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X-ray investigation of bowl-like compounds

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The mesophases of bowl-like compounds were first proposed in 1982, and the compounds have recently been synthesized. We have found that some bowl-like compounds can form disordered crystalline phase that have long-range positional order, but with strong fluctuations in position and orientation. Their side chains are in a molten state. X-ray diffraction has shown that two new homologues in the hexa-*n*-alkylcarboxytribenzocyclononene series are stacked in triclinic systems with space group $P\bar{1}$. The parameters of a unit cell, the densities of the compounds and the expansion coefficient are given. Modelling of a unit cell is presented, which confirms the up-down asymmetry of the molecules, but there is no microscopic ferroelectricity. However, one-dimensional antiferroelectricity may exist. The results are compared with disc-like molecules, as well as with higher homologues of the bowl-like compounds.

1. Introduction

Mesophases of bowl-like molecules were first proposed by Lin [1], and the compounds were synthesized more recently by Zimmermann *et al.* [2] and Malthete and Collet [3]. They called the molecules pyramidal-shaped and cone-shaped respectively; here we use the terms bowl-like or bowl-like. The molecules are three-dimensional in a physical sense, and can exhibit mesophases as do the one-dimensional rod-like and two-dimensional disc-like compounds. The bowl-like compounds are attracting some interest at present.

As shown in figure 1, the bowl-like molecules that have so far been reported to exhibit the mesophases are all derivatives of tribenzocyclononene, with R being either OC_nH_{2n+1} , $OC(O)C_nH_{2n+1}$, $OC(O)C_6H_4C_nH_{2n+1}$ or $OC(O)C_6H_4OC_nH_{2n+1}$. They consist of a cone-shaped rigid core and six identical flexible side chains attached to the core, each containing several carbon atoms. The configuration creates a remarkable difference from conventional liquid-crystal molecules (e.g. rod-like and disc-like ones) in physical properties. In consequence, the structure of the bowl-like compounds is an important subject for investigation. One class of bowl-like molecules is the hexa-*n*-alkylcarboxytribenzocyclononene series (abbreviated HATB), their molecular formulae have the form shown in figure 1. Zimmermann *et al.* [2] have synthesized the $n = 7-14$ HATB homologues possessing mesophases. Malthete and Collet [3] have synthesized the $n = 9, 11, 15$ HATB homologues, two of which ($n = 9, 11$) have been investigated by Levelut *et al.* [4] by means of X-ray diffraction experiments. The structure of the two HATB homologues with $n = 9, 11$ shows the classical columnar phases and a hexagonal or oblique lattice in a two dimensional array with a disordered array in the third dimension. The lower members of the homologous series of HATB may be important, as predicted by Lin [5], and so we limit our attention to the two lower HATB homologues with $n = 5$ and 6. We denote them by HATB (5) and HATB (6) respectively. Differential-scanning calorimetry and optical-polarizing

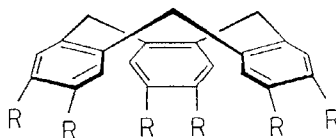


Figure 1. Bowlic molecules; hexasubstituted tribenzocyclononenes, $R = \text{OC(O)C}_n\text{H}_{2n+1}$.

microscopy show that a phase transition occurs at 152°C for HATB(5) and 153°C for HATB(6). When the temperature is less than 152°C HATB(5) exhibits a texture quite distinguishable from the $n = 7$ and 9 cases, as shown in figure 2. For temperatures greater than 152°C the compound becomes isotropic.

We have investigated the structure of HATB(5) and HATB(6) using X-ray diffraction. We give the crystallographic system, the space group and the parameters for the unit cell. The modelling of the phase will be discussed later in the paper.

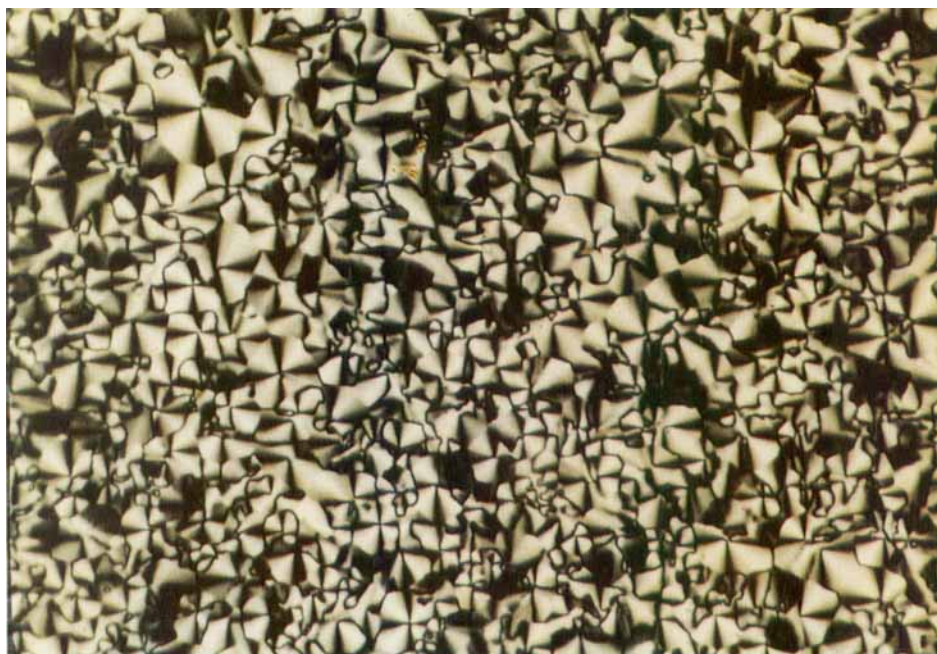
2. Experiments

The X-ray experiments were carried out with a Rigaku X-ray diffractometer. Scattering through a diffraction angle 2θ of more than 2° was measured using a goniometer at intervals of 2θ of 0.1° ; scattering through less than 9° degrees was collected by a linear position-sensitive detector at intervals of 0.05° . The monochromatic X-ray beam was the CuK_α line with wavelength λ of 1.54 \AA . The samples were 1 mm thick and were held in an oven whose temperature was controlled to within $\pm 0.5^\circ\text{C}$. The experiments were performed at 30°C, 80°C, 113°C, 140°C, 152°C (all in the disordered crystalline phase) and 153°C (just above the disordered-crystal-isotropic transition). The experimental results were similar for all the mesophases. Low-angle diffraction peaks were mostly observed, and higher-order reflections were not found. The even reflections ($h00$) were not of higher intensity than odd ones. However, despite the Debye-Waller factor, the ($h00$) reflections did not show a significant decrease with scattering vector, as did the ($0h0$) ones. In addition, a broad diffuse scattering was found at $2\theta \approx 20^\circ$, which reflects the liquid-like distribution of the side chains of the bowlic compound. As the temperature increased above 152°C, all the diffraction peaks disappeared, but the diffuse scattering remained. In addition, one more broad diffuse scattering appeared, which indicates the random distribution of the centres of mass of the molecular cores. The two diffuse scattering peaks were similar to those of all the discogens in the isotropic phase.

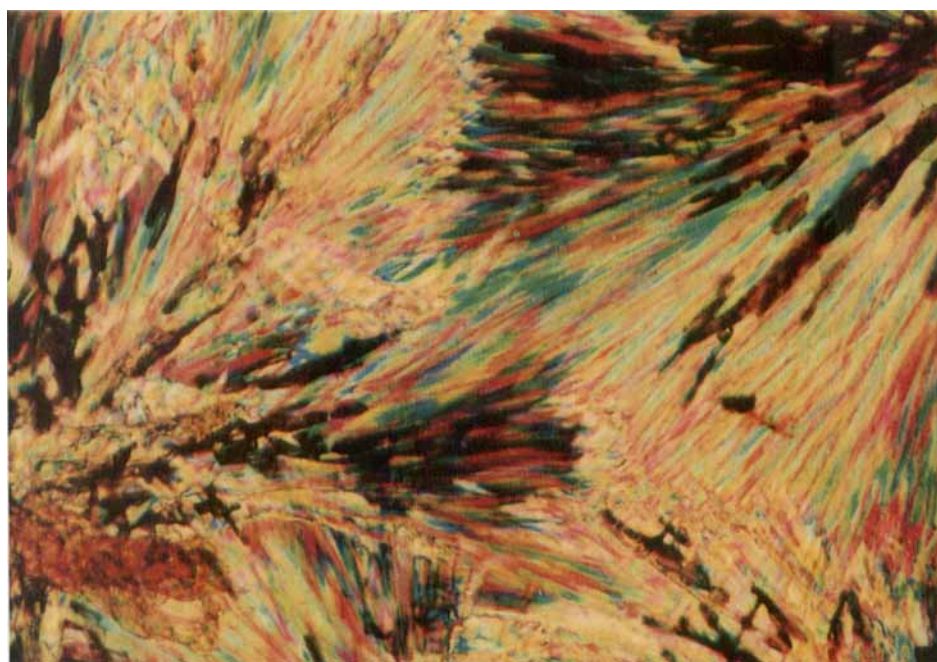
3. Crystallographic system, space group and unit-cell parameters

The experimental data were analysed by using our knowledge of the steric shape of the bowlic molecules. The structure of HATB(5), including the crystallographic system, the space group, the unit-cell parameters and the calculated density, as well as the number of molecules in the unit cell, are summarized in table 1. Table 2 gives a comparison of the measured and calculated values of the scattering vector Q ($= 4\pi \sin \theta/\lambda$) for the individual reflections from the sample of HATB(5).

The crystallographic system is triclinic with a space group $P\bar{1}$, the only symmetrical element of which is the inversion centre. In fact, the existence of an inversion centre was derived from two facts: one was the $Z = 2$ value, and the other results from the shape and dimensions of the bowlic molecules. Hence this implies that there is no



(a)



(b)

Figure 2. Photomicroscopic textures of (a) HATB(9) at 100°C and (b) HATB(5) at 100°C, obtained from cross-polarizing microscopy (magnification $\times 320$).

Table 1. Summary of crystallographic data for HATB (5) at 140°C.

Molecular formula:	$C_{57}H_{78}O_{12}$
Molecular weight:	954
Crystal system:	Triclinic
Space group:	$P\bar{1}$
Unit-cell parameters:	
$a = 30.5 \text{ \AA}$	$\alpha = 95.2^\circ$
$b = 22.1 \text{ \AA}$	$\beta = 113.4^\circ$
$c = 4.86 \text{ \AA}$	$\gamma = 77.1^\circ$
	$V_c = 2870 \text{ \AA}^3$
	$Z = 2$
Calculated density:	1.10 g/cm^3

Table 2. Diffraction data for HATB(5) at 80°C.

Reflection	Scattering vector $Q/\text{\AA}^{-1}$		Intensity
	Calculated	Measured	
100	0.2331	0.2349	Strong
010	0.2918	0.2918	Strong
110	0.3338	0.3345	Very strong
$1\bar{1}0$	0.4093	0.4127	Strong
200	0.4661	0.4625	Strong
210	0.4963	0.4909	Very weak
120	0.5821	0.5832	Very weak
020	0.5837	0.5832	Very weak
220	0.6676	0.6827	?
$1\bar{2}0$	0.6716	0.6827	?
300	0.6992	0.6827	?
$2\bar{2}0$	0.8186	0.8102	Weak
030	0.8755	0.8739	Weak
400	0.9322	0.9306	Weak
330	1.0014	1.0154	Weak
$\bar{1}\bar{1}1$	1.3524	1.3536	Strong
$\bar{1}11$	1.3918	1.3953	Strong
001	1.4238	1.4238	Strong
011	1.4623	1.4656	Very Strong
101	1.5379	1.5359	Strong
$1\bar{1}1$	1.5660	1.5775	Strong

second-harmonic generation effect. The crystalline phases of the bowlic compounds are biaxial. There are two bowlic molecules in the unit cell, one up and the other down. More details concerning the structure of the bowlic compounds will be discussed later. The experiments found that the unit-cell parameters α , β , γ and a , b , c change little with increasing temperature; for example, the changes in a , b , c were less than 2 per cent, while those in α , β , γ were less than 3 per cent as the temperature increased from 30°C to 140°C. From the specific volume calculated for the range of 30–140°C, the average expansion coefficient $\bar{\kappa}$ of the bowlic sample of HATB(5) may be obtained as $2.3 \times 10^{-4} \text{ K}^{-1}$, which is two or three times smaller than that of the mesophases of conventional rod-like molecules (see e.g. [6]) at temperatures below the liquid-crystal–isotropic transition, where the κ may diverge.

4. The disordered crystalline phase

There were a few peaks in the X-ray diffraction patterns, so that we could not determine more exactly the structural details at the atomic level. The sharp diffraction peaks at low reflections are evidence that the bowlic molecules are arranged with long-range three-dimensional positional order. But the diffraction intensity fell off rapidly with scattering vector, and no higher orders of reflection were observed, which may imply that the density wave of the center of mass for the molecular cores is approximately sinusoidal. By contrast, the density wave of a crystal phase is a sum of quite sharp gaussian functions, and the corresponding diffraction peaks are very sharp too. The difference between them is in the number and intensity of the diffraction peaks. The bowlic phase of HATB(5) below 152°C may therefore be interpreted as a disordered crystalline phase [7]. However, the side chains of the compounds are in a liquid-like disordered state, which is responsible for the broad diffuse scattering at diffraction angles of about 20°. These characteristics can be compared with those of rod-like molecules. Ordered liquid crystals, for example the monoclinic smectic G and J phases and the cubic D phase, have three-dimensional positional order, but there is significant local disorder in both the position and orientation in these phases. We may therefore use the alternative term of ordered mesophase for the bowlic compounds.

5. Molecular stacking and discussion

We designate the outside normal to the bowl head of the molecule by the vector $\mathbf{1}$; then the outside normal to the bowl bottom is the vector $-\mathbf{1}$. Molecules with the same direction $\mathbf{1}$ or $-\mathbf{1}$ are stacked in columns, whose axes make a tilt angle of about 25° with respect to the vectors $\mathbf{1}$ or $-\mathbf{1}$, which is similar to the discotic liquid-crystal phase D_h (see e.g. [8]). The columns are arranged in a two-dimensional array. The bowlic cores are regularly distributed in the columns. The molecules with directions $\mathbf{1}$ and $-\mathbf{1}$ form an interpenetrating simple triclinic lattice. An inversion around the centre transforms a molecule with director $\mathbf{1}$ into a molecule with director $-\mathbf{1}$ with such a transformation the two molecular sites differ within a vector $\frac{1}{2}\mathbf{a}$. The space group of the low-temperature phase of the bowlic compound is $P\bar{1}$. The stacking of the bowlic molecules is shown schematically in figure 3. Two conclusions can be obtained from the model. The bowlic molecules are three-dimensional in a physical sense, and the 'up' and 'down', i.e. $\mathbf{1}$ and $-\mathbf{1}$, of the molecules are not equivalent. This differs from the situation for disc-like molecules, which have up-down symmetry. On the other hand, the numbers of molecules with directions $\mathbf{1}$ and $-\mathbf{1}$ are equal in a very small macroscopic site, so that there is up-down symmetry at the macroscopic level; there is therefore no ferroelectricity, but one-dimensional antiferroelectricity may exist along the \mathbf{a} axis.

The disc-like molecules, hexa-*n*-alkanoates of triphenylene (HAT), have some similarity to HATB in their chemistry and shape despite the difference in the cores of the two kinds of molecules. X-ray diffraction shows that the disc-like molecules are arranged in columns and the average separation of the molecular cores of HAT ($n = 7$) in the columns [9] is 4 Å, and the minimum gap of the cores of HAT ($n = 3$) in columns [10] is 3.43 Å. However, the separation in the bowlic molecules HATB(5) is 4.4 Å, greater than that for disc-like molecules. This reflects the geometrical features of the bowlic molecules. The bond angles and distances of the crown cores of the non-substituted tribenzocyclononene, which are the same as the cores of HATB,

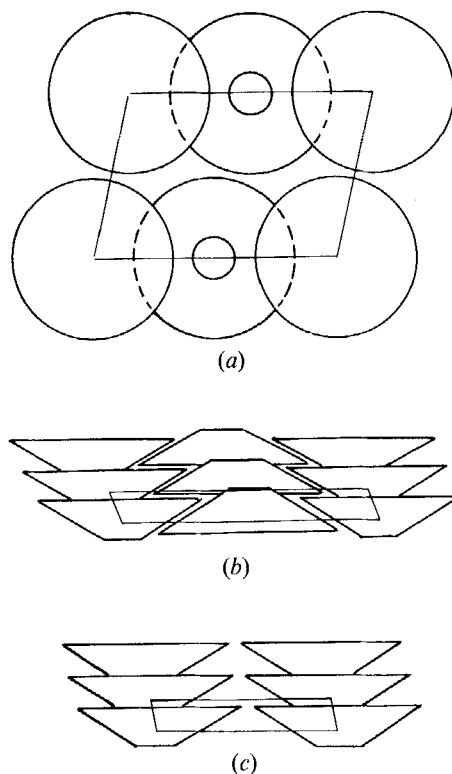


Figure 3. The packing of bowl-shaped molecules of HATB(5) and HATB(6) in the low-temperature phase. It is a triclinic system with space group $P\bar{1}$. The bowls represent the bowl-shaped molecules. Viewed along the direction of (a) $\mathbf{b} \times \mathbf{a}$, (b) $\mathbf{c} \times \mathbf{a}$, (c) $\mathbf{c} \times \mathbf{b}$.

have been measured by Cerrini *et al.* [11]. According to the data, the side plane of the aromatic ring of HATB makes a dihedral angle of about 40° with the bowl-head plane, and so the cone-shaped rigid core contributes an additional 1.2 \AA or 1.8 \AA in thickness on the basis of the [9] or [10] respectively. In addition, if we add the contribution of the flexible paraffinic chains the thickness will of course be much greater than the experimental value of 4.4 \AA . Obviously, there must be an overlap of the bowl-shaped molecules within the columns; in other words, the bottoms of the bowls penetrate into the interior of the nearest neighbours within the same columns.

The calculated density of HATB(5), $D = 1.10 \text{ g/cm}^3$ is in very reasonable agreement with some data of [9] and [10]. A direct measurement of the density is not available. One of the parameters $b = 22.1 \text{ \AA}$ of the unit cell of the triclinic system of HATB(5) corresponds to the diameter of the bowl. There are many conformations of the side chains as a result of their flexibility, but we may discuss the results by comparison with the corresponding disc-like molecules. In order to explain the value of the parameter $a = 30.5 \text{ \AA}$, we have to take into account the interception of two neighbouring columns with parallel and antiparallel directions $\mathbf{1}$ and $-\mathbf{1}$. The interception is approximately 6.8 \AA in width, which is approximately the same value as the projection of the flexible side chain onto the plane perpendicular to the axis of the bowls. The experiment by Levelut *et al.* on the bowl-shaped compounds HATB with $n = 9$ and 11 showed that for HATB(9), $a = 35.35 \text{ \AA}$, $b = 25.49 \text{ \AA}$, $\gamma = 99.1^\circ$, and

that the separation of the cores in the columns $d > 4 \text{ \AA}$. We have also performed X-ray experiments on the bowlic compound; the results were nearly the same as those obtained by Levelut *et al.*; for example, for HATB(9), $a = 34.33 \text{ \AA}$, $b = 25.65 \text{ \AA}$, $\gamma = 100.4 \text{ \AA}$. A more detailed discussion will be published elsewhere.

The results for another bowlic compound, HATB(6), were similar to those for the lower homologue with $n = 5$, but the unit-cell parameters increased (a by 3.5 \AA and b by 1.8 \AA), which results from the additional methylene group in each side chain.

6. Conclusion

The bowlic compounds HATB(5) and HATB(6) exhibit a disordered crystalline phase. They have long-range three-dimension positional order, but with strong local disorder in both position and orientation. In addition, the side chains of the compounds are in a liquid-like state. More work is needed to study some physical properties, for example the shear viscosity and the shear modulus, neutron scattering or dielectric relaxation should be employed to probe the dynamics of the compounds. The symmetry of the phase is that of a triclinic system; the space group is $P\bar{1}$. There are two molecules, one up and the other down in the unit cell. Therefore there should be no ferroelectricity and no second-harmonic generation effect. However, one-dimensional antiferroelectricity may exist. The results show that the crystalline phases are biaxial. The calculated density of the compound HATB(5) is 1.10 g/cm^3 , the expansion coefficient is about $2.3 \times 10^{-4} \text{ K}^{-1}$. On the basis of the analysis, a stacking model has been presented.

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