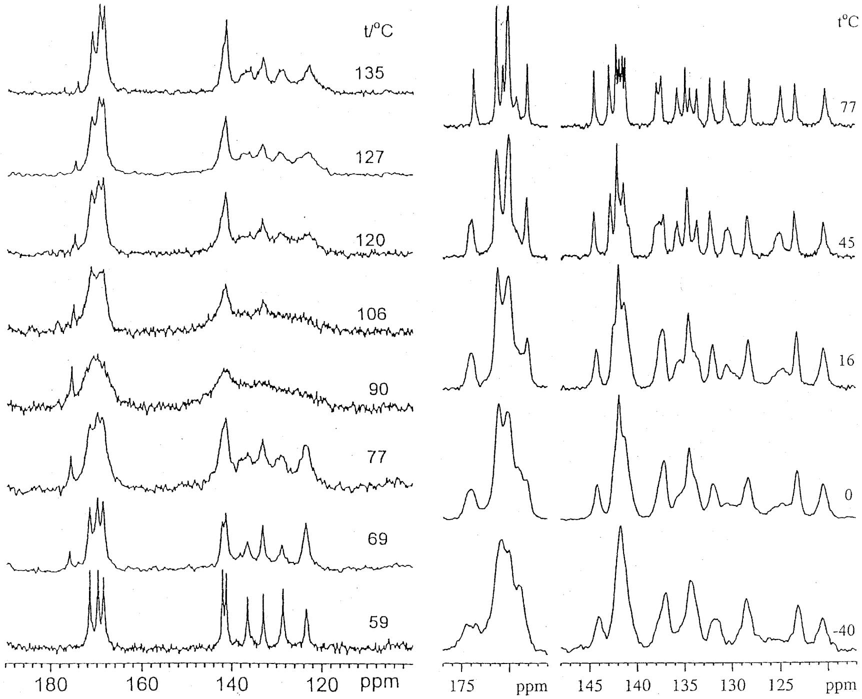

FIGURE 3 Carbon-13 magic angle spinning (MAS) NMR spectra of the crown (left) and saddle (right) mesophases of TBCN-8 at the indicated temperatures. Spinning frequency: 5 kHz.

non-equivalent side chains. These peaks remain relatively sharp upon heating the sample until about 60°C. Further heating results in gradual broadening of all peaks and eventual narrowing. This behavior is characteristic of dynamic processes, but the line shapes, as such, do not disclose the mechanism of the process. To elucidate its nature we performed a 2D MAS exchange experiment in the slow regime (61°C). The result is shown on the left hand side of Figure 4.

It exhibits besides the main diagonal, which is always observed in such experiments, also cross-peaks arranged in off diagonal lines parallel to the main diagonal. Their presence is due to exchange and their arrangements indicate that the exchange involves molecular reorientation (rather than isomerization). Because of the three-fold symmetry of the TBCN molecules we assume that the dynamic process involves three-fold molecular jumps within the columns. To obtain the kinetic parameters for this process from the dynamic spectra of Figure 4 we compared them with simulations

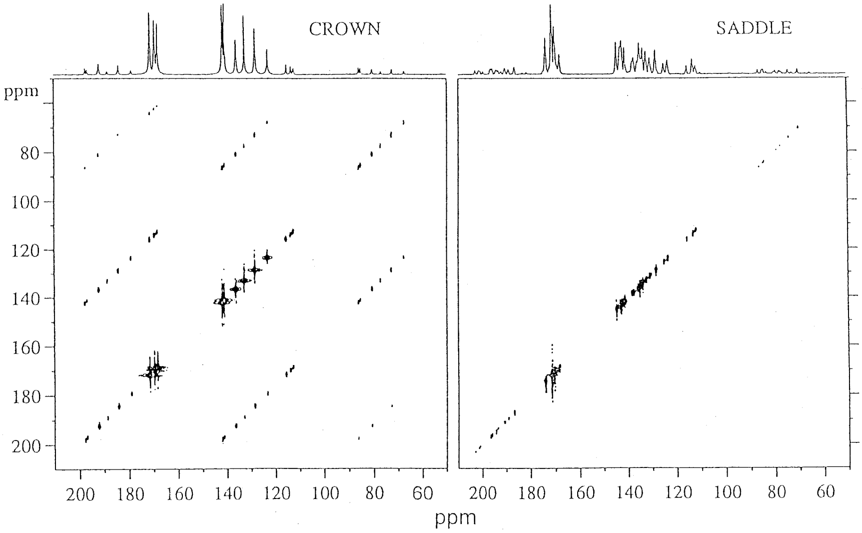

FIGURE 4 Carbon-13 rotor synchronized 2D exchange spectra for the crown (left) and saddle (right) isomers of TBCN-8 in the mesophase region. One dimensional projection spectra are depicted at the top. Experimental details for the crown: 61°C; spinning rate, 4.2 kHz; mixing time, 1 s. Corresponding details for the saddle: 80°C; 4.4 kHz; 10 s.

calculated for the appropriate magnetic parameters and different assumed rates [15,16]. In practice only spectra in the slow and fast regime could be analyzed. Excessive overlap between peaks prevented quantitative analysis of the spectra in the intermediate regime. The results, in terms of an Arrhenius plot, are shown in Figure 5. They correspond to the following kinetic parameters: $A = 3.1 \times 10^{22} s^{-1}$ and $\Delta E = 130.1$ kJ/mol.

These parameters are unusually large. The pre-exponential factor is several orders of magnitude higher than expected for dynamic processes in general, while the activation energy is much too high for molecular reorientation in liquid crystals or even soft solids. As proposed by Dunitz, [17] most likely these unusually high values reflect the fact that the barrier for the molecular reorientation decreases with increasing temperature. Such a temperature dependent barrier will result in a steep slope and a large intercept for a k vers. 1/T plot. It can be argued that the effect reflects the loosening, with increasing temperature, of the molecular stacking within the mesophase columns.

Similar carbon-13 measurements were performed on the saddle isomer of TBCN-8. Examples of spectra are shown on the right hand side of Figure 3. The spectrum shown in the top trace (corresponding to 77°C) remains

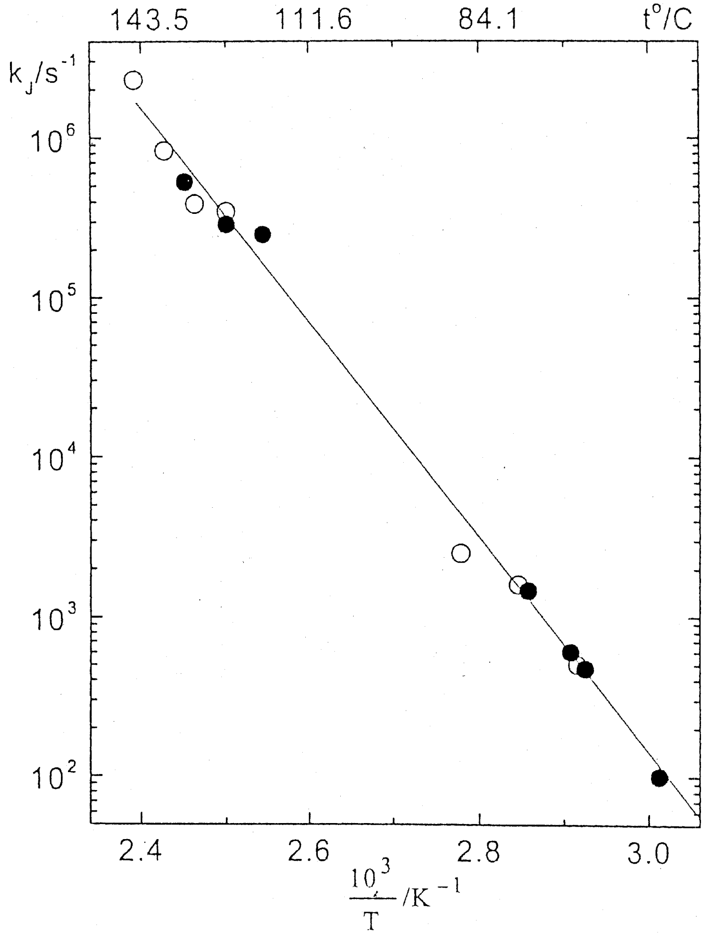

FIGURE 5 Arrhenius plot for the three-fold jump process in the mesophase of the crown form of TBCN-8. The results were obtained from spectra of the type shown in the left hand side of Figure 3. Open and solid symbols correspond to spectra recorded at 5 kHz and 10 kHz, respectively.

essentially unchanged on heating up to the clearing temperature. It exhibits several unresolved carboxylic signals (around 170 ppm) and eighteen well-resolved aromatic peaks in the region 120 ppm to 145 ppm. This is exactly the number of non-equivalent carbons in a static saddle conformer. We thus conclude that the saddle isomer is not reorienting, in the mesophase on the NMR time scale. In fact, even in the ultraslow regime no motion could be observed, as evidenced by the 2D exchange spectrum shown on the right hand side of Figure 4. This spectrum was recorded at 80°C with a mixing time of 10 s and no traces of cross-peaks can be observed. This stiffness of the saddle molecules towards reorientation may be understood in terms of their stacking modes within the columns (see Fig. 6). While the crown conformers can easily slip around the columnar axis without much distortion, the saddle molecule cannot do so without severe deformation.

The lack of reorientational motion in the saddle mesophase is nevertheless somewhat surprising. In an earlier deuterium NMR study [12] of columnar mesophases derived from tetrabenzo-cyclododecatetraene (see Fig. 1c) it was found that the molecules do undergo intracolumnar reorientation, despite the fact that their core is not smooth. These molecules acquire a sofa shape that would be expected to hinder intracolumnar reorientation in much the same way as in the saddle isomers of the TBCN derivatives. It was shown that in the tetrabenzo case the molecules reorient *via* a combined motion involving pseudorotation and rotation. This mechanism ensures that the stacking mode of the molecules before and after reorientation remains unchanged. In principle one would expect a

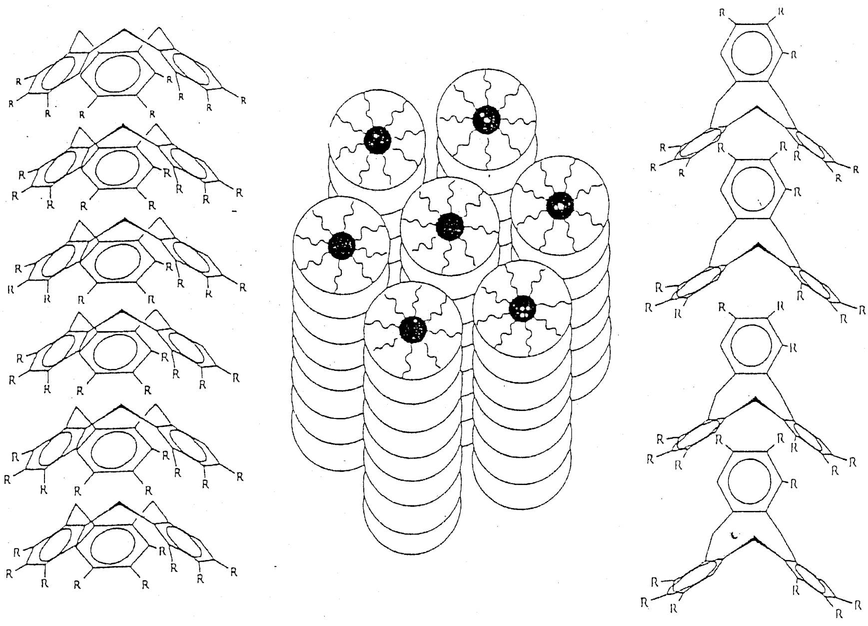

FIGURE 6 Schematic diagrams of a hexagonal columnar mesophase (center) and the stacking mode of the crown (left) and saddle (right) conformers within the columns.

similar mechanism for the saddle TBCN derivatives, which are also flexible, undergoing fast pseudorotation in solution. Apparently in this case the stacking is too tight to allow such a process to take place.

As indicated, the shape of the carbon-13 MAS spectrum of the saddle isomer remains unchanged on heating to above 77°C (right hand side of Fig. 3). However, on cooling (probably super-cooling) gradual line broadening sets in, as may be seen in the other traces displayed in the figure. We believe that the sharp signals observed in the high-temperature region of the mesophase reflect fast averaging of distorted saddle conformations. On cooling, these high-amplitude librations gradually freeze out, resulting in a distribution of twisted saddle forms. This, in turn, results in a distribution of isotropic chemical shifts and an inhomogeneous broadening of the MAS spectra. Close examination of these spectra shows that the broadening is selective; some of the peaks broaden more than others. This selectivity may be due to the fact that one of the benzene rings in the saddle conformation (perhaps the one sticking up) undergoes a larger distribution (libration amplitude) and hence in a larger inhomogeneous broadening. Support for this interpretation is lent by the fact that the low-temperature limiting broadening is independent of the MAS spinning speed.

SUMMARY AND CONCLUSIONS

It was shown that nonaalkanoyloxy TBCN can exist in two isomeric forms, crown and saddle. For sufficiently long alkanoyloxy chains both isomers are mesogenic, exhibiting hexagonal columnar phases. The two forms do not interconvert (or only very slowly) in the solid and mesophase, but they isomerizes rapidly in the melt (and at sufficiently high temperatures also in solution – the half life being of the order of a day at 60°C, but reduces to less than a minute above 100°C). The clearing temperatures of the crown isomers are always higher than those of the corresponding saddle, resulting in a special coupling between isomerization and phase transformation.

While the crown isomers crystallize and usually show clear melting transitions, the saddle form resist crystallization and probably only exists as a mesophase or (at low temperatures) as a supercooled mesophase. The lattice parameters of both isomers in the mesophase are similar for corresponding homologues, but their dynamic properties are quite different. The rigid crown core reorients freely within the columnar phases on the time scale of milliseconds to microseconds. On the other hand the saddle isomers, which in solution or in the melt are flexible, are rigidly packed within the columns and do not reorient even on the time scale of many minutes. However, in the mesophases of the latter the cores seem to undergo high amplitude librations, which gradually freeze out on cooling to room temperature and below.

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