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# A deuterium NMR study of the discotic mesophase of hexa-hexyloxytriphenylene

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Résumé. — La mésophase discotique obtenue dans les cristaux liquides de l'hexa-hexyloxytriphénylène est étudiée en résonance magnétique nucléaire du deutérium. Les spectres de deux composés isotopiques, sélectivement deutérés ont été obtenus : dans le premier cas, toutes les positions aromatiques ont été substituées, et dans le second la substitution a été réalisée sur le carbone en  $\alpha$  des chaînes latérales. Le benzène deutéré (C<sub>6</sub>D<sub>6</sub>) dissous dans l'hexa-hexyloxytriphénylène normal a aussi été mesuré. Les échantillons, préparés par refroidissement lent du liquide et placés dans un champ magnétique suffisamment puissant (> 20 kgauss), fournissent des domaines où les directeurs sont distribués uniformément dans un plan perpendiculaire à la direction du champ magnétique. Une fois formés les différents domaines conservent leurs orientations originales (au moins dans un champ aussi grand que 21 kgauss) permettant dès lors d'enregistrer des spectres dans différentes orientations du champ magnétique. Les résultats de ces expériences fournissent des données sur la répartition du directeur et sur le paramètre d'ordre de la partie aromatique rigide du cristal liquide. Le paramètre d'ordre de la partie aromatique rigide de la molécule est compris entre 0,90 et 0,95 dans la région de la mésophase et est très faiblement dépendant de la température même au voisinage du point de clarification. Les résultats des splittings quadrupolaires des deutérons suggèrent que les chaînes latérales alkylées sont largement désordonnées. Ceci est en accord avec la courte valeur du rayon effectif des colonnes discotiques, obtenue par les études des rayons-X de certaines mésophases discotiques. Finalement il a été démontré qu'il est possible d'obtenir une mésophase discotique présentant un domaine unique. Ceci a été obtenu à partir du liquide, par un refroidissement lent effectué dans un champ magnétique, l'échantillon tournant suivant un axe perpendiculaire à la direction du champ. Le domaine unique se forme avec son directeur s'orientant parallèlement à l'axe de rotation.

Abstract. — The discotic liquid crystalline mesophase of p-n-hexa-hexyloxytriphenylene was studied using deuterium NMR spectroscopy. Spectra of two selectively deuterated isotopic species were recorded : (i) in which all aromatic positions were substituted, and (ii) in which the substitution was made in the  $\alpha$ -carbon side-chains. Measurements were also made on a deuterated probe compound ( $C_6D_6$ ) dissolved in normal hexa-hexyloxytriphenylene. Samples prepared by slow cooling of the isotropic liquid in a sufficiently strong magnetic field (> 20 kgauss) consist of domains whose directors are evenly distributed in a plane perpendicular to the field direction. Once formed, the various domains conserve their original orientation (at least in a field as high as 23 kgauss) thus making it possible to record spectra at different orientations of the magnetic field. The results of such experiments provide information on the distribution of the director and on the order parameter of the liquid crystal. For the rigid aromatic moiety of the molecules the order parameter ranges between 0.90 and 0.95 in the mesophase region and is very weakly temperature dependent even close to the clearing point. The results for the quadrupole splittings of the aliphatic deuterons suggest that the alkyl side chains are quite disordered. This is in agreement with the short effective radius of the discotic columns determined by X-ray studies in certain discotic mesophases. Finally it is demonstrated that a single domain of the discotic mesophase can be obtained by allowing the mesogen to cool slowly from the isotropic liquid in a magnetic field, while spinning the sample about an axis perpendicular to the field direction. The single domain is formed with its director parallel to the spinning axis.

1. Introduction. — The existence of a new type of liquid crystalline phases in compounds composed of disc-like molecules was recently demonstrated by two groups of researchers. In 1977 Chandrasekhar, Sadashiva and Suresh [1] first reported that certain members of the homologous series of benzene hexa-*n*-alkanoates (I) exhibit liquid crystalline mesophases, and a year later Billard, Dubois, Tinh and Zann [2] reported similar observations on hexa-substituted derivatives of triphenylene (II).



In a recent review Billard [3] described several other compounds which exhibit such mesophases. These mesophases have been termed discotic liquid crystals. They share the common feature that they consist of molecules with a flat aromatic rigid part to which several (usually six) alkyl chains are bonded in a symmetric way along the periphery of the rigid central part. Several different phases have already been identified, including nematic, cholesteric and a number of columnar (discotic) mesophases [4].

The purpose of this paper is to explore the suitability of NMR spectroscopy to elucidate the structure of these discotic phases. NMR has been used extensively in the past to study structures of many thermotropic liquids [5] but it has not yet been applied in connection with the discotics. In preliminary experiments we have tried both <sup>1</sup>H NMR of normal mesogens and <sup>2</sup>D NMR of deuterated compounds. In both cases we recorded spectra of the neat liquid crystals as well as of probe molecules dissolved in the mesophase. We found that the deuterium results were very informative while the proton spectra were usually poorly resolved and uninterpretable.

Specifically we studied the discotic phase of p-nhexa-hexyloxytriphenylene,  $R = OC_6H_{13}$  in II, (THE6) which has the phase diagram [6]

### Solid $\stackrel{68}{\longleftrightarrow} D \stackrel{99}{\longleftrightarrow} Iso$ .

Here Iso stands for isotropic liquid, and D for discotic mesophase. This mesophase was studied previously by X-ray diffractometry [7] in two other members of the hexa-alkoxytriphenylene series, i.e. n = 5,7. It was shown to belong to the D<sub>ho</sub> class, i.e. to a mesophase in which the molecules are stacked in columns which in turn form a regular hexagonal array. The spacing between the columns was found to be 18.94 Å and 21.94 Å for the n = 5 and 7 respectively. These spacings are somewhat shorter than the diameters of

the corresponding molecules with fully stretched chains, indicating the presence of disorder in the chain conformation (« diablo » or « octopus » like molecules) [8]. Within the columns the average spacing between the molecules is 3.59 Å. A study of some triphenylene ester derivatives [9] show that in the solid phase the molecules are associated in pairs with an interspacing distance of 3.43 Å.

We have prepared two specifically deuterated species of THE6, one in which the deuterium is substituted in the six available aromatic sites (THE6-ard<sub>6</sub>), and a second one in which the deuterium is substituted in the  $\alpha$ -positions of the six hexploxy side chains (THE6- $\alpha d_{12}$ ). Measurements were also made on deuterated probe molecules C<sub>6</sub>D<sub>6</sub> dissolved in normal THE6. The deuterium NMR results obtained with THE6-ard<sub>6</sub> provide information on the order parameter of the rigid moiety. These results are discussed in section 3.1. Detailed information on the ordering of the mesophase could be obtained from spectra recorded at different orientations with respect to the magnetic field. The analysis of these results is described in sections 3.2 and 3.3. Finally in section 3.4 we discuss the data obtained for the aliphatic deuterons in THE6- $\alpha d_{12}$  and provide a preliminary analysis of the results in terms of the chain conformation. The experimental procedures including the synthesis of the isotopically labelled compounds are summarized in section 2.

2. Experimental. — 2.1 PREPARATION OF COM-POUNDS. — The synthesis of the hexa-alkoxytriphenylenes was first performed by Destrade *et al.* [6]. Here we give a short description of the synthetic route used by us for both the normal and deuterated species used in the present study. The overall scheme is given in the following diagram :



Hexa-methoxytriphenylene (III) was prepared by reacting veratrole (o-dimethoxybenzene) with chloranil (tetrachlorobenzoquinone) in sulfuric acid [6]. The excess chloranile was removed by sublimation

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and the resulting hexa-methoxytriphenylene was purified by column chromatography with  $CHCl_3$  as eluent (Yield : 62 %).

Hexa-hydroxytriphenylene (IV) was obtained by refluxing III in a 1:1 mixture of acetic acid and concentrated hydrobromic acid (48 %) for 24 hours (Yield : 75 %). The desired product, hexa-hexyloxytriphenylene (THE6), was finally obtained by refluxing IV with excess of *n*-hexylbromide in ethanol (95%) in the presence of potassium bicarbonate. The reflux was conducted under nitrogen for 24 hours. The resulting product contained traces of high molecular weight impurities which were removed by column chromatography on Silica-Gel using as eluent a 1:1 mixture of methylene chloride and n-hexane, followed by increasing the proportion of methylene chloride. The final product was recrystallized from ethanol (Yield : 72 %). It should be emphasized that the use of ethanol as a solvent in the refluxing stage is preferable to that of dimethylformamide used in reference [6] since in the latter solvent a considerable amount of partially alkoxylated triphenylenes are produced which are difficult to remove.

The deuterated species THE6-ard<sub>6</sub> and THE6- $\alpha d_{12}$ were prepared using appropriate deuterated starting materials, i.e. perdeuterated hexa-hydroxytriphenylene (IV) and  $\alpha$ -d<sub>2</sub>-hexylbromide respectively. Perdeuterated-IV was obtained in the same way as normal IV except that the refluxing mixture contained DBr and CH<sub>3</sub>COOD in D<sub>2</sub>O. In addition to the demethylation reaction, the refluxing also induced exchange of the aromatic hydrogens. NMR analysis showed that the degree of deuteration of the aromatic sites was ~ 60 %.  $\alpha$ -d<sub>2</sub>-hexylbromide was obtained from ethylhexanoate by first reducing it with LiAlD<sub>4</sub> to  $\alpha$ -d<sub>2</sub>hexylalcohol followed by bromination with red phosphoruous and bromine. The deuterium content of the end product was ~ 98 % (by NMR).

The phase transition temperatures of the compounds were determined by microscopy using a Mettler FP-52 hot stage. The melting and clearing temperature (in °C) were respectively 68 and 99 for normal THE; 65 and 96 for THE- $\alpha d_{12}$ ; and 67 and 95, for THE6-ard<sub>6</sub>.

2.2 NMR MEASUREMENTS. — Most NMR measurements were performed on a Bruker WH-270 spectrometer operating at 41.45 MHz for deuterium, using the pulsed Fourier Transform mode. The temperature of the sample was controlled with a BST 100/700 unit which was modified to have a resolution of 0.1 °C. The absolute temperature was repeatedly calibrated using Fluke 2190A digital thermometer. Since the calibration varied from day to day it is felt that the absolute temperature may have been off by as much as 2 °C. We therefore present the results relative to the mesophase-isotropic liquid clearing point temperature, defined as  $T_c$ .

The experiments which required sample rotation could not be performed in the WH-270 spectrometer,

since the natural rotation axis in this (superconducting) spectrometer lies parallel to the magnetic field. Rotation experiments were therefore performed on a Bruker WH-90 spectrometer which uses a conventional electromagnet (deuterium frequency 13.81 MHz)

Samples of the neat deuterated compounds were prepared by filling about 0.7 g mesogen into a 10 mm (o.d.) tube, degassing by repeated freeze-thaw cycles and sealing under vacuum. Samples containing a solution of deuterated benzene ( $C_6D_6$ ) in normal THE6 were prepared by adding a weighed amount of deuterated benzene to a sample containing the mesogen after the degassing stage, then cooling it down to liquid nitrogen temperature, pumping and finally sealing under reduced pressure. The probe concentration was 6.6 wt. % and its clearing point,  $T_c = 77.5$  °C.

We have also prepared samples in which the mesogen was enclosed in a small capsule which could be placed in a 10 mm sample tube both parallel and perpendicular to its axis. These capsules were made from a 7 mm tube, and their « long axis » (i.e. along the original tube's axis) was between 8 and 9 mm. The capsules contained about 0.15 g mesogen.

3. **Results and discussion.** — The deuterium NMR spectrum in liquid crystalline mesophases is usually dominated by the quadrupole interaction [5]. If we neglect the effect of dipolar interactions and consider a single uniaxial liquid crystalline domain the spectrum from a single type of deuterium consists of a doublet with spacing

$$v_{Q} = S\left(\frac{3 e^{2} qQ}{2 h}\right) \frac{1}{2} (3 \cos^{2} \gamma - 1) \frac{1}{2} (3 \cos^{2} \theta - 1) \quad (1)$$

where  $(e^2 qO/h)$  is the quadrupole interaction constant, S the orientational order parameter of the molecular symmetry axis,  $\gamma$  the angle between the C-D bond direction and the molecular axis and  $\theta$  the angle between the director and the external magnetic field. In writing equation (1) we assumed an axially symmetric quadrupole tensor ( $\eta = 0$ ) for the C-D bond and a mesogen of molecules possessing a symmetry axis  $C_n$  with  $n \ge 3$ . From the known magnetic susceptibility tensor of the aromatic rings we expect the mesophase molecule to prefer an orientation in which the molecular rigid planes lie parallel to the magnetic field, and the director perpendicular to it ( $\theta = \pi/2$ ). Since all perpendicular orientations are equally probable we expect the discotic phase to break up into many domains with their directors normal to the external field and a random azimuthal distribution (see Fig. 1). This picture is consistent with susceptibility measurements on analogous discotic compounds [18]. In the next sections we show that the NMR spectra are also consistent with this picture and provide additional information on the order parameter and the distribution of the domains.



Fig. 1. — A schematic diagram of the domain distribution in a sample formed by slow cooling of the discotic mesogen in a magnetic field. The discs represent the liquid cystalline molecule and the n's are the directors of the various domains. They lie in the XY plane while the magnetic field is parallel to Z.

3.1 THE ORIENTATIONAL ORDER PARAMETER. — In figure 2 are shown examples of spectra from a 2 : 1 mixture of THE6-ard<sub>6</sub> and THE6- $\alpha d_{12}$  in the mesophase region. The outer and inner doublets in this figure correspond respectively to the aromatic and  $\alpha$ aliphatic deuterons. We have measured the quadru-



Fig. 2. — <sup>2</sup>D NMR spectra of specifically deuterated hexa-hexyloxytriphenylene in the mesophase region. The sample consists of a 2 : 1 mixture of THE6-ard<sub>6</sub> : THE6- $\alpha$ d<sub>12</sub>. The outer and inner doublets correspond respectively to the aliphatic and aromatic deuterons, while the centre peak in the lower spectrum is due to traces of isotropic material.

pole splittings in this mixture as well as in neat samples of THE6-ard<sub>6</sub> and THE6- $\alpha$ d<sub>12</sub> over the whole mesophase region and the results are shown in figure 3. The samples used to record these spectra were prepared by slowly cooling the mesogen from the isotropic region down to the discotic phase within the magnetic field of the WH-270 spectrometer (63 kgauss). The configuration of this magnet is such that its field is parallel to the sample tube axis so that the directors distribute in the radial plane. Indeed rotation of the sample about this axis during cooling of the mesogen and/or during recording of the spectra after cooling, did not affect the lineshape. The relatively sharp peaks



Fig. 3. — Quadrupole splittings for the aromatic  $v_Q^{ar}$  and  $\alpha$ -aliphatic,  $v_Q^a$ , deuterons of deuterated hexa-hexyloxytriphenylene as function of temperature in the mesophase region. The open circles correspond to measurements on neat THE6-ard<sub>6</sub> and THE6- $\alpha d_{12}$  separately, while the filled points correspond to a 2 : 1 mixture of these isotopic species. The scale on the upper right hand side gives the order parameter of the aromatic part using equation (2). The curve at the bottom gives the ratio of the quadrupole splittings for the  $\alpha$ -aliphatic and aromatic deuterons.

observed in the spectra indicate very little distribution in the orientation of director about  $\theta = \pi/2$ , and also of course that the rotational and translational diffusion of the mesogen molecules is fast on the NMR time scale.

To derive the order parameter, S, from these results, we use equation (1) and suitable values for the angle  $\gamma$ and the quadrupole splitting constant  $e^2 qQ/h$ . For the aromatic deuterons the latter quantity is taken [11] as 183 kHz while  $\gamma$  is clearly  $\pi/2$ , so that

$$v_o^{\rm ar} = 68.6 \ S \ kHz$$
 (2)

Using this relation the ordinate on the right hand side of figure 3 which gives the order parameter S was recalibrated.

A striking feature of these results is the relatively high value of S (0.90-0.95) and its very weak temperature dependence even close to the clearing point. It is reminiscent of the behaviour predicted by Onsager for rod-like objects undergoing excluded volume interaction [12]. This model may indeed be a very suitable one for the discotic phase. It seems plausible to assume that the dominant intermolecular interaction between the discotic molecules is along their symmetry axis thus stabilizing the formation of columns, which in turn serve as the rigid rods in the Onsager model. It should be noted that the results for S in figure 3 are the first of their type for discotic phases and so no comparison with other systems can be made at this stage.

3.2 DOMAIN DISTRIBUTION AND MAGNETIC FIELD ROTATION EXPERIMENTS. — In the above we have assumed that the discotic sample prepared by slow cooling from the isotropic liquid in the magnetic field, consists of domains with directors homogeneously distributed in a plane perpendicular to the original orientation of the magnetic field (Z-direction in figure 1). To prove this picture and in order to learn more about the distribution of the domains we performed experiments in which NMR spectra of the aligned samples were recorded at different orientations of the magnetic field. The configuration of the WH-270 superconducting magnet is not suitable for such experiments since the natural rotation axis of the sample tube is parallel to the magnetic field direction. We have therefore performed these experiments in the WH-90 spectrometer where sample rotation can be made about an axis perpendicular to the field direction. It turned out however that the deuterium powder signals from the neat deuterated THE6-ard<sub>6</sub>, and THE6- $\alpha d_{12}$  samples were very distorted due to their wide spectral range. We therefore used the signal from a probe molecule ( $C_6D_6$ , 6.6 wt. %) dissolved in normal THE6. Because of the smaller spread of the spectrum of this sample the distortion problem did not appear and good quality powder signals could be obtained [13]. We assume that the small amount of probe added, does not affect the nature of the phase. It should be noted however that addition of solvents



Fig. 4. — <sup>2</sup>D NMR spectra of a 6.6 wt. % solution  $C_6D_6$  in the discotic mesophase of THE6 (T = 56.5 °C). The spectra on the left are experimental and were obtained from a sample which was aligned in a magnetic field (0°) and then rotated by 30°, 60° and 90° about an axis perpendicular to the field. The spectra on the right are theoretical, and were computed using equation (3) and the best fit parameters K = 315 Hz;  $1/T_2 = 10$  Hz;  $\sigma = 3.75^\circ$ .

to discotic mesogens may in certain cases result in a lyotropic phase [14].

Towards the end of this study we prepared a sample of hexa-heptyloxytriphenylene with perdeuterated alkyl side chains (THE7- $d_{90}$ ). The deuterium spectrum from the methyl groups in this compound also exhibited sufficiently small splitting so that good quality powder signals could be obtained. In the following we report rotation pattern experiments on both these samples, i.e. normal THE6 containing  $C_6D_6$  and THE7- $d_{90}$ .

The samples were slowly cooled in the magnetic field from the isotropic phase to a few degrees below  $T_c$ . After some time the temperature was reduced to about 10-20 °C below  $T_c$  and the spectrum recorded as function of the rotation angle about the sample-tube longitudinal axis (the X-axis in figure 1). Results of spectra obtained at selected rotation angles are shown in figures 4 and 5. The spectra are typical of « two dimensional powders » with the directors distributed in a plane [15] and the magnetic field inclined to the plane's normal by the rotation angle  $\alpha$ .



Fig. 5. — Same as figure 4 but for the CD<sub>3</sub> spectrum in THE7-d<sub>90</sub> (T = 75 °C). The best fit parameters used for the simulated spectra are K = 185 Hz;  $1/T_2 = 17$  Hz;  $\sigma = 3.75^{\circ}$ .

For the actual simulation of the spectra it was necessary to assume a certain degree of out of plane distribution of the directors. Assuming that this distribution is Gaussian the experimental spectra could very accurately be simulated by convoluting a Lorentian lineshape over the whole angular distribution

$$I(v)^{\alpha} = \sum_{m=\pm 1} \int_{-\pi/2}^{\pi/2} d\varphi \int d\beta \cos \beta \times \\ \times \exp(-\beta^2/2 \ \sigma^2) \ (1/T_2) / \{ (1/T_2)^2 + [v - v^m(\alpha, \varphi, \beta)] \}$$
(3)

where

$$v^{m}(\alpha, \varphi, \beta) = v_{0} + mK \frac{1}{2} \left[ 3\cos^{2}\theta(\alpha, \varphi, \beta) - 1 \right]$$
$$K = S\left(\frac{3e^{2}qQ}{4h}\right) \frac{1}{2} \left( 3\cos^{2}\gamma - 1 \right)$$

and

 $\cos \theta(\alpha, \varphi, \beta) = \cos \alpha \sin \beta + \sin \alpha \cos \beta \sin \theta$ .

In these equations  $\sigma^2$  is the variance of the out of plane distribution,  $1/T_2$  is the natural linewidth, and the angles  $\alpha$ ,  $\beta$  and  $\varphi$  are defined in figure 6. In practice the double integration was performed by summation over  $\varphi$  at intervals of 2 degrees and summation over  $\beta$ at one degree intervals between  $-4\sigma$  and  $+4\sigma$ . It may be seen in figures 4 and 5 that the theoretical spectra reproduce closely the details of the experimental results. (The slight asymmetry in the experimental spectra around  $\alpha = \pi/2$  is believed to be caused by the effect of the anisotropic macroscopic magnetic susceptibility of the bulk on the centre frequency,  $v_0$ , of the various domains. The effect could be accounted for by adding a term  $\delta[3\cos^2\theta(\alpha, \varphi, \beta) - 1]$  to  $v_0$ .) The theoretical spectra were calculated using the best fit parameters, K,  $1/T_2$  and  $\sigma$  as indicated in the figure captions. The quantities K and  $1/T_2$  are characteristic of the probe molecule used, but the distribution parameter  $\sigma$  depends on the ordering of the mesophase and provides information on the texture of the sample.



Fig. 6. — The coordinate system used to compute the rotation experiments. Z is the original direction of the magnetic field which is arbitrarily confined to lie in the YZ plane and  $\alpha$  is the rotation angle in this plane. n represents a director with azimuthal angle  $\varphi$  and  $\beta$  its deviation from the XY plane.

The main conclusions from these experiments are that in the presence of a sufficiently strong magnetic field the discotic domains grow with their director perpendicular to the external field. When the phase has completely formed from the isotropic liquid and then cooled down several degrees ( $\sim 10 \text{ °C}$ ) below  $T_c$ , the structure locks itself and anchors to the sample wall. At this stage it will not reorient on rotation of the magnetic field at least of strength up to 23 kgauss. The situation is similar to that observed in the usual thermotropic smectics [16].

3.3 DISCOTIC SINGLE DOMAINS. — Levelut et al. [10] have shown that single domain discotics can be prepared by allowing the mesophase to grow within a rotating magnetic field. We have prepared such single domains for our NMR experiments. A mesogen sample was slowly cooled from the isotropic liquid to just below the clearing point and left at that temperature for one to two hours while spinning the sample in the magnetic field about an axis, X, perpendicular to the field axis. During spinning, those domains which nucleate with their director parallel to X do not experience any magnetic torques, while those which are formed in a general direction experience alternating torques which tend to align them parallel to the X-direction. The only exceptions are the domains with directors in the YZ plane, but these are metastable and are driven out from this plane by small fluctuations. Eventually most domains orient themselves parallel to X and upon further cooling the mesogen the director remains fixed, resulting in a homogeneously aligned sample. Its structure can be maintained as long as the mesophase does not crystallize or is not heated up too close to the clearing point.

To prove the single crystal nature of samples prepared as above we performed two types of rotation experiments. First we checked the spectrum of the sample at various orientations of the magnetic field with the X axis perpendicular to the magnetic field, i.e. the original orientation of the sample. The resulting spectra exhibited a single sharp doublet with a constant splitting independent of orientation as would be expected for a single domain with a director



Fig. 7. — <sup>2</sup>D NMR spectrum of a single domain sample of a  $C_6D_6$  solution in normal THE6 (T = 77 °C). The single domain was prepared by spinning the sample about an axis perpendicular to the magnetic field while cooling it from the isotropic liquid. The sample was then tilted by 90°, and spectra were recorded for different orientations,  $\theta$ , of the original spinning axis (X) with respect to the magnetic field.



Fig. 8. — As in figure 7 for the methyl resonance of THE7-d<sub>90</sub> (T = 67 °C). The spectrum of the methylene deuterons lies outside the region of the figure except for the  $\theta = 55^{\circ}$  where they also contribute to the central peak.

u (Hz)

parallel to the rotation axis. The second experiment was done using mesogen samples enclosed in a small capsule as described in the experimental section. We first placed the capsule in a 10 mm tube with its « long axis » parallel to the tube's axis, and prepared a single crystal in exactly the same way as described above. Then we replaced the capsule in the tube but reoriented by 90°, so that the director now lay perpendicular to the tube's axis. Precaution was taken to prevent the mesophase from solidifying by performing the manipulation as quickly as possible and immersing the tube in a hot bath during the operation. After placing the sample back into the magnetic field, rotation experiments were performed again. Selected spectra for both a  $C_6D_6$  solution in THE6 and the  $CD_3$ groups of THE7-d<sub>90</sub> are shown in figures 7 and 8. They clearly show the single crystal nature of the samples. In particular note the coalesced signal around the magic angle and the fact that the splittings at 0° and  $\pi/2$  are related by a factor 2. On the other hand between 0° and  $\pi/2$  the lines are quite broad indicating a significant degree of distribution in the director orientation. The uniaxiality of the phase is demonstrated by the angular dependence of the quadrupole splitting. A plot of the quadrupole splitting of the methyl deuterons in THE7-d<sub>90</sub> obtained from spectra of the type shown in figure 8 is given in figure 9. In this figure the orientation  $\theta = 0$  was adjusted to coincide with the orientation of the sample that gave maximum splitting and the full line traces the function  $K \frac{1}{2}(3\cos^2 \theta - 1)$  with K = 334 Hz.



Fig. 9. — The quadrupole splitting of the CD<sub>3</sub> deuterons in THE7d<sub>90</sub>, from experiments of the type shown in figure 8, as function of the rotation angle  $\theta$ .

3.4 Quadrupole splitting from the  $\alpha$ -aliphatic DEUTERONS AND CHAIN CONFORMATION. --- We now turn to the results obtained from the THE6- $\alpha d_{12}$ , i.e. the compound in which the hydrogen bonded to the chains  $\alpha$ -carbons where substituted by deuterium. A plot of the quadrupole splitting,  $v_Q^{\alpha}$  versus temperature is shown together with the corresponding plot for the aromatic deuterons in figure 3. From the data in this figure we note that both  $v_0^{ar}$  and  $v_0^{\alpha}$  decrease with temperature in the mesophase region. However the ratio  $v_Q^{\alpha}/v_Q^{ar}$  is not constant but rather decreases from about 0.48 at 55 °C to 0.43 at 97 °C. The temperature dependence of  $v_0^{ar}$  reflects, as discussed above, the decrease in the order parameter of the molecular rigid moiety. If the aliphatic chains were also rigid they should exhibit an identical temperature dependence as the aromatic deuterons. The fact that the ratio  $v_0^{\alpha}/v_0^{\alpha r}$  is temperature dependent indicates that the conformation of the alkyl chains changes with



Fig. 10. — Molecular structures for the two extreme models for chain conformation discussed in the text. (a) The alkoxy oxygen and the  $\alpha$ -carbon are coplanar with the aromatic ring. (b) The alkoxy oxygen and  $\alpha$ -carbon lie in a plane perpendicular to the aromatic ring.

temperature. In the rest of this section we discuss possible conclusions that can be derived from this effect.

We consider two limiting models. In the first model we assume that the triphenylene rings, the alkoxy oxygens and the  $\alpha$ -carbons are coplanar (Fig. 10*a*), and allow the CD<sub>2</sub>R group to reorient about the oxygen  $\alpha$ -carbon bond (R is the end part of the aliphatic chain,  $C_5H_{11}$ ). The CD<sub>2</sub>R group can occupy three rotameric states; a « trans » rotamer with the R group coplanar with the aromatic ring, and two « gauche » states obtained from the « trans » by  $\pm 120^\circ$  rotation about the oxygen  $\alpha$ -carbon bond. Assuming fast chain isomerization and tetrahedral bond angles ( $\tau$ ) for the  $\alpha$ -carbon bonds, the following expression for  $v_{\alpha}^{\alpha}/v_{\alpha}^{\alpha}$  is obtained

$$\frac{v_Q^2}{v_Q^2} = q_r \frac{(P_t + \frac{1}{2}P_g)\frac{1}{2}(3\cos^2\delta - 1) + \frac{1}{2}P_g\frac{1}{2}[3\cos^2(\pi/2) - 1]}{\frac{1}{2}[3\cos^2(\pi/2) - 1]} = -q_r P_t$$
(4)

where  $P_t$  and  $P_g$  are the probabilities for the trans and gauche rotamers respectively,  $(P_t + P_g = 1)$ ,  $\delta = 1/2(\pi - \tau)$ , and  $q_r$  is the ratio of the quadrupole



Fig. 11. — A semilog plot of  $P_i/P_g$  versus reciprocal absolute temperature in the mesophase region of THE6. The ratio  $P_i/P_g$  was calculated from equation (4) using the model shown in figure 10a.

splitting constants of a deuteron in aliphatic and aromatic bonds. We take [11] for the aliphatic deuteron the value 168 kHz so that  $q_r = 168/183 = 0.918$ . Thus, this model predicts opposite signs for  $v_Q^a$  and  $v_Q^{ar}$ , with  $|v_Q^a/v_Q^{ar}|$  ranging between zero (for all-gauched), to 0.92 (for all-trans). The experimental values 0.43 to 0.48 for  $|v_Q^a/v_Q^{ar}|$  correspond to  $P_t/P_g \sim 1$  with a slight increase of  $P_g$  with increasing temperature. In figure 11 are plotted numerical values for  $P_t/P_g$ derived from the experimental data versus reciprocal temperature. From the slope of this curve a free energy difference

$$\Delta G = G_{g} - G_{t} = 1.4$$
 kcal./mole

between the gauche and trans is obtained.

We next consider the second extreme model in which the alkoxy oxygens and the  $\alpha$ -carbons lie in a plane perpendicular to the aromatic plane (Fig. 10b) and again assume three possible rotamers : a « trans » rotamer with R in a trans position with respect to the aromatic carbon bounded to the oxygen, and two gauche rotamers obtained by  $\pm$  120° rotation. For this case we have

$$\frac{v_Q^2}{v_Q^{ar}} = q_r \frac{(P_t + \frac{1}{2}P_g)\frac{1}{2}(3\cos^2 58.2 - 1) + \frac{1}{2}P_g\frac{1}{2}(3\cos^2 81.5 - 1)}{\frac{1}{2}[3\cos^2(\pi/2) - 1]} = q_r(0.55 - 0.38P_t)$$
(5)

where we took for the COC bond angle [17] a value of 118°. This model predicts equal signs for  $v_Q^a$  and  $v_Q^{ar}$  over the whole mesophase range with  $v_Q^a/v_Q^{ar}$  ranging from 0.50 (for all gauche) to 0.16 (for all trans). The experimental values of  $v_Q^a/v_Q^{ar}$  correspond in this model to  $P_u/P_g \simeq 0.25$  with a significant increase with temperature of the trans form. An analysis similar to that described for the first model gives

$$\Delta G = G_{g} - G_{l} = -7.2 \text{ kcal./mole}.$$

From the limited experimental data it is not possible to decide between the two extreme models or any intermediate one. Determination of the relative signs of  $v_Q^{\alpha}$  and  $v_Q^{ar}$  would be helpful, but this we could not do. The results for  $\Delta G$  and the temperature dependence of  $P_t/P_g$  favour however the first model in which the oxygen- $\alpha$ -carbon bonds are coplanar with the aromatic ring. The estimated  $\Delta G$  value of 1.4 kcal./mole calculated for this case is very close to that generally accepted [18] for the trans-gauche isomerization equilibria in alkyl chains ( $\sim 0.6$  kcal./mole), but the agreement should not be taken too seriously due to the simplified model used in the analysis. At any rate the results for  $P_t/P_g$  at the  $\alpha$ -carbon indicate considerable deviation from an all-trans extended chain. Most probably there is even more disorder at successive carbon atoms along the chain. We hope to be able to study this point in more detail by deuterium NMR of perdeuterated chains. At this moment we can only say that the chains are definitely not stretched radially in the aromatic plane but are rather disordered or perhaps bent into a perpendicular direction. The result is shortening of the effective radius of the discotic columns as was indeed observed by X-ray measurements [7].

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