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Mesomorphic and dynamic properties of discotic alkanoyloxybenzene dimers as studied by X-ray and NMR: The effect of spacer length

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The preparation and mesomorphic properties of four members of the homologous series of dimers, alkandioic acid bis[pentakis(*n*-heptanoyloxy)phenyl] esters $[(C_6H_{13}COO)_5C_6OC(O)(CH_2)_{(n-2)/2}]_2$ with $n = 6$, 8, 12 and 14, are reported. They are henceforth referred to as T*n*. Between -100°C and the isotropic liquid (I) the four compounds exhibit, with increasing temperature, the phase sequence $Cr \rightarrow P \rightarrow I$, where Cr is a solid and P is an intermediate phase which is crystalline for T6 and T8, and columnar discotic for T12 and T14. The mesophases of T12 and T14 are completely miscible with that of the corresponding monomer, hexaheptanoyloxybenzene (BHA7) and thus are identified as of type Col_{rd}. This assignment is confirmed by X-ray measurements which also provide the lattice parameters for the two-dimensional columnar array. Deuterium and carbon-13 NMR measurements indicate that the side chains in the P(Cr) phases of T6 and T8 are dynamically disordered, while the benzene core is rigid. In the P(Col) mesophases of T12 and T14, the side chains are also disordered, but in addition the benzene cores undergo high amplitude planar librations. Analysis of the carbon-13 spectra of the carboxyl groups in the latter compounds shows a distribution of librational amplitudes around a mean value of about one rad with a variance of $\sim 0{\cdot}14\ \mathrm{rad}^2$. The structure of the mesophases can be visualized as columns consisting of stacked monomeric units. The monomers are linked via spacers to their counterparts in neighbouring columns. The stacking level of the monomeric units in neighbouring columns is not correlated. Some pairs are stacked at the same level, resulting in loose spacers and high librational amplitudes, while other pairs are stacked at different levels with a corresponding tightening of the spacers and reduced librational amplitudes.

1. Introduction

Compounds consisting of disc-like molecules with several alkyloxy or alkanoyloxy side chains often exhibit one or several liquid crystalline mesophases [1]. These so-called mesophases of discotic molecules are usually columnar with the molecules stacked into rod-shaped aggregates, which in turn are arranged in two-dimensional arrays with various symmetries [2]. Columnar mesophases are also exhibited by discotic dimers in which pairs of discotic molecules are linked via suitable spacers [3–13]. Examples of such discotic dimers include derivatives of benzene [3], triphenylene [4–9], orthocyclophane [10] and multiethynes [11]. For such dimers to be mesogenic the spacer must be long enough to allow sufficient orientational freedom of the dimer components. The mesophases exhibited by such dimers are isomorphic with those of the corresponding monomers. Their thermal range of stability is, however, usually larger. Discotic dimers often serve as precursors for main chain polymers which may also exhibit columnar mesophases of even higher thermal stability [4–8]. In the mesophases of discotic dimers and polymers the monomeric units are visualized as residing in neighbouring columns, as shown schematically in the diagram below. Such a stacking restricts the orientational freedom of the monomeric units [14–16]. In particular, they cannot undergo complete reorientation as in the corresponding monomeric analogues [14, 17, 18] and their motion is limited to planar librations whose amplitudes depend on the spacer length. The minimum spacer length required for the appearance of a mesophase is evidently related to these librational motions. If the spacers are too short,

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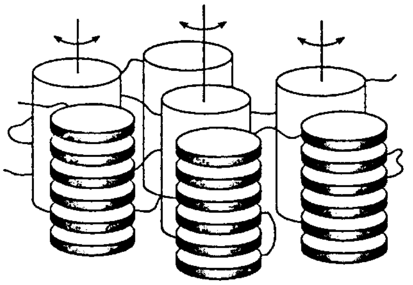
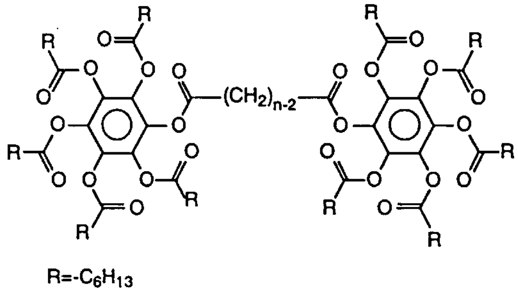


no motion is possible and a mesophase will not form, while for long spacers, high amplitude librations are allowed opening the possibility for mesophase formation. The nature of these restricted motions was earlier studied by deuterium NMR in dimers and main chain polymers of discotic triphenylenes [9, 15, 16]. The results showed a heterogeneous dynamic behaviour with some monomeric units exhibiting larger librational amplitudes than others.

In the present work we extend the study of the motional modes of discotic dimers to the family of benzene hexa-alkanoates. Specifically we have investigated the mesomorphic and dynamic properties of the alkandioic acid bis[pentakis(*n*-heptanoyloxy)phenyl] esters $[(C_6H_{13}COO)_5C_6OC(O)(CH_2)_{(n-2)/2}]_2$ with $n = 6$, 8, 12 and 14.



In the case of the triphenylene dimers, the analysis of the results in terms of a distribution of motional modes was complicated by the fact that the experimental (deuterium) NMR line shapes depended on both the librational amplitudes and rates [9]. It was felt that in the present case of the benzene dimers the librational rates would be faster, yielding line shapes corresponding to the extreme fast exchange regime. This should allow more conclusive evidence for the distribution in the librational amplitudes and an estimate of the distribution width.

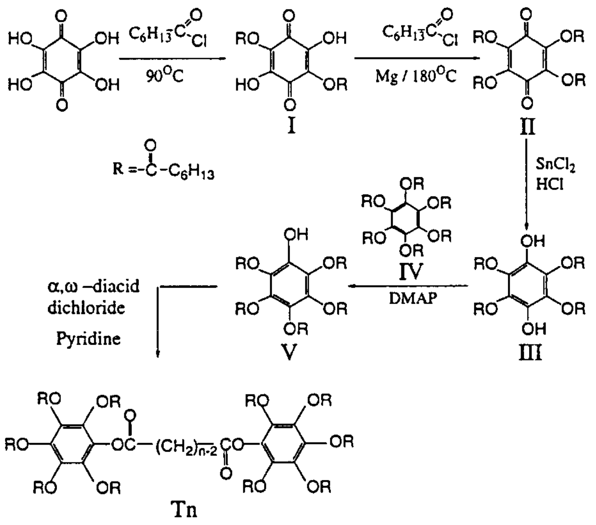
The polymorphism of the benzene hexa-alkanoate monomers (BHA*m*, where *m* is the number of carbons in the side chains) has been studied by thermophysical methods [19, 20], as well as by X-ray diffraction [21–23] and NMR spectroscopy [14, 17, 18]. Homologues of this series display a series of solid–solid transitions, while those with $m = 7$, 8 are also mesomorphic and exhibit a high temperature rectangular columnar phase of the Col_{rd} type. The various solid–solid transitions are accompanied by an increase in the degree of disorder in the side chains, but the core remains essentially rigid throughout the solid range. In contrast, in the mesophase whole molecules undergo free reorientation, very fast on the NMR time scale [18].

Two members of the family of the BHA7 dimers were described earlier by Lillya and Murthy [3]. The spacers in these dimers contained 10 and 20 carbons. Following Lillya and Murthy we refer to these compounds as T*n* where T stands for 'twin' and *n* refers to the number of carbons in the spacer. They showed that while T20 is mesogenic, T10 is not. Our measurements indicate that T6 and T8 are also not mesogenic, but that T12 and T14 are. It thus appears that the critical spacer length for inducing mesomorphism in this homologous series corresponds to twelve (or eleven) carbons. All four compounds show, however, a similar polymorphism, with just two phases between −100°C and the isotropic liquid phase. We present X-ray diffraction, carbon-13 and deuterium NMR measurements on these phases and compare them with those of BHA7. As will be seen, the mesophases of the high-*n* dimers are indeed isomorphic with that of BHA7. They have similar unit cell parameters to the latter, but a wider thermal stability range. Their NMR spectra are interpreted in terms of fast librational motions with a distribution of librational amplitudes.

2. Experimental

2.1. *Material preparation*

Four twins of pentaheptanoyloxybenzene were prepared with a spacer containing 6, 8, 12 and 14 carbons. A general scheme of the synthetic route is shown below:



2,5-diheptanoyloxy-*p*-benzoquinone (**I**) was prepared by heating 10 g of dried tetrahydroxy-1,4-benzoquinone (Aldrich) and 50 ml of *n*-heptanoyl chloride to 90°C for 60 h while stirring. The crystallized product was filtered, triturated with *n*-pentane, filtered again and crystallized from ethanol, yielding red–yellow crystals (m.p. 226–227°C) of **I**. Tetraheptanoyloxy-1,4-benzoquinone (**II**) was prepared by mixing 1 g of **I** with 20 ml of *n*-heptanoyl chloride and a few grains of Mg. The flask containing the mixture was inserted in an oil bath (preheated to 180°C) for exactly 15 min. The resulting clear light-yellow solution was immediately distilled under reduced pressure and the residue recrystallized from ethanol, yielding yellow crystals (m.p. 60°C) of **II**. Tetraheptanoyloxy-1,4-dihydroxybenzene (**III**) was prepared by shaking a solution of 0·5 g of **II** in 20 ml of diethylether with a solution containing 1·5 g of $SnCl_2$ in 15 ml of 1 N HCl, within a separatory funnel for 45 min. After separating the aqueous phase, the procedure was repeated using a freshly prepared $SnCl_2$ solution. The nearly colourless ether solution of **III** was washed with saturated aqueous NaCl, dried with Na_2SO_4 and evaporated until a white crystalline mass was formed; this was then filtered (m.p. 115–124°C). Note that due to acyl-migration this procedure yields a mixture of the three isomers, *o*-, *m*- and *p*-tetraheptanoyl-*o*-, *m*- and *p*-dihydroxybenzene (only one of which is shown in the scheme above). This, however, does not affect the next steps of the synthesis and no separation is needed.

Pentaheptanoyloxyphenol (**V**) was obtained by *trans*-esterification between the tetraheptanoyloxy derivative (**III**) and hexaheptanoyloxybenzene (**IV**) [24]. The latter compound was prepared from hexahydroxybenzene by esterification with *n*-heptanoyl chloride [15]. A solution of 128 mg of 4-dimethylaminopyridine in 3 ml dry THF was added dropwise, while stirring, to a solution containing 650 mg of **III** and 1·43 g of **IV** dissolved in 10 ml of dry THF. The mixture was heated to 45°C for 4 h. After cooling, the mixture was diluted with 300 ml of *n*-hexane and shaken 3 times with H_2O, when a pH of 7 was reached. The hexane solution was dried and evaporated under vacuum to yield a white, slightly pinkish solid, consisting of a mixture of **III**, **IV** and predominantly **V**. The product distribution was checked by TLC (1/4 ethyl acetate/*n*-hexane, silica plate) in a Pancaldi solution (1 g $CeSO_4$, 21 g $(NH_4)_2MoO_4$, 31 ml H_2SO_4, 470 ml H_2O) with heat drying until deep blue spots were observed. To separate the desired compound (**V**) a flash chromatography column was prepared (MATREX silica gel 60 Å, Amicon Corp. Danvers MA) with 2·5 cm inner diameter and 15 cm filling height. The column was flashed with N_2 gas (≈2 bar) followed by rinsing with 100 ml of ethyl acetate/500 ml of *n*-hexane, rendering the column free of air bubbles. The reaction mixture was loaded and pressure reapplied. The fractions collected containing **V** were evaporated and dried on a manifold line.

The desired twin compounds were prepared by reacting **V** with the appropriate α,ω-diacid dichloride. For example, in the case of the $n = 14$ spacer, 390 mg of **V** were dissolved in 6 ml of very dry CH_2Cl_2 and 60 mg of dry pyridine. The solution was stirred at 0°C and 65 mg of $ClOC(CH_2)_{12}COCl$ in 2·5 ml of CH_2Cl_2 were quickly added. The reaction mixture was kept at 0°C for two hours and then overnight at room temperature and checked for reaction completion by TLC. The reaction mixture was diluted with 100 ml of CH_2Cl_2, shaken twice with 25 ml of 1 N HCl and twice with 25 ml of 2% $NaHCO_3$, then washed with H_2O, dried over Na_2SO_4 and evaporated at room temperature. The resulting oil was crystallized from ethanol, yielding 320 mg of T14. Proton NMR spectra of all the twin compounds so prepared were completely consistent with the expected formulae.

For the deuterium and carbon-13 NMR measurements, three kinds of specifically labelled compounds were prepared; (i) twins labelled with carbon-13 at the ten carbonyl carbons of the heptanoyloxy side chains ($Tn\text{-}^{13}C_{10}$); (ii) twins deuteriated at the α,ω-methylenes of the spacers ($Tn\text{-}\alpha d_4$) and (iii) twins labelled with carbon-13 at the carboxyl carbons of the spacer ($Tn\text{-}^{13}C_2$). Compounds (i) were prepared as described above using $1\text{-}^{13}C$ labelled *n*-heptanoyl chloride [25]. Compounds (ii) were prepared using the appropriate $\alpha,\omega\text{-}d_4$-diacid dichloride in the final step of the synthesis [26]. Isotopomers (iii) were prepared using the appropriate $\alpha,\omega\text{-}^{13}C_2$ spacer; the required materials were specifically synthesized for each case. For example, to prepare the spacer with $n = 6$, 5·18 g of 1,4-dibromobutane were added dropwise to a solution of 2·64 g of $K^{13}CN$ ($^{13}C = 99\%$) in 3 ml of H_2O/14 ml EtOH. The mixture was boiled for 3 h, treated with conc. HCl (10 ml) and hydrolysed to the $^{13}C_2$-diacid for 24 h. After extraction with ether, the solvent was removed and the diacid heated with $SOCl_2$ for 5 h and the product isolated by distillation under high vacuum, yielding 1·8 g of $^{13}C_2$-adipic acid dichloride.

2.2. *Physical methods*

X-ray diffraction, as well as polarizing optical microscopy and differential scanning calorimetry measurements, were carried out as described in a recent publication from this laboratory [27]. The NMR measurements were performed using a Bruker CXP300 spectrometer equipped with a BVT1000 variable temperature unit operating at 46·07 and 75·46 MHz for deuterium and carbon-13, respectively. High power probes were used with 5 mm solenoid coils. The deuterium spectra were recorded using the quadrupole echo method (90° pulse width 2·5 μs; time interval between the 90° pulses 20 μs; recycle times ranging from 0·5 to 3 s). The carbon-13 spectra were recorded under low power broad band proton decoupling using a 90°-τ-180°-τ-*acquisition* echo sequence (90° pulse width 3 μs; delay between pulses 30 μs; recycle times ranging from 10 to 300 s). Longitudinal relaxation times were measured using both inversion recovery and saturation recovery techniques.

3. Results and discussion

3.1. *Phase behaviour and miscibility experiments*

Differential scanning calorimetry (DSC) measurements for the four twin compounds were carried out between -100°C and 120°C. The thermograms in the range above room temperature are shown in figure 1. They all show two phases below the isotropic liquid (I). The transition parameters are also summarized in table 1. In this table, Cr stands for a low (room) temperature solid phase and P for a high temperature intermediate phase. We show below that this intermediate phase is solid for T6 and T8 and liquid crystalline for T12 and T14. No additional transitions below 40°C down to -100°C were detected in the DSC thermograms of the T*n* compounds, although several solid–solid transitions were observed for BHA7 [18, 19]. The Cr–P transitions in all compounds are rather broad ($\sim$5°C) and not always observed on second heating due to supercooling of the P phase.

Table 1. Transition temperatures and (in brackets) transition enthalpies for BHA7 and some twin dimers, T*n*.[a]

Compound	Cr	°C(kJ mol^{-1})	P	°C(kJ mol^{-1})	I
BHA7	●	80·6(32·2)	●	86·1(21·5)	●
T6	●	74·9(33·2)	●	115·6(58·0)	●
T8	●	61·3(1·0)	●	94·0(40·1)	●
T12	●	75·0(38·3)	●	96·8(41·4)	●
T14	●	77·0(45·9)	●	91·3(40·6)	●
T10[b]	●	—	—	128(—)	●
T20[b]	●	112(90)	●	121(26)	●

[a] For T6 and T8, Cr and P are solid phases labelled, respectively, Cr$_2$ and Cr$_1$ in figure 1. For BHA7, T12 and T14, Cr is a solid phase (Cr) and P is a Col$_{rd}$ mesophase.

[b] From reference [3].

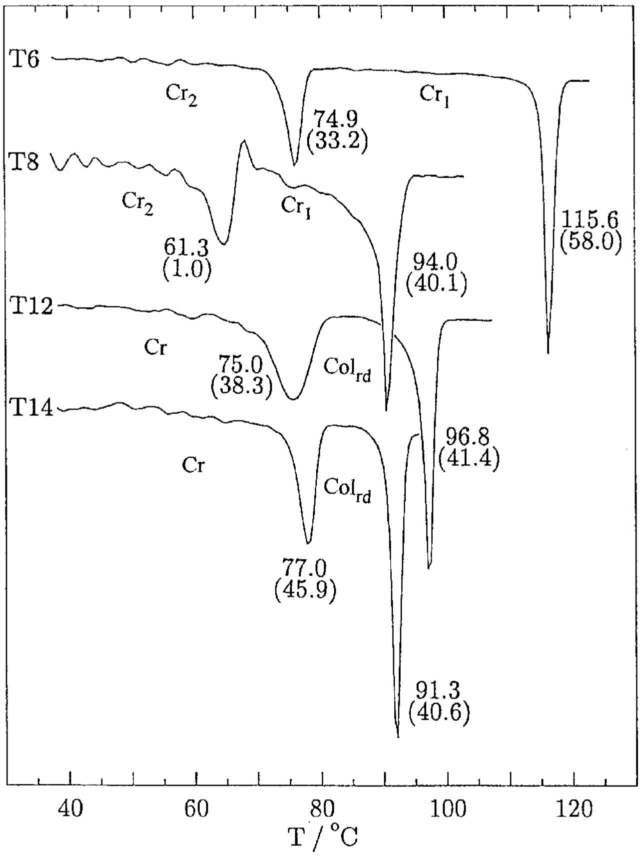


Figure 1. Differential scanning calorimetry (DSC) thermograms of the four twin dimers, T*n*, studied in the present work; only the range 40°C to 120°C is shown. Transition temperatures (in °C) and (in brackets) transition enthalpies (in kJ mol^{-1}) are indicated; heating rate 10 K min^{-1}. The Cr are crystalline phases and Col$_{rd}$ is a columnar mesophase.

Under an optical polarizing microscope the P phases of T6 and T8 exhibit grainy textures with very small domains, while for T12 and T14 fan-shaped areas are observed, suggestive of columnar mesophases. To confirm the identity of the P phases in the various T*n* compounds, we checked their miscibility with the Col$_{rd}$ phase of BHA7, using contact preparations and a polarizing optical microscope [28]. No miscibility was observed between the monomer and T6 or T8, while the intermediate phases of T12 and T14 showed complete miscibility with the Col$_{rd}$ phase of BHA7. This confirms unequivocally that the P phases of the latter homologues are columnar of type Col$_{rd}$. More detailed DSC measurements were performed on weighed mixtures of BHA7 and T14. The resulting phase diagram showed continuous monotonic Cr–P and P–I transitions over the entire range. While the lack of miscibility of the P phases of T6 and T8 does not exclude the possibility that they are also mesogenic, it is very likely that they are not. This is further confirmed by the X-ray measurements described below.

3.2. *X-ray measurements*

The X-ray structure of the columnar mesophases of the BHA*n* monomers were determined earlier [21, 22] and established as rectangular disordered, Col$_{rd}$. For BHA7 the unit cell parameters at 86°C were found to be $a = 28·5$ Å and $b = 17·7$ Å with $a/b = 1·61$ [2]. This ratio differs only slightly (by 7%) from the corresponding ratio in an ideal two-dimensional hexagonal lattice, $3^{1/2}$. We have re-examined the BHA7 mesophase at 82°C (table 2) and also measured the positions of the X-ray diffraction peaks of the Cr and P phases for the four T*n* compounds studied in the present work. Examples for the T6 and T14 compounds along with the $\mathrm{Col}_{\mathrm{rd}}$ phase of BHA7 are shown in figure 2. At room temperature all four T*n*s exhibit a multitude of diffraction rings indicating that the Cr (room temperature) phases are highly ordered solids. The diffraction patterns of the high temperature phases, P, are quite different for the low- and high-*n* twins. For T6 and T8 the patterns are essentially solid-like, although the rings are somewhat broadened due perhaps to the setting-in of chain disorder. On the other hand, for T12 and T14 the diffraction patterns in the P phase closely resemble that of the $\mathrm{Col}_{\mathrm{rd}}$ phase of BHA7. For T14, four diffraction rings are observed in the low angle region (*d*-spacing larger than 8 Å) which can be indexed on a rectangular lattice with $a = 28{\cdot}6$ Å and $b = 17{\cdot}5$ Å (see table 2), although the innermost peaks (11 and 20) are barely resolved due to the near hexagonal symmetry ($a/b = 1{\cdot}63$). For T12 only two low angle diffraction peaks are observed. When interpreted in terms of a similar rectangular phase (unresolved 1 1/2 0 and 0 2/1 2 with peak widths as those for T14), one obtains $a = 28{\cdot}4$ Å, $b = 17{\cdot}3$ Å, ($a/b = 1{\cdot}64$), i.e. even closer to hexagonal symmetry. In both compounds, a broad reflection at ~4·5 Å due to the alkyl chains is also observed, but no peak due to the intracolumnar stacking could be detected. This is consistent with the classification of the P phase of T12 and T14 as a $\mathrm{Col}_{\mathrm{rd}}$ mesophase. Mixtures of T14 and BHA7 in the mesophase region showed cell parameters intermediate

Table 2. *d*-Spacings of the diffraction peaks in the $\mathrm{Col}_{\mathrm{rd}}$ mesophases of BHA7 (at 82°C) and T12 and T14 (at 83°C), and the two-dimensional lattice parameters derived therefrom. The numbers in parentheses are calculated *d*-spacings. All data are in Å.

	d-spacings							Lattice parameters	
Compound	1 1	2 0	2 1	0 2	1 2	2 2	Diffuse	*a*	*b*
BHA7	15·3	14·3	11·4	8·9	8·6	7·6	4·7		
	(15·22)	(14·45)	(11·24)	(8·95)	(8·55)	(7·61)		28·9[b]	17·9[b]
T12	14·5[a]	14·5[a]	—	8·5[a]	8·5[a]	—	4·5		
	(14·78)	(14·20)	(10·97)	(8·65)	(8·30)	(7·39)		28·4	17·3
T14	14·9	14·3	—	8·7	8·3	—	4·5		
	(14·93)	(14·30)	(11·07)	(8·75)	(8·37)	(7·47)		28·6	17·5

[a] Unresolved doublet.

[b] These values, for 82°C, may be compared with 28·5 and 17·7, respectively, reported by Levelut [2] for 86°C

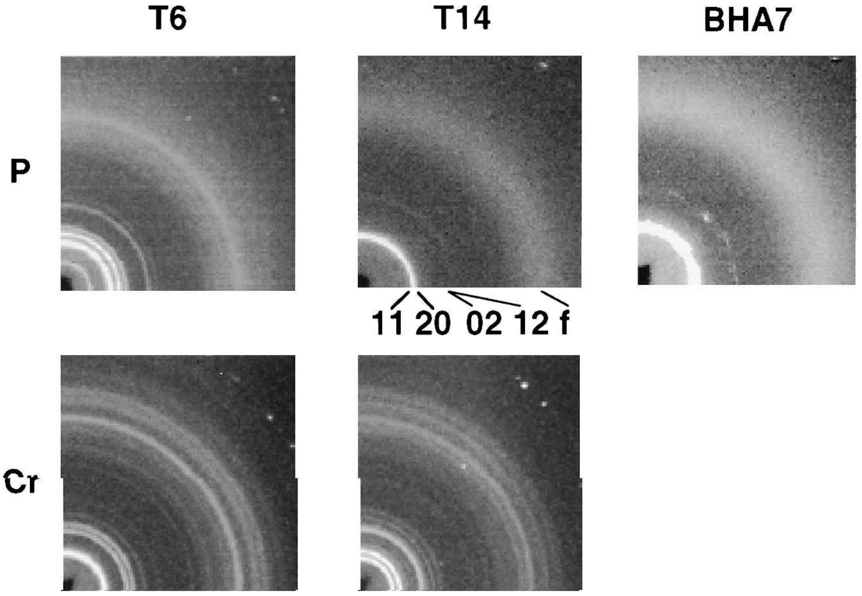


Figure 2. X-ray diffraction patterns for T6, T14 and BHA7. Bottom: room temperature solid phases for T6 (Cr_2) and T14 (Cr). Top: high temperature phases of T6 (Cr_1), T14 ($\mathrm{Col}_{\mathrm{rd}}$) and BHA7 ($\mathrm{Col}_{\mathrm{rd}}$). The Miller indices for the barely resolved, 1 1, 2 0 and 0 2, 12 reflections of the T14 mesophase are indicated. f indicates the halo due to scattering from the alkyl chains.

between the two neat compounds. The isomorphism of the mesophases in BHA7 and the T*n* compounds indicates that the columnar arrangement for the twins is similar to that for the monomers. In particular, from the unit cell areas ($\sim 500\,\text{Å}^2$) we conclude that there are two monomeric units per unit cell. The calculated specific surface per column ($1{\cdot}6 \times 10^7\,\text{cm}^2\,\text{g}^{-1}$) is approximately 10% smaller than for BHA7 [2]. This reduction may reflect the effect of the spacer.

3.3. *Deuterium NMR measurements*

The different nature of the P phases in T6 and T8, in comparison with those in T12 and T14 is also reflected in the deuterium NMR spectra of the T*n*-αd4 isotopomers. Examples of such spectra for T6 and T14 are shown in figure 3. In the low temperature solid phase, the spectra of the α-methylene deuterons in both compounds are similar and correspond to that of a rigid solid with a quadrupole splitting parameter of $3e^2qQ.4h = 110\,\text{kHz}$ and $\eta = 0{\cdot}06$. In the P phase of T6 the width of the spectrum halves and its shape corresponds to that of an asymmetry parameter of $\eta \sim 1$. This indicates partial averaging of the static quadrupole tensor due to some fast motion of the α-methylene groups. An $\eta = 1$ value corresponds to a two-site jump of $\sim 70°$ as would be expected for a methylene group undergoing fast *trans*-gauche-isomerism. This is consistent with the X-ray results which indicate a certain degree of disorder in the otherwise ordered P phase of T6 and T8. As will be seen from the carbon-13 NMR, the benzene core in these phases remains rigid, so that the disorder must be related to the spacer and alkanoyloxy side chains. On the other hand, the deuterium NMR spectrum of T14-αd4 in the P-phase is quite different. Its overall width is considerably narrower than in T6 and the line shape exhibits several features which indicate a more complex motion involving not only the chains, but also the cores of the discotic molecules. In the next sections we attempt to characterize the latter motion in some detail, using the carbon-13 NMR spectrum of the carboxylate groups.

3.4. *Carbon-13 NMR measurement*

Two types of carbon-13 labelled isotopomers were prepared. T*n*s labelled in the carboxylate groups of the heptanoyloxy side chains, T*n*-^{13}C$_{10}$, and T*n*s labelled in the two carboxylate groups of the spacer, T*n*-^{13}C$_2$. The two types of isotopomers gave essentially the same NMR spectrum, suggesting that the carboxylate groups are rigidly fixed to the benzene ring and that their spectrum reflects the motional state of the super-disc consisting of the benzene ring and the six carboxylate groups.

In the low temperature solid phase (Cr), where the molecules are rigid on the NMR time scale, the carbon-13 spectra of both T6-^{13}C and T14-^{13}C are identical and correspond to a uniaxial chemical shift tensor (see figure 4). This axial symmetry is accidental and not required by symmetry, not even by the local symmetry of the carboxylate group. Earlier measurements indicate that the most shielded principal direction lies normal to the carboxylate plane [29, 30]. On this basis we identify one of the perpendicular components (at 125 ppm) with

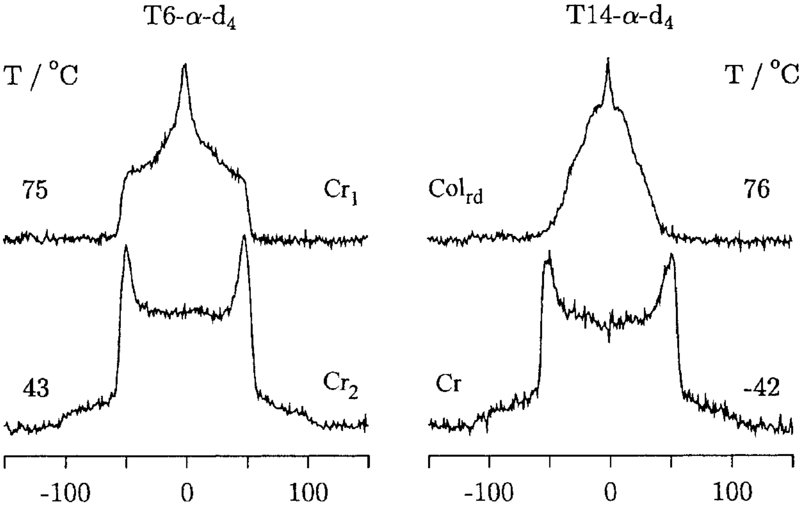


Figure 3. Deuterium quadrupole echo NMR spectra, at 46·07 MHz, of T6-αd$_4$ (left) and T14-αd$_4$ (right) at the indicated temperatures. The bottom traces correspond to the low (room) temperature solid phases, Cr, while the top traces correspond to P which is a solid (Cr) phase for T6 and a mesophase (Col$_{rd}$) for T14.

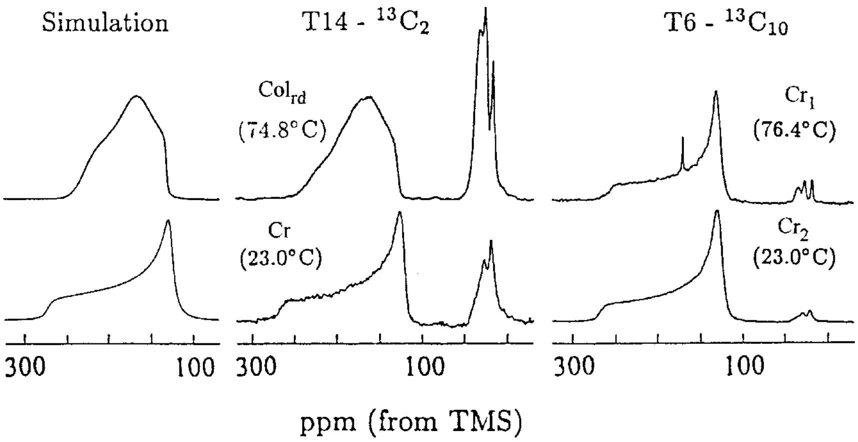


Figure 4. Carbon-13 NMR spectra, at 75·46 MHz, of T6-$^{13}C_{10}$ (right column) and T14-$^{13}C_2$ (middle column), at the indicated temperatures. The bottom traces correspond to the low (room) temperature (solid) phases, Cr, while the top traces correspond to P, which is a solid phase (Cr_1) for T6 and a mesophase (Col_{rd}) for T14. In the left column are shown simulated spectra for T14, calculated with the following parameters: for Cr, $\Delta\delta = 150$ ppm, $1/T_2 = 500\ s^{-1}$; for Col_{rd}, $\Delta\delta = 135$ ppm, $\eta = 1{\cdot}45$, $u = 0{\cdot}475$, $1/T_2 = 500\ s^{-1}$.

the normal to the OC(O) moiety. The other two components (at 125 and 270 ppm) lie within the carboxylate plane, but we cannot tell their orientation.† Within the Cr phase, the chemical shift anisotropy, $\Delta\delta = \delta_\parallel - \delta_\perp$, decreases gradually with increasing temperature. For example, for T6 $\Delta\delta$ decreases from about 145 ppm at −10°C to 130 ppm near the transition to the P phase, although the spectrum remains uniaxial. In the same temperature range, the carbon-13 T_1 increases from about 19 to 28 s (see figure 5). These changes in the spectrum must be due to fast local motion of the carboxylate groups, related to effects of pretransition to the P phase. However, they are of low amplitude and cause only a small reduction in the carbon-13 chemical shift tensor.

The transition to the high temperature P phase results in different carbon-13 spectra for T6 and for T14. For T6 there is a further small discontinuous reduction in $\Delta\delta$ (from 128 to 123 ppm) and T_1 decreases from 28 to 13 s, but the spectrum remains solid-like and uniaxial. In T14 the spectrum changes more drastically; its overall width reduces to less than 80% of its value in the solid phase, with one of the $\delta_\perp$ components remaining essentially unchanged. The general behaviour of the carbon-13 spectrum in the P phase is thus consistent with the assignment of a solid for T6 (and T8) and a mesophase for T14 (and T12).

3.5. *The restricted librations in the Col_{rd} mesophase*

The carbon-13 spectrum in the mesophase of T14 (and T12) corresponds approximately to an average biaxial chemical shift tensor with an asymmetry parameter of ~0·5. Within the mesophase region, the line shape remains essentially unchanged, with T_1 around 7 to 8 s, suggesting that it corresponds to a fast exchange limit of some averaging process. It is, however, not possible to fit the line shape with a single set of average chemical shift parameters. Following our earlier work on the triphenylene dimer [9], we therefore assume that the observed line shape corresponds to a superposition of sub-spectra with a distribution of chemical shift parameters due to a distribution in the librational amplitudes of the various monomeric units. According to this model, the monomeric units undergo fast, high amplitude librations within their respective columns. The librations are restricted by the spacers which link each monomeric unit to its counterpart and the degree of restriction is determined by the relative positions of the two units in the adjacent column. When the two monomeric units are at about the same level, the libration amplitude is high, while for other relative positions it reduces according to their vertical separation. The effect of such a motion on the chemical shift tensor in the fast exchange limit is to reduce the overall anisotropy and in general results in a biaxial average chemical shift tensor. It may be seen in figure 4 that one of the perpendicular static components, $\delta_\perp$, remains essentially unchanged. This will always be the case for an axially symmetric tensor undergoing two-site jumps, but not for a general reorientational motion. The observation that $\delta_\perp$ remains unchanged therefore suggests that the

† In an earlier publication from this laboratory on BHA*n* [18, 31, 32], we mistakenly identified the parallel feature of the carbon-13 carboxylate group with the normal to the carboxylate plane. This error does not affect the rest of the analysis in these papers.

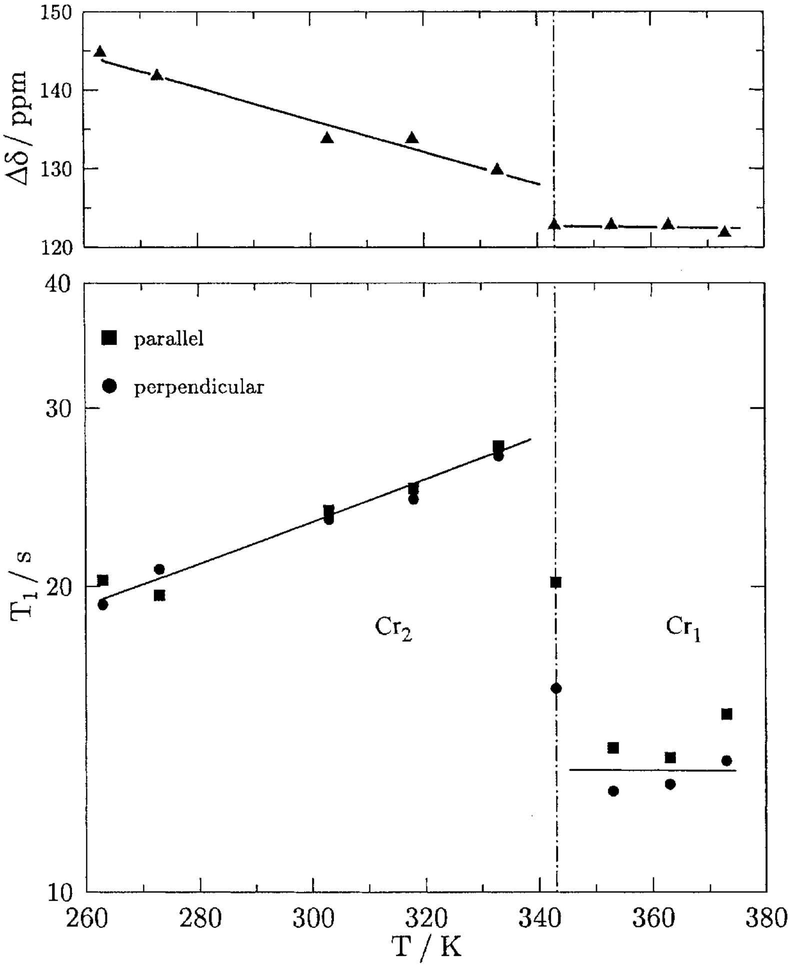


Figure 5. The temperature dependence of the carbon-13 longitudinal relaxation times (bottom) and chemical shift anisotropy (top) in the solid phases, Cr(Cr_2) and P(Cr_1), of T6-$^{13}C_{10}$. The squares and circles in the T_1-results correspond, respectively, to the parallel and perpendicular features in the powder spectrum.

unique principal component, $\delta_\parallel$ lies in, or close to, the librational plane. Under such conditions the principal components of the average chemical shift tensor of a particular site, i, in the mesophase become

$$\begin{aligned}\langle\delta_{11}\rangle^i &= \frac{2}{3}\Delta\delta\left\langle\frac{1}{2}(3\sin^2\theta-1)\right\rangle \\ \langle\delta_{22}\rangle^i &= -\frac{1}{3}\Delta\delta \qquad (1)\\ \langle\delta_{33}\rangle^i &= \frac{2}{3}\Delta\delta\left\langle\frac{1}{2}(3\cos^2\theta-1)\right\rangle^i\end{aligned}$$

where θ is the reorientation angle of $\delta_\parallel$ and the angular brackets indicate averages of the θs in site i. Since $\langle\delta_{22}\rangle^i$ is identical for all sites, i, and the sum $\langle\delta_{11}\rangle^i+\langle\delta_{22}\rangle^i+\langle\delta_{33}\rangle^i$ is zero, the contribution from each site to the powder spectrum in the fast motion limit depends on just one variable which can be defined as

$$\eta^i = \frac{\langle\delta_{11}\rangle^i-\langle\delta_{33}\rangle^i}{\langle\delta_{22}\rangle^i}. \qquad (2)$$

This definition of an asymmetry parameter is not conventional because the range of η extends from 3 ($\theta=0$) to -3 ($\theta=\pi/2$), rather than the usual range of 0 to 1. However, it is convenient because then η does not cross through singular values.

As indicated above, the experimental spectrum of the carboxylate carbon-13 does not correspond to a single biaxial tensor, but rather to a superposition of subspectra with a distribution of asymmetry parameters. To fit this spectrum we assumed a Gaussian distribution in η^i about a mean value, η,

$$P(\eta_i) = \frac{1}{(2\pi u^2)^{1/2}}\exp\left[-\frac{(\eta^i-\eta)^2}{2u^2}\right] \qquad (3)$$

where u is the variance of the distribution. There are thus two parameters to fit the spectrum, i.e. the mean value η and the width of the distribution, u. A very reasonable fit to the experimental spectrum was indeed obtained, as may be seen in the left hand column of figure 4, for $|\eta| = 1{\cdot}45$ and $u = 0{\cdot}475$. Essentially the same results were obtained for T12.

Various models can be assumed for the librational motions, including two-site jumps with a distribution in the jump angle, libration in a harmonic-like potential of various widths, etc. An attractive model is one in which the librations occur within flat potentials, i.e. for each site the libration is restricted to a range between $-\theta_i$ and $+\theta_i$ with equal probability within this range and zero outside it. Then

$$\begin{aligned}\langle \delta_{33} \rangle^i &= \frac{2}{3}\Delta\delta \left\langle \frac{1}{2}(3\cos^2\theta - 1) \right\rangle \\ &= \frac{2}{3}\Delta\delta \frac{1}{2\theta_i}\int_{-\theta_i}^{\theta_i} \frac{1}{2}(3\cos^2\theta - 1)\,\mathrm{d}\theta \\ &= \frac{1}{6}\Delta\delta[1 + 3\,\mathrm{sinc}(2\theta_i)] \\ \langle \delta_{11} \rangle^i &= \frac{1}{3}\Delta\delta - \langle \delta_{33} \rangle^i = \frac{1}{6}\Delta\delta[1 - 3\,\mathrm{sinc}(2\theta_i)]\end{aligned} \tag{4}$$

and

$$\eta^i = 3\,\mathrm{sinc}(2\theta_i) \tag{5}$$

where $\mathrm{sinc}(2\theta_i) = \sin(2\theta_i)/(2\theta_i)$. In terms of this model, taking $\eta > 0$, the average width of the potential well is $2\theta = 111° = 1{\cdot}94$ rad with a variance of $\sim 0{\cdot}14\ \mathrm{rad}^2$.

4. Summary and conclusion

We have confirmed the earlier finding of Lillya and Murthy [3] that the twin dimers of BHAn with sufficiently long spacers can form columnar mesophases isomorphic with those of the monomers. When the spacer length is short (for the case of the BHA7 dimers, shorter than 11 carbons) no mesophases are formed. However, for sufficiently long spacers (about twice the length of the side chains or longer) very similar mesophases are obtained as for the monomers, although with higher thermal stability. In the mesophase of the BHAn monomers, the molecules undergo fast planar reorientation. Likewise, in the Tn dimers, the molecules also undergo a fast planar motion, which is however, restricted to high amplitude librations. The motion is in the extreme fast limit of the NMR time scale and no kinetic parameters can therefore be derived from the spectral line shape. However, the latter could be used to determine the distribution in the librational amplitude. Assuming a flat potential, the results show that the average libration amplitude is about one radian, with a Gaussian distribution of 0·38 rad. This distribution reflects the inhomogeneity in the stacking arrangement of the dimers in neighbouring columns.

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