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A deuterium NMR investigation of polymorphism in benzene pizzanes

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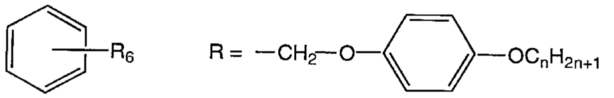
The polymorphism of three members of the homologous series hexa(*p*-alkoxyphenoxymethyl) benzene (benzene pizzanes) with 5, 6 and 7 carbons in the alkoxy chains and several of their deuteriated isotopomers have been investigated by differential scanning calorimetry, polarizing optical microscopy, X-ray diffraction and deuterium NMR spectroscopy. These homologues exhibit several solid phases and a high temperature M phase, which is isomorphic in the three homologues and whose nature is discussed. In the solid phases, the benzene cores of the molecules remain rigid, but the side chains are mobile, as reflected by rapid π-flips of the benzene rings in the side chains. It is found that there are two types of such benzene rings, differing in the rates of flips. In the M phase the molecules undergo fast overall reorientation and the side chains are even more disordered than in the solid phases. However the X-ray measurements do not provide a clear cut determination as to whether this phase is crystalline or mesomorphic. Mixing of the benzene pizzanes with *p*-xylene yields lyomesophases, which appear to belong to the D_{ho} class.

1. Introduction

About a decade ago Kok *et al.* [1] described the phase sequences and X-ray diffraction patterns of a number of *p*-alkoxyphenoxymethyl substituted benzene and naphthalene compounds. Because of the resemblance of their molecular 'super-disc' structure to the Italian pizza, these discotic compounds were termed 'Pizzanes'. As is often the case [2–4] for discotic compounds, the pizzanes too, exhibit a series of solid–solid phase transitions with increasing degree of mobility and disorder, before the liquid crystalline or liquid phases are reached. It is thus of interest to study the ordering and the dynamic properties of these compounds in the various solid and mesomorphic phases.

In the present work we use deuterium NMR of specifically deuteriated benzene pizzanes in combination with X-ray diffraction, polarizing optical microscopy and differential scanning calorimetry to characterize their phase behaviour. These compounds, [hexa(*p*-akloxyphenoxymethyl) benzenes] are ethers comprising a central hexamethylenebenzene and six *p*-alkoxyphenyloxy moieties. We label them as P*n,* where *n* is the number of carbons in the alkoxy chains.



The homologues with $n=5$, 6 and 7 exhibit a sequence of solid–solid transitions leading to a high temperature phase which was tentatively assigned by Kok *et al.* [1] as a disordered rectangular columnar mesophase [D_{rd}). Nevertheless, on the basis of later X-ray measurements they concluded that this phase is a 'special type of crystal, the nature of which still has to be determined'. In the following, we shall refer to this high temperature phase as the M phase. We have prepared deuteriated isotopomers of the P5, P6 and P7 pizzanes with deuterons in the phenoxy rings ($Pn-d_b$) of the side chains and in the benzene-bound methylenes ($Pn-d_m$). The analysis of the NMR spectra of these isotopomers shows that rapid π-flips of the side chain benzene rings already occur in the solid phases preceding the M phase, but it appears that there are two types of side chain with very different mobilities. The spectra in the M phase indicate that in this phase the molecules undergo fast, non-cylindrically symmetric, reorientation.

The mesomorphic properties of discotic compounds may sometimes be modified by the formation of charge transfer complexes with suitable electron acceptors

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[5, 6]. Even when the high temperature solid phase is not mesomorphic, mesomorphism can be induced by addition of apolar solvents [7–9]. These induced lyomesophases are sometimes columnar with two dimensional lattices, but usually they are nematic columnar. They exhibit high molecular mobility and may be stable over wide temperature ranges. This induced mesomorphism is attributed to loosening of the intercolumnar interaction between the discotic molecules, providing 'lubrication' for the motion by the solvent molecules. The very formation of such lyomesophases may, with certain reservation, be considered as an indication that the original thermotropic phase is also discotic columnar.

To help in characterizing the high temperature M phases of the Pn pizzanes ($n=5$–7) we examined their interaction with an electron acceptor compound and with various apolar organic solvents. No induced mesomorphism was found with trinitrofluorenone; however, three homologues were found to form stable enantiotropic lyomesophases with p-xylene. For the $n=6$ homologue, we constructed a detailed phase diagram by differential scanning calorimetry and polarizing microscopy, and investigated its properties by X-ray diffraction and deuterium NMR.

2. Experimental

The three homologues of the benzene pizzanes which show a high temperature M phase, i.e. P5, P6 and P7, were synthesized as described in [1]. The products were recrystallized twice from petroleum ether/ethanol, purified by column chromatography (silica, CH_2Cl_2 : n-hexane 8 : 2) and then crystallized again.

Two types of isotopomers were prepared in which, respectively, the benzene rings in the side chains (P$n-d_b$) and the methylenes bound to the centre core (P$n-d_m$) were deuteriated. The intermediates for these isotopomers were synthesized as follows. Perdeuteriated hexamethylbenzene was prepared from the corresponding normal compound by exchange with D_2O over a Pt catalyst in a pressure vessel at 300°C for seven days. Three consecutive exchange runs were performed yielding a 98% enriched product. This was then used to prepare perdeuteriated hexabromomethylbenzene as described in [10]. The 4-n-alkoxyphenols, deuteriated in the aromatic sites were prepared as described in [11]. All compounds gave the expected proton NMR spectra.

The deuterium NMR measurements were performed at 46·07 MHz on a high power Bruker CXP300 spectrometer equipped with a BVT1000 variable temperature unit. The spectra were recorded using a quadrupole echo sequence with a time interval between pulses of 20 μs. Typical 90° pulse widths were around 2·5 μs. Longitudinal relaxation rates were measured by inversion recovery followed with a quadrupole echo sequence for detection. Further details are given in the figure captions.

Polarizing optical microscopy observations were made using a Zeiss Universal microscope equipped with a Mettler FP52 heating stage. The coloured pictures reported here were taken with transmitted light using crossed polarizers. The phase transition temperatures and associated enthalpies were measured by differential scanning calorimetry using a Mettler DSC30 with a heating/cooling rate of 5 K min^{-1}.

3. Results and discussion

3.1. *Phase sequences*

The phase sequences of the Pn compounds studied in the present work were obtained by DSC on heating and are summarized in the table. In addition to the high temperature M phase, the compounds exhibit two or three solid polymorphs, labelled Cr$_1$, Cr$_2$ and Cr$_3$. The data in the table were confirmed by polarizing optical microscopy and, where applicable, they are consistent with those reported in [1]. In the following sections we describe deuterium NMR measurements made on the Cr phases and more extensive studies also involving X-ray diffraction, DSC and optical polarizing microscopy of the M phases. These studies show that, at least, the M and the Cr$_1$ phases in all three homologues are isomorphous.

3.2. *Deuterium NMR of the Cr phases*

Examples of deuterium NMR spectra of P5 labelled in the benzene rings of the side chains (P5-d_b) are shown in figure 1. At low temperatures (below −40°C) the

Table Phase transition temperatures, in °C, and (in brackets) transition enthalpies, in kJ mol^{-1}, for P5, P6 and P7.

Compound	Cr$_3$		Cr$_2$		Cr$_1$		M		I
P5			•	−3·1	•	64·5	•	96·3	•
				(14·9)		(14·3)		(24·6)	
P6	•	−1·8	•	13·9	•	76·6	•	83·4	•
		(0·4)		(1·2)		(20·2)		(20·4)	
P7	•	−66	•	−13·7	•	66·8	•	71·2	•
		(5·0)		(12·2)		(29·8)		(17·1)	

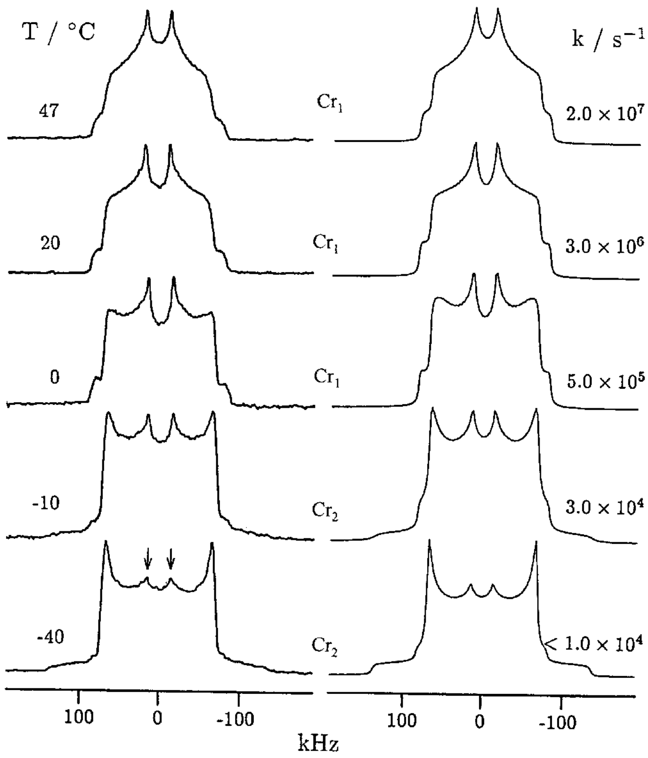

Figure 1. (left) Deuterium NMR spectra of the benzene ring deuterons of P5-d_b in the Cr_2 and Cr_1 phases at the indicated temperatures. The spectra were recorded by the quadrupole echo method with intervals between pulses of 20 μs and Fourier transformation with a line broadening (exponential apodization) of 200 Hz. The arrows in the −40°C spectrum indicate the frequencies for which the T_1 results of figure 3 are recorded. (right) Simulated superposition spectra consisting of two components at a ratio of 1:2; both components correspond to an axially symmetric quadrupole coupling tensor ($\nu_Q = 133$ kHz) undergoing 118° two-site jumps. For the intensity 1 component (F), the rate is constant at 2×10^7 s^{-1}, while the rates for the intensity 2 component (S) are as indicated in the figure. For the calculations, a line width parameter $1/T_2 = 8 \times 10^3$ s^{-1} was used.

spectrum exhibits a rigid solid pattern, corresponding to a quadrupolar splitting constant of $\nu_Q = 3e^2qQ/4h = 133$ kHz and $\eta \leq 0{\cdot}04$. With increasing temperature within the Cr phases, typical dynamic features of two-site jumps appear [12–14] leading, at high temperatures, to a spectrum of an average biaxial quadrupole coupling tensor with $\langle \nu_Q \rangle = 83$ kHz and $\eta = 0{\cdot}60$. This fast exchange limit spectrum corresponds to a two site jump process in which the unique principal direction of the deuterium quadrupole interaction tensor rapidly flips by ±60° about an average orientation. Such a spectrum would be expected for the *ortho*-deuterons in a benzene ring rapidly undergoing π-flips about its *p*-axis. Detailed analysis of the spectra, involving comparison with simulated spectra [15, 16] shows, however, that the situation is more complicated and that they actually consist of a superposition of two sub-spectra with relative intensities of 1:2. The weaker of the two components, which we term F, is temperature independent. In the low temperature spectra, it is responsible for the pair of weak inner horns and the small shoulders just outside the main perpendicular features, observed already in the Cr_2 phase at −40°C (see figure 1). This sub-spectrum thus has the same $\langle \nu_Q \rangle$ and η values as determined for the whole spectrum at high temperatures and consequently must also correspond to rapid π-flips of the benzene rings. To yield an average fast limit spectrum we must assume that the flip rate, k, of this component is faster than 10^6 s^{-1} even at −40°C. In practice we arbitrarily set its value at 2×10^7 s^{-1} in the simulations.

The line shape of the second component of the spectrum, which we designate S, is temperature dependent and can readily be interpreted in terms of the π-flips of the benzene ring, but with much slower rates, falling within the dynamic regime of deuterium NMR. By suitable choices of flip rates, overall spectra consisting of a 1:2 superposition of the F and S components can be simulated which satisfactorily fit the experimental results. Examples of such spectra for P5 are shown in the right hand column of figure 1. These spectra were calculated for a switching angle of ±59°, which gave somewhat better fitting than ±60°. Very similar results were obtained for the P6-d_b and P7-d_b isotopomers and the resulting Arrhenius plots, for all three homologues, for the switching rate in the S component are shown in figure 2. It may be seen that for P5 and P6, where the temperature range of the measurements includes the two solid phases, Cr_1 and Cr_2, there is a discontinuity in the Arrhenius plots at the phase transition region.

Deuterium NMR measurements of the methylene deuterons of the Pn − d_m isotopomers in the Cr phases showed a static spectrum up to the M phase, where its width reduces discontinuously to about 88% of its rigid value. We will discuss the dynamic properties of the M phase in the next section. For the Cr phases we may conclude that the molecular cores remain rigid over the entire temperature range, while the benzene rings in the side chains undergo fast π-flips. Such a process is often found in solid systems [12–14]; however, in the present case there are two distinct types of benzene ring in the crystal at a population ratio of 1:2 with quite different kinetic properties. This may reflect the presence of two types of molecule in the crystal or two types of side chain bound to the same molecule. We speculate that the latter is more likely, with each molecule having two more mobile and four less mobile chains. Since the crystal structure is not known it is not possible to tell for sure.

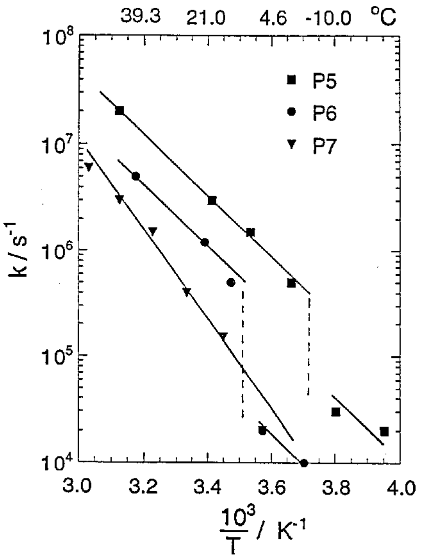

Figure 2. Arrhenius plots for the two-site jump rate constants of the benzene rings in the S components of the solid phases of the P5, P6 and P7 homologues.The vertical dashed lines correspond to the Cr_1–Cr_2 phase transition temperatures of P5 and P6.

We have also performed T_1 (inversion recovery and saturation) measurements on the aromatic deuterons of the P5-d_b homologue over the entire region of the Cr phases. The magnetization growth was followed for several features of the spectrum. In general the growth curves were bi-exponential reflecting the two components in the spectrum and the results were accordingly fitted to two T_1-relaxation times. As an example the results obtained at the frequencies corresponding to the 'inner horns' (see arrows in bottom trace of figure 1) of the spectrum are shown in figure 3. In these plots the filled symbols, with the shorter T_1s, correspond to the F component, while the empty symbols, which exhibit a discontinuity at the Cr_1 to Cr_2 transition corresponds to the S component. For both curves, T_1 decreases with increasing temperature, indicating that the condition $\omega_0\tau > 1$ applies, where ω_0 is the Larmor frequency of the deuterons and τ is a correlation time. To check whether the T_1s of the S component are controlled by the flipping of the benzene ring, or by a faster process, we use the equation [17]

$$\frac{1}{T_1}=\frac{3}{16}\left(\frac{\omega_Q}{\omega_0}\right)^2\tau^{-1}$$

which applies to the two-site, ±60° switching process, in the $\omega_0\tau > 1$ regime, with $\omega_Q = 2\pi\nu_Q$. Inserting for $\tau = k^{-1}$ from figure 2, yields T_1 values which are about an order of magnitude longer than observed experimentally for the S component. This indicates that some other relaxation mechanisms overshadow the effect of the π-flips. A similar analysis for the F component, but reversing the procedure and computing k from the experimental T_1 of figure 3 gives k (at 250 K) $\lesssim 0{\cdot}6\times10^8$ s^{-1}, which is consistent with the fact that the spectrum is already in the fast exchange regime ($k > \omega_Q$) at low temperatures.

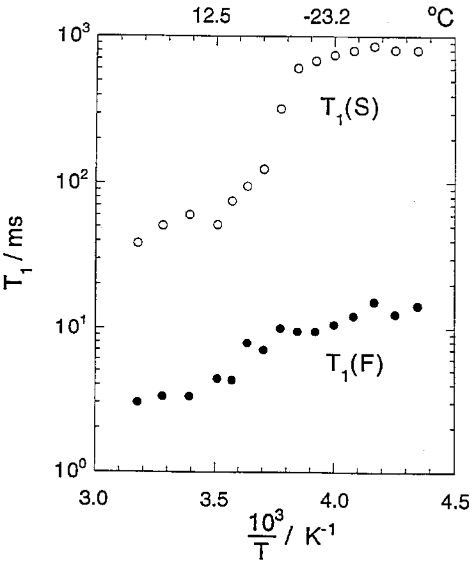

Figure 3. Plots of the two T_1s of the benzene deuterons of P5-d_b in the Cr_1 and Cr_2 phases. The results correspond to the 'inner horns' in the spectrum (see arrows in the −40°C spectrum of figure 1). The full and open symbols correspond, respectively, to the F and S components of the spectrum.

3.3. *The M phase*

3.3.1. *X-ray diffraction*

Kok *et al.* [1] have tentatively identified the M phase as a columnar discotic mesophase of the D_{rd} class on the basis of three sharp Bragg reflections compatible with a two dimensional rectangular lattice, which they observed in the low angle regime. We have repeated the X-ray diffraction measurements on powder samples of P5, which shows the widest range of M phase, using a Searle low angle camera with CuK$_\alpha$ radiation. For the Cr_1 phase, at room temperature, a multitude of diffraction peaks was observed characteristic of crystalline phases. Upon initial heating to the M phase region, the diffraction pattern consisted of superposition of weak, diffuse rings plus some additional peaks, apparently due to residual crystallites. Further heating within the M phase, produced three diffraction halos, corresponding to d-spacings of 4·6, 8·2 and 20 Å. No additional low angle diffraction maxima, as reported by Kok *et al.* [1] were seen in our diffraction patterns. However, when the M phase was reached by cooling from the isotropic liquid, at approximately 77°C, a number of sharp Bragg reflections reappeared, as if the sample consisted of a few large well ordered domains. This was apparently also observed by Kok *et al.* [1] causing them to conclude that the M phase is crystalline, after all.

3.3.2. *Polarizing optical microscopy and binary phase diagrams*

Microscopy texture studies were mainly performed on P5, which, as mentioned above, exhibits the widest range of M phase. The Cr_I to M transition was expressed by small changes in the defects and birefringence colours. On slow cooling from the isotropic liquid, the M phase appears only after supercooling about 8 to 10°C. It grows into large homogeneous domains with rectilinear boundaries (see figure 4). The growth rate is strongly anisotropic. Pressing with a steel needle results in cracks, but almost no flow. Essentially the same behaviour was observed for the M phases in the P6 and P7 homologues. Contact preparations of P5 with P6 and of P6 with P7 showed complete miscibility of the M phases, and indicates that the solid Cr_I phases are also isomorphous.

To substantiate these observations we recorded the phase diagrams of the three binary systems P5/P6, P6/P7 and P5/P7, by performing DSC measurements on gravimetrically prepared mixtures. The results are shown in figure 5. These diagrams confirm the isomorphicity of both the M and Cr_I phases in the three homologues. Interestingly, the phase diagram of the P5/P7 system shows a large miscibility gap in the M phase region. Apparently the extra two methylene groups per side chain render the P5 and P7 homologues sufficiently different in size to prevent common packing [18]. Note the multiplicity of experimental points in the region of the phase diagram where [P6]/[P7] = 1·5 to 4. This is due to the fact that in preliminary experiments several transitions were observed in this region of the phase diagram within the M phase region. They gradually disappeared, however, when the samples were kept for long periods (two days) in the isotropic phase. This suggests that the self diffusion in these mixtures is especially slow.

3.3.3. *Deuterium NMR spectroscopy*

To gain more information on the dynamic properties of the M phase, we refer again to the deuterium NMR spectra of the side chain methylenes and benzene rings. Examples of spectra for P5-d_m and P5-d_b are shown in figures 6 and 7, respectively. The spectrum of methylene deuterons in the Cr phases (see figure 6 (*a*)) is typical of a rigid system with a nearly axially symmetric quadrupole coupling tensor ($\nu_Q = 122$ kHz, $\eta \lesssim 0{\cdot}07$). On heating to the M phase (figure 6 (*b*)), there is a reduction in the overall width of the spectrum and several new features appear which suggest that it comprises two sub-spectra.

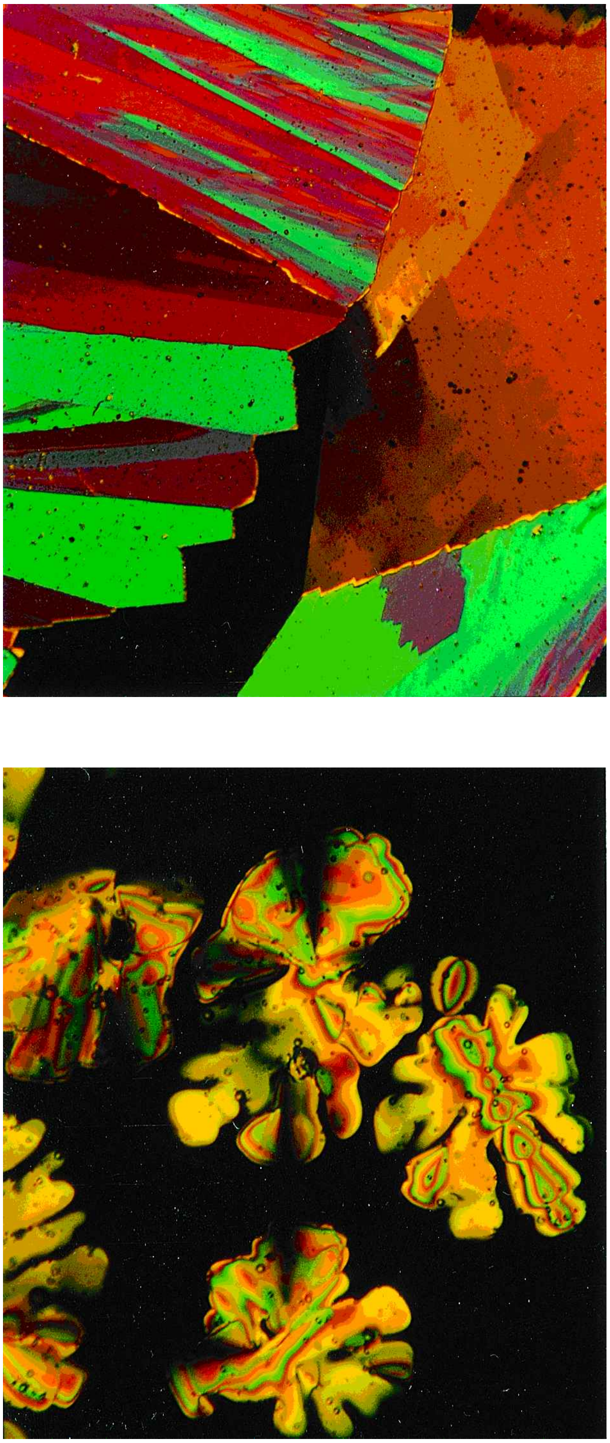

Figure 4. Polarizing optical microscopy pictures of (top) the M phase at 78°C (×80) and (bottom) the lyotropic phase in a 29 wt% *p*-xylene mixture at 39°C (×200).

When the spectrum of the M phase is recorded on cooling from the isotropic liquid, the pattern changes and becomes characteristic of a multi-domain and/or partially aligned sample (figure 6 (*c*)). The same general

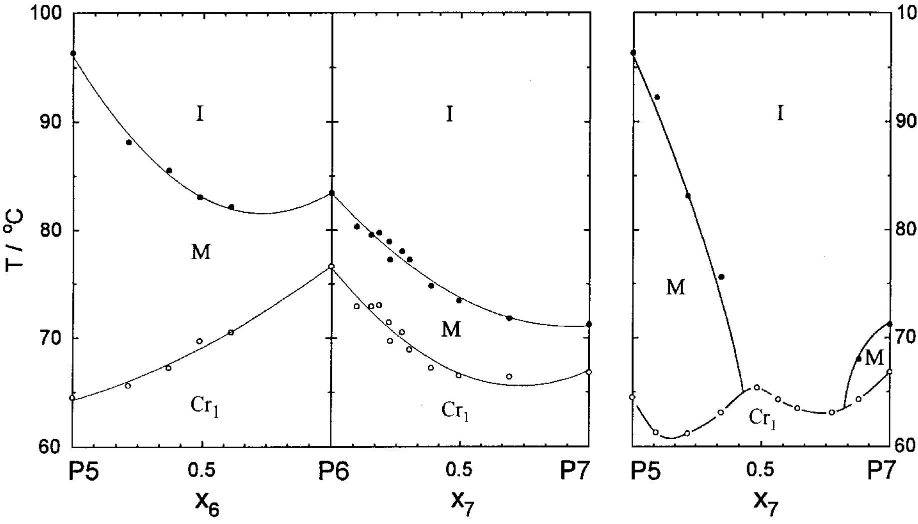

Figure 5. Binary phase diagrams obtained from DSC measurements on binary mixtures of P5/P6, P6/P7 and P5/P7.

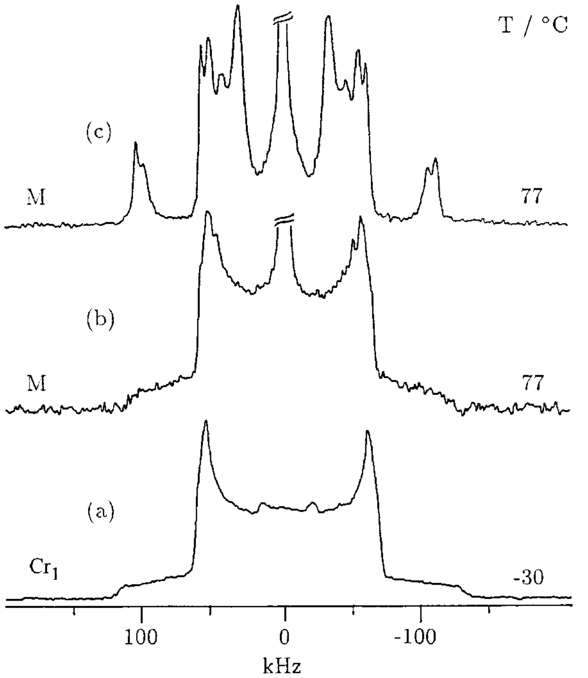

Figure 6. NMR spectra of the methylene deuterons in P5-d$_m$. *(a)* Spectrum in the Cr$_1$ phase; *(b)* spectrum in the M phase obtained on heating from K$_1$; *(c)* spectrum in the M phase obtained on cooling from the isotropic liquid.

behaviour is also observed for the benzene ring deuterons. On heating Cr$_1$, the spectrum changes discontinuously into a complex lineshape (figure 7 *(a)*) which appears as a superposition of a narrow biaxial component and a broad, featureless, background signal. When the sample is cooled from the isotropic liquid (figure 7 *(b)*) the latter component does not reappear, while the line shapes of the narrow component exhibit sharp features characteristic of a partially aligned or multi-domain sample. We therefore identify the broad background signal observed on first heating as due to residual untransformed Cr$_1$, while that of the narrow component is due to neat M phase. This is consistent with the X-ray results described above and is further supported by inversion recovery measurements, some spectra of which are shown in figure 7 *(c)*. It may seen that the two components recover at different rates, with $T_1(\mathrm{M}) > T_1(\mathrm{Cr}_1)$. For a recovery time of 3 ms the signal is essentially that of (inverted) M with the same parameters as for the narrow component of the spectrum ($\langle \nu_Q \rangle = 81$ kHz, $\eta = 0{\cdot}27$).

A likely interpretation of the deuterium spectra in the M phase is in terms of an overall rapid molecular reorientation within a non-axially symmetric phase, i.e. fast, non-cylindrical, planar reorientation. For such a motion the spectrum of the methylene deuterons is very sensitive to the dihedral angle $\mathrm{C_b'}$–$\mathrm{C_b}$–C(methylene)–O moiety, where $\mathrm{C_b'}$–$\mathrm{C_b}$ are neighbouring carbons in the central benzene core. When this angle differs from 0° (or 180°), the two methylene deuterons become inequivalent and should yield different average quadrupole interaction parameters, as apparently observed in the experiments. There is, however, insufficient information in the experimental spectra to estimate this dihedral angle for a biaxial phase. A quantitative analysis for the P5-d$_b$ spectra is even more difficult because it is affected by several motions and depends on the detailed conformational equilibria of the side chains.

3·4. *The lyomesophases of the Pn compounds*

To shed more light on the nature of the M phase we decided to examine whether new mesophases are induced when the P*n* compounds are mixed with electron acceptors or with apolar solvents. Contact preparations

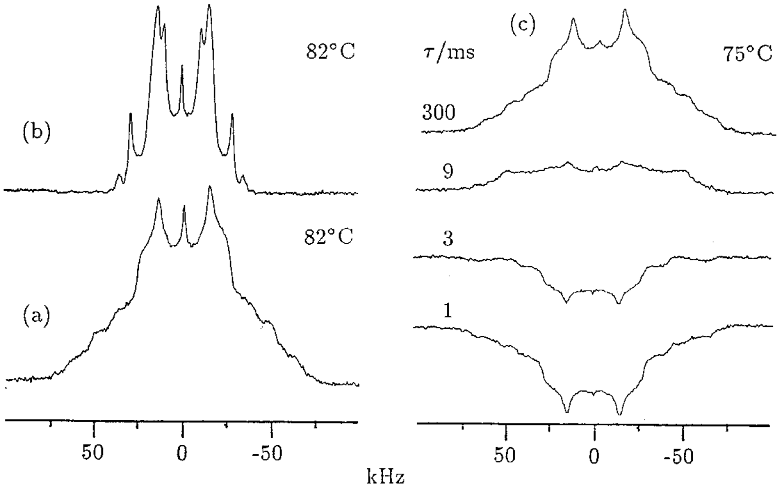

Figure 7. NMR spectra of the aromatic deuterons of P5—d_b in the M phase. *(a)* Spectrum obtained on heating from Cr_I; *(b)* spectrum obtained on cooling from the isotropic liquid; *(c)* a sequence of inversion recovery spectra at the indicated recovery time.

of the benzene pizzanes with 2,4,7-trinitro-9-fluorenone (TNF), showed reddish-brown colouring in the contact zones, suggesting the formation of charge transfer complexes. However, no indication of mesophase induction was observed.

Attempts to induce mesomorphism with apolar solvents were more successful. We investigated, by polarizing optical microscopy, contact preparations of the P*n* compounds with a variety of apolar organic solvents including tridecane, heptane, cyclohexane and *p*-xylene. Of these, the last led to the formation of well defined enantiotropic lyomesophases with all three pizzanes ($n = 5$ to 7). The appearance of these lyomesophases when the mixtures were cooled from the isotropic liquid was characterized by the formation of fluid digitization (finger-like) domains (see figure 4), often with a homeotropic alignment, indicating that the phase is uniaxial. On further cooling, the textures developed into mosaic domains with focal conic-like shapes, characteristic of two dimensional hexagonal columnar mesophases, especially those with high intercolumnar order. Hence we tentatively identify this phase as D_{ho}.

For the P6/*p*-xylene system, which exhibits the widest range of mesophase, we also constructed a detailed phase diagram as shown in figure 8. This diagram was set up from gravimetrically prepared mixtures by DSC measurements and subsequently checked by polarizing microscopy. When the *p*-xylene concentration exceeded 5 wt % a multitude of transitions was observed within the solid phase, as indicated by the open squares. These are at least partly due to different stages of phase separation of the *p*-xylene and P6. The other symbols, however, correspond to well defined transitions between the indicated phases. The D_{ho} phase exists in the concentration range 11 to 37 wt % of *p*-xylene. The clearing process becomes broader with increasing solvent content leading to the biphasic region, as indicated by the shaded area in figure 8. The maximum clearing temperature of the D_{ho} mesophase corresponds to the M/D_{ho}/I triple point (53°C at 10 wt % of *p*-xylene). A similar situation applies to P5, while for P7 there seems to be a real maximum in the phase diagram with a sharp clearing point for the M phase at 55°C.

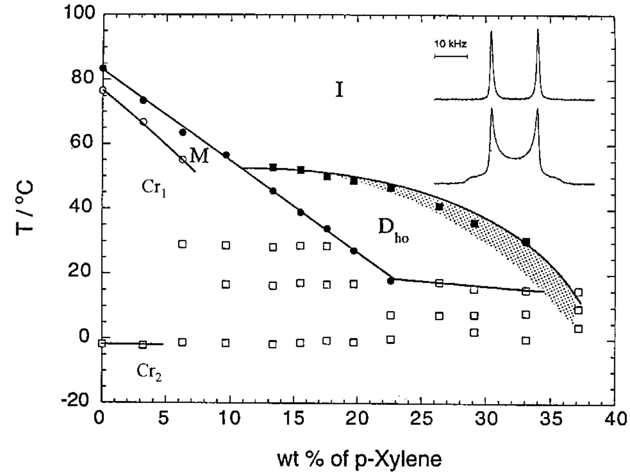

Figure 8. The binary phase diagram of the P6/*p*-xylene system. The points were experimentally obtained by DSC. Open squares correspond to transitions observed within the solid P6/*p*-xylene mixtures, apparently due to various stages of phase separation; the other symbols reflect transitions between well defined phases as indicated. The shaded area corresponds to the isotropic-D_{ho} biphasic region; the insets are deuterium NMR spectra of P6-d_b containing 27·8 wt % of *p*-xylene at 20°C. The top spectrum is of an aligned sample obtained on cooling from the isotropic liquid inside the magnetic field; the bottom spectrum is for the same sample, but obtained on cooling outside the magnet before inserting in the NMR spectrometer.

We were unable to substantiate definitively the assignment of this lyomesophase as D_{ho} by X-ray diffraction. Nevertheless, a sample of P6 with 28 wt % of *p*-xylene, which was cooled from 45°C to 25°C, showed clearly two low diffraction angles with a spacing ratio of $1:7^{1/2}$ (with a spacing of 9·4 and 25 Å) and possibly a third one at $3^{1/2}$ (14·4 Å), as would be expected for the (2 1), (1 0) and (1 1) diffractions of a two-dimensional hexagonal structure. The calculated lattice parameter for this structure is $a \sim 29$ Å. No diffraction corresponding to the intracolumnar stacking distance could however be observed.

Deuterium NMR spectra of a mixture containing P6-d_b and 27·8 wt % of *p*-xylene recorded at 20°C are shown in the inset of figure 8. The bottom spectrum was obtained by allowing the sample to cool into the lyomesophase outside the magnetic field, before inserting it into the NMR probe. It corresponds to a powder sample of a uniaxial quadrupole coupling tensor with $\langle \nu_Q \rangle =$ 28·4 kHz. When the same sample is warmed to the isotropic liquid and cooled again within the magnetic field to the lyomesophase region, a sharp doublet, as shown by the top spectrum, corresponding to an aligned sample is obtained. The doublet splitting in this spectrum is identical to the separation of the perpendicular features in the powder spectrum. These results confirm that the lyomesophase is uniaxial and indicate that it aligns with its director perpendicular to the magnetic field (i.e. $\Delta\chi < 0$), as is usually the case for discotic mesophases [19].

4. Summary

We have studied the various phases of three homologues of the benzene pizzane series, P5, P6 and P7, i.e. those exhibiting a high temperature M phase. All homologues are highly polymorphic, exhibiting besides the M phase two or three solid phases. Using deuterium NMR we have shown that in the solid phases the centre cores of the pizzane molecules are rigid on the NMR time scale, while the side chains are mobile as reflected by the flipping of the benzene rings in the side chains. Such gradual increase in mobility of the side chains is often found in discotic mesogens and may therefore suggest that the M phase, which precedes the isotropic phase, is mesomorphic.

The identification of the M phase as a solid or a genuine mesophase is, however, complicated because of conflicting evidence from the different experiments. Polarizing microscopic observation of large homogeneous domains with rectilinear boundaries, the anisotropic growth rate, the rigidity and the low fluidity are indicative of a highly ordered ('crystalline') phase. On the other hand, the high molecular mobility as reflected in the extensive averaging of the deuterium quadrupole coupling interaction and, particularly, the alignment observed in the magnetic field, favour its identification as a mesophase. In fact the biaxial spectrum of the P5-d_b deuterons is consistent with the original assignment of a D_{rd} phase by Kok *et al.* [1]. However, this assignment was based on X-ray results that could not be reproduced by our own measurements. The induction of a columnar lyomesophase, by the addition of *p*-xylene to the M phase also favours the identification of the latter as a mesophase or at least as a solid with a stacked molecular structure, as often found in discotic mesogenic solids. It is noteworthy that of the apolar solvents tried, only the aromatic one was effective in inducing lyomesomorphism. This may indicate that the dominant mechanism for the formation of the D_{ho} phase involves intercalation of the *p*-xylene between the stacked P*n* molecules, thus loosening the intracolumnar interactions. This is in contrast to the alkane solvents which mainly affect the intercolumnar interactions, usually leading to the formation of nematic columnar mesophases. The ambiguous X-ray results for the M phase preclude a clear-cut assignment of this phase at present.

The definition of Kok *et al.* [1] that it is 'a special type of crystal' may still hold, but perhaps 'a special type of mesophase' is more appropriate.

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