Liquid Crystals
Publication details, including instructions for authors and subscription information:
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To cite this Article Zamir, S. , Spielberg, N. , Zimmermann, H. , Poupko, R. and Luz, Z.(1995) 'On the solid polymorphs of the discotic mesogen hexa-octanoyloxytriphenylene', Liquid Crystals, 18: 5, 781 — 786
To link to this Article: DOI: 10.1080/02678299508036690
URL: http://dx.doi.org/10.1080/02678299508036690

LIQUID CRYSTALS, 1995, VOL. 18, NO. 5, 781–786

On the solid polymorphs of the discotic mesogen hexa-octanoyloxytriphenylene

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(*Received 12 August 1944; accepted 8 October 1994*)

In an earlier study by van Hecke *et al.*, it was shown that the discotic mesogen hexa-octanoyloxytriphenylene (HAT8) crystallizes in four different solid forms, depending on the thermal history of the sample. The present study is an attempt to characterize three of these solids in more detail using X-ray, carbon-13 and deuterium NMR techniques. It is shown that van Hecke's modification *IV* is a metastable amorphic solid, while modifications *III* and *II* are highly ordered crystalline solids. Both are apparently monoclinic, but with different unit cell dimensions. In all solid phases, the triphenylene core is static on the NMR time-scale, but the side chains are disordered to different degrees in the different modifications. Further NMR studies on the discotic mesophase of HAT8 are also reported.

1. Introduction

Discotic mesogens often exhibit a sequence of solid–solid transitions below the melting temperature to the mesophase. This phenomenon was extensively investigated by Sorai and co-workers [1] using thermocalorimetric measurements for a number of discotic systems, including hexa-alkanoyloxybenzenes (HAB*n*) [2–4], hexa-alkanoyloxytriphenylenes (HAT*n*) [5, 6] and hexa-alkyloxytriphenylenes (HET*n*) [6, 7]. This solid-state polymorphism was interpreted as reflecting the gradual melting of the side chains as the melting temperature to the mesophase is approached. The hypothesis was subsequently confirmed by NMR studies [8] although, as it turned out, the details are somewhat more subtle than originally thought [9].

In most cases the phase sequence involves a series of enantiotropic solids and the phase transitions are reversible. A special situation was encountered in hexa-octanoyloxytriphenylene (HAT8) where four different solid modifications were found, each transforming to the mesophase upon heating, but at different temperatures [5]. The different forms were generated by different sample preparation procedures and some could be interconverted to others by suitable thermal treatment. A summary of the melting entropies and temperatures of the various solids is given in table 1. Thus solid *IV* which is obtained by fast cooling (quenching) of the mesophase melts at 69°C, solid *III* which is obtained by crystallization from a solution melts at 75°C, while two other solids (*II* and *I*) obtained by thermal annealing melt at 87°C and 90°C, respectively. In the present work we attempt to characterize these solids further using both X-ray and solid-state NMR techniques, as well as kinetic studies of their interconversion using differential scanning calorimetry (DSC). Although our

Table 1. Melting entropies and melting temperatures of the four solid modifications of HAT8. Adapted from [5].

Solid phase	Method of preparation	m.p./°C	Melting enthalpy/kJ mol^{-1}
I	Annealing at 88°C	90	24·21
II	Annealing at 75°C for several hours	87	25·44
III	Crystallization from solution	75	34·77
IV	Fast cooling of the mesophase or isotropic liquid	69	34·8†

† From present work.

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results do not provide full details on the structures of the various solids, they show distinct differences in their molecular packing and side chain disorder.

The structure of the mesophases of the HAT*n* discogens was studied earlier by both X-ray [10] and NMR techniques [11, 12]. For HAT8 the mesophase is biaxial-columnar with a two dimensional p2gg (or $P2_1/a$ [13]) lattice. In contrast to the situation in the solid phases where the triphenylene core is rigid (on the NMR time-scale), in the mesophase the entire molecules reorient rapidly about the columnar axis and the aliphatic side chains are highly disordered.

2. Experimental

For the present study we use isotropically normal HAT8 for the X-ray measurements and four specifically labelled isotopomers for the NMR studies. These include HAT8 carbon-13 labelled in the carboxy groups, as well as HAT8 specifically deuteriated in the aromatic sites and in the α and β-methylenes of the side chains. The preparations of the normal and isotopically labelled compounds are given in [11, 12, 14]. The DSC, X-ray and NMR measurements were as described in several earlier publications from this laboratory [9, 15].

3. Results and discussion

3.1. *Sample characterization and DSC measurements*

To study the conditions under which the different solid forms can be generated and their interconversion kinetics, we found it convenient to use DSC. For example, a DSC thermogram of an old sample, originally crystallized from a solvent is depicted in the bottom trace (*a*) of figure 1. It clearly corresponds to a mixture of several solids; the weak endothermic peak at 13°C is a solid–solid transition of one of the solid forms. Then comes a strong melting peak at 69°C due to solid *IV*, which is followed by a weak exothermic signal due to partial crystallization of the mesophase. At 76°C another melting peak appears due to solid *III*, which is also followed by a weak exothermic signal. Finally at around 90°C a double peak is observed, apparently due to solids *I* and *II*. Above this temperature the sample is entirely in the mesophase which persists until the clearing point at 130°C.

When the thermogram of a freshly crystallized sample is recorded, a completely different pattern is observed with a strong melting peak at 76°C as shown in trace (*d*) of figure 1. This sample corresponds to solid *III*, with only a very minute amount of the higher melting solid modifications. On the other hand when the DSC thermogram of a freshly quenched sample is examined, the main melting peak is at 69°C, as shown in trace (*c*). The latter thermogram also shows a small exothermic peak due to transformation to one of the high melting solid forms, followed by its melting peak at around 88°C. Finally a sample that was kept between 70 and 76°C for several hours gave the thermogram shown in trace (*b*), with a melting peak at 88°C. It must therefore correspond to solid *II*. No attempt was made to obtain the other high temperature melting form (solid *I* of van Hecke *et al.*) since it requires lengthy annealing over a narrow temperature range [5], and in the following we shall therefore describe X-ray and NMR studies of only three solids, which we

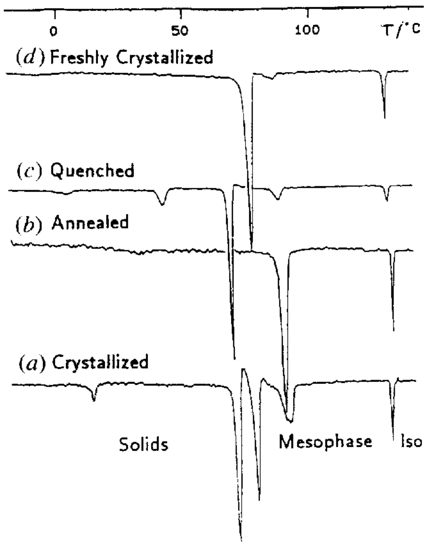

Figure 1. Differential scanning calorimetry thermograms of various solid samples of HAT8. All traces were recorded on heating at 10°C per minute. (*a*) An 'old' crystallized sample exhibiting melting peaks of all four solid forms, (*b*) a solid annealed at 71°C, (*c*) a quenched solid, and (*d*) a 'freshly' crystallized solid.

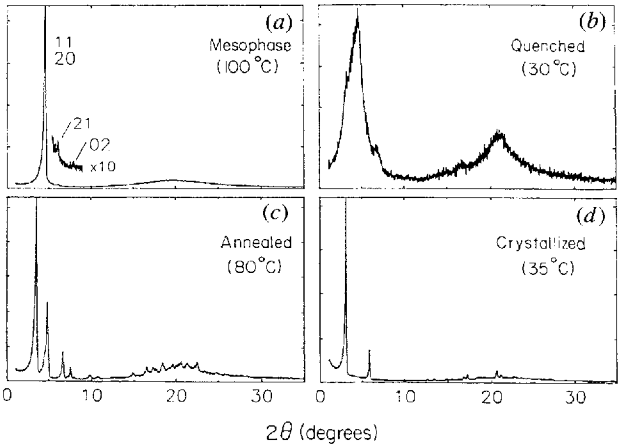

Figure 2. X-ray powder diffractograms of various HAT8 phases. (*a*) The mesophase at 100°C, (*b*) quenched solid at 30°C, (*c*) annealed form at 80°C, and (*d*) crystallized solid at 35°C.

Table 2. Lattice dimensions of some solid phases of the HAT*n* series.

Phase	System	*a*/Å	*b*/Å	*c*/Å	*β*/degrees	*Z*	Reference
HAT4	Hexagonal†	18·85	41·13	18·85	120	12	[17]
HAT5	Monoclinic‡	33·69	20·60	53·57	128·58	24	[17]
HAT6	Monoclinic‡	35·41	21·58	53·60	128·58	24	[17]
HAT8 (*III*)	Monoclinic§	38·43	21·00	71·28	128·0	24	Present work
HAT8 (*II*)	Monoclinic‖	48·93	18·01	61·90	128·0	24	Present work

† Identified as space group R$\bar{3}$c. To facilitate comparison with the other homologues we have chosen *b* to be the unique hexagonal axis, rather than *c*.

‡ Identified as space group C2/c.

§ Assumed to belong to C2/c.

‖ Assumed to belong to P2/c.

term, 'quenched' (solid *IV*), 'crystallised' (*III*) and 'annealed' (*II*). In addition, we report some new NMR results on the mesophase of the HAT8 compound. The various phases were prepared on the basis of the observations described in this section.

3.2. *X-ray measurements*

In figure 2 are shown X-ray diffractograms of the mesophase (*a*) and three solid ((*b*), (*c*) and (*d*)) forms of HAT8. The diffractogram of the mesophase is typical of columnar discotics, although only very few features are observed. The broad peak at $2\theta \sim 15°$ to 25° is due to scattering from the disordered side chains and from the stacking periodicity of the molecules in the (disordered) column. In the low angle region ($2\theta < 10°$), a strong signal is observed at $2\theta = 4{\cdot}5°$ and two very weak ones at $2\theta = 6{\cdot}0$ and 7·5°. These results are identical to those of Levelut [10] who was able to interpret them in terms of a rectangular p2gg lattice with unit cell dimensions of $a = 37{\cdot}8$ Å and $b = 22{\cdot}2$ Å. The mesophase was accordingly classified as D_{rd}, or in the notation of Dubois and Billard, as D_B [16]. The ratio $a/b = 1{\cdot}70$ is however very close to $\sqrt{3} = 1{\cdot}73$, indicating an almost hexagonal symmetry. This is reflected in the fact that the 20 and 11 reflections are not resolved.

Figure 2 (*b*) depicts the diffractogram obtained from a quenched sample. It exhibits two broad bands at around $2\theta \approx 4°$ and 20° with essentially no fine structure, and corresponds to an amorphic or disordered solid.

The diffractograms of the annealed and crystallized forms (see traces (*c*) and (*d*) of figure 2) show sharp diffraction peaks, as would be expected from ordered solids. These reflections could be indexed on a number of different monoclinic and orthorhombic lattices, but not on lattices of higher symmetry. Since we are unable uniquely to index these patterns, we drew upon earlier results [17, 18] obtained for the lower homologues of the HAT*n* series ($n = 4, 5, 6$). These compounds are not mesomorphic and their crystal structure was determined by X-ray investigations on single crystals. The lattice parameters for these solids are summarized in table 2. Accordingly we have attempted to index the powder diffraction patterns of solids *II* and *III* of HAT8 on monoclinic lattices. A good fit was obtained with the parameters listed in table 2.

In several samples we were able to follow the interconversion between various solid forms by X-ray measurements taken as a function of time. One such experiment is shown in figure 3, where the low-angle region of the diffractograms of a freshly prepared crystallized sample is presented. The bottom trace (*c*) was obtained at 40°C and corresponds to the pure crystallized form. The sample was then slowly heated to 60°C, and the diffractograms recorded after two and five hours are shown in traces (*b*) and (*c*), respectively. The time evolution clearly shows the gradual transformation of the crystallized solid to the annealed form, a diffractogram of

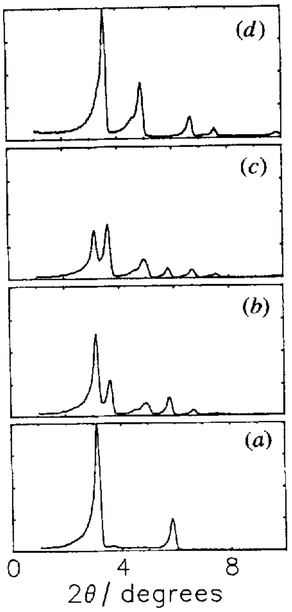

Figure 3. X-ray diffractograms in the low-angle region of HAT8 samples. (*a*) A freshly crystallized solid at 40°C, (*b*) same as (*a*) after two hours at 60°C, (*c*) same as (*a*) after five hours at 60°C, and (*d*) an annealed solid.

which is shown in trace (*d*). Similar transformations of the crystallized to the annealed form could also be effected at somewhat lower temperatures, but not below 45°C. This suggests the existence of a crossing point between the free energy curves of solids *III* and *II* at a somewhat higher temperature than 17°C, calculated by van Hecke *et al.*, for solids *III* and *I* [5].

3.3. *NMR spectra of the solid forms*

The deuterium spectrum of the aromatic deuterons was essentially identical for all solid forms and consisted of a typical powder pattern (see figure 4) with a full spectral width of $\nu_Q = \frac{3}{2}(e^2qQ)/h = 266$ kHz and $\eta = 0{\cdot}05$, characteristic of a rigid system. Likewise the carbon-13 spectrum of the carboxy group was the same for all solid forms and exhibited (see figure 5) an essentially axially symmetric chemical shift tensor with $\sigma_\perp = 128$ ppm and $\sigma_\parallel = 261$ ppm (relative to TMS, see table 3). These values are similar to those found for other carboxy groups attached to aromatic moieties with rigid structures [9]. The axial symmetry of the chemical shift tensor is apparently accidental with $\sigma_\parallel$ pointing perpendicular to the plane of the carboxy group [19, 20]. The results therefore indicate that the triphenylene ring and the directly attached carboxy groups are completely rigid in all solid forms.

The side chains exhibit a totally different behaviour as may be judged by the deuterium NMR spectra of the α- and β-methylene deuterons depicted in figure 6. The two upper rows in this figure correspond to the α-deuterons, while the bottom two relate to the β-deuterons. For each pair of rows, the top one corresponds to the annealed solid and the bottom one to a quenched sample. The main points to notice are that the spectra are temperature dependent within the solid phases and that they are different for the different forms. This indicates that the methylene groups of the side chains undergo temperature dependent conformational changes within the solid phases, but no attempt was made to analyse these effects quantitatively.

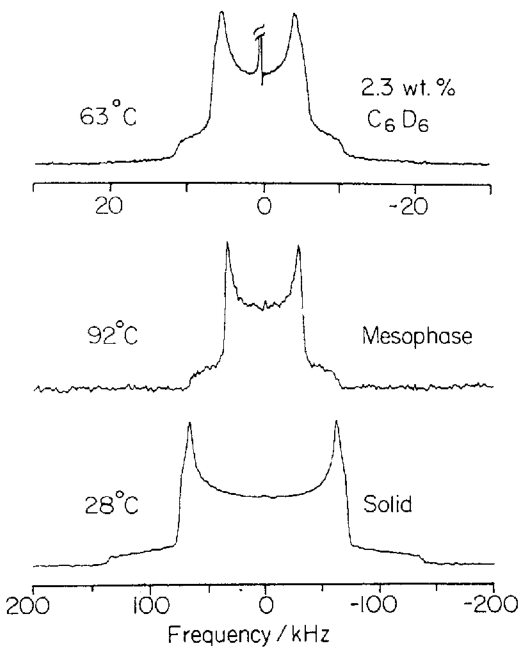

Figure 4. Deuterium NMR spectra of, bottom: HAT8 deuteriated in the aromatic sites in the solid state at 28°C, middle: HAT8 deuteriated in the aromatic sites in the mesophase at 92°C, top: C_6D_6 dissolved in the mesophase of isotopically normal HAT8 (2·3 wt %) at 63°C.

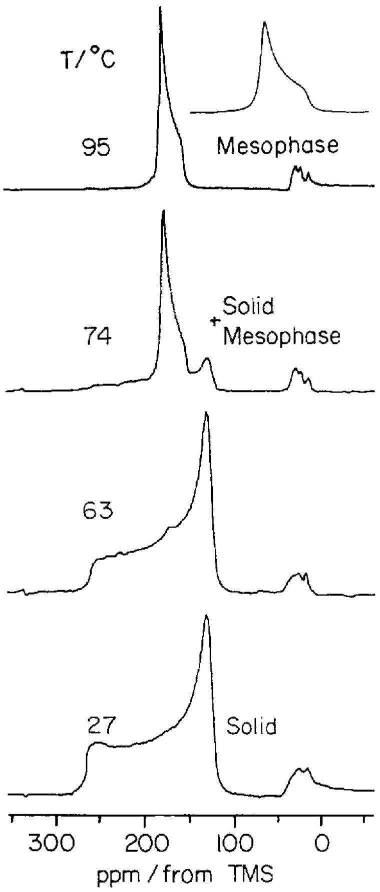

Figure 5. Carbon-13 NMR spectra of HAT8 enriched to 98 per cent in the carboxy groups. The band at ~ 20 ppm is due to the naturally abundant carbon-13 in the aliphatic chain, while the signal in the region 100 to 300 ppm is due to the carboxy carbon. The traces at 27°C and 63°C are for the solid; at 74°C melting sets in and the spectrum at 95°C is of the mesophase. The expanded spectrum of the carboxy carbon, inserted in the top trace, has a total range of 100 ppm.

3.4. *NMR spectra of the mesophase*

The deuterium NMR spectrum of HAT8 in the mesophase region has been extensively studied earlier [11, 12]. In particular the spectrum of the aromatic deuterons could be used to determine the orientational

Table 3. Carboxy carbon-13 chemical shift and aromatic deuteron quadrupole interaction parameters for HAT8 in the solid phase and in the mesophase.

	Carboxy carbon-13†				Aromatic deuterons	
Phase	σ_{iso}‡	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\Delta\sigma$§	ν_Q	η
Solid	170·4	261	128	133	266	0·05
Mesophase	170·4	155	178	−23	−126	~0

† Relative to TMS.
‡ Taken from [9], assumed to be identical to that in HAB*n*.
§ $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$.

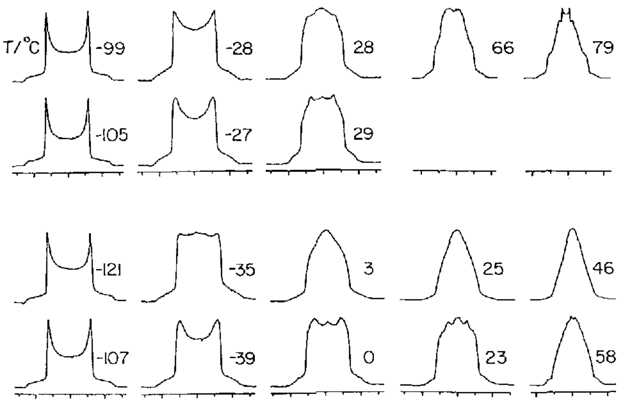

Figure 6. Deuterium NMR spectra of HAT8 deuteriated in the α-methylene groups (upper two rows) and the β-methylene groups (lower two rows). In each case, the top row corresponds to an annealed solid and the bottom row to a quenched sample. The scale between ticks is 50 kHz for all spectra.

order of the aromatic moiety within the mesophase region. An example of such a spectrum is shown in the middle trace of figure 4. It exhibits a uniaxial powder pattern with an overall splitting of $|\nu_Q| = 126$ kHz. This reduction in the quadrupole splitting has been interpreted in terms of fast planar reorientation of the molecules within the columns of the discotic mesophase and a further reduction by $S = 0{\cdot}94$ due to orientational disorder of the triphenylene C_3 axis. Hence in table 3, ν_Q for the aromatic deuterons in the mesophase is given a negative sign. The carbon-13 spectrum of the carboxy group behaves similarly to the aromatic deuterons in that in the mesophase it exhibits an axially symmetric average chemical shift tensor with parameters as shown in table 3. Note that as for the quadrupole interaction of the deuterons, the sign of the carbon-13 chemical shift tensor in the mesophase is reversed with respect to that in the solid. The fact that these average tensors appear axially symmetric reflects the weak biaxiality of the mesophase. The average quadrupole tensors of the α- and β-methylene deuterons, on the other hand, are clearly biaxial, and when the mesophase is doped with a small amount of deuteriated benzene, its deuterium spectrum also exhibits a pattern characteristic of an asymmetric tensor (see top trace in figure 4). For a rigid molecule with threefold or higher symmetry in an orthorhombic mesophase, all (second rank) magnetic tensors should have the same asymmetry parameters [11]. For the real HAT8 molecules, this does not apply, since in the mesophase they consist of a mixture of conformers. The essentially perfect axial symmetry of the aromatic deuterons and carboxy carbon tensors may suggest that the cores of the HAT8 molecules, consisting of the triphenylene moiety and its adjacent carboxy groups, experience a local uniaxial symmetry, while the biaxial nature of the phase is predominantly reflected in the ordering of the side chains. A pictorial visualization of such a model would be columns consisting of stacked cores, whose planes are nearly perpendicular to the axes of the columns and which undergo small, but nearly equal fluctuations in the *ac* and *bc* planes of the mesophase. The ordering of the side chains may however be different in these two planes.

If the carboxy groups in the mesophase remain rigidly attached to the triphenylene core as in the solid, an estimate of the angle, θ, between the perpendicular to the triphenylene and carboxy planes could be made from the relation

$$\Delta\sigma\,(\text{meso}) = \Delta\sigma\,(\text{solid})\,S\tfrac{1}{2}(3\cos^2\theta - 1).$$

Inserting the experimental results from table 3 and $S = 0{\cdot}94$ yields $\theta \sim 63°$, which is very close to that measured for diphenylsuccinate ($\sim 64°$) [21] and to values calculated by molecular mechanics for similar moieties (56°) [18]. However this is most likely fortuitous, since there is no reason to assume that the carboxy group remains rigid with respect to the triphenylene ring in the mesophase. For example, in the (biaxial) mesophase of the alkanoyloxybenzene derivatives, the carbon-13 chemical shift tensor of the aromatic moiety is axially symmetric, while that of the carboxy group is strongly asymmetric.

This research was supported by the Israel Science Foundation administered by the Israel Academy of Sciences and Humanities.

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