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Mesomorphic behaviour of 4-benzoyloxybenzoic acid and its binary mixture with 4-acetoxybenzoic acid

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The nematic liquid crystalline property of 4-benzoyloxybenzoic acid (BBA) was observed by polarizing microscopy and X-ray diffraction. The structure of the hydrogen-bonded BBA dimer was verified by FT-IR, and the axial ratio (l/d) of the rod-like molecule was calculated to be 5·8, which is large enough to exhibit a liquid crystalline phase. The mesophase was stable at 240°C. At higher temperatures, for example, 270°C, the *trans*-esterification side reaction occurred. The binary phase diagram of BBA and 4-acetoxybenzoic acid shows the eutectic temperature at 175°C.

1. Introduction

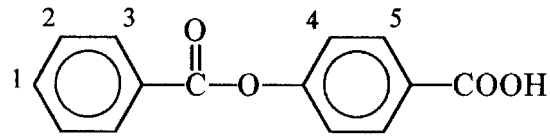
4-Benzoyloxybenzoic acid (BBA) was prepared long ago [1–3], however, the liquid crystalline (LC) properties, to our knowledge, have never been reported in the literature. The liquid crystallinity of rod-like molecules is attractive both for theoretical and rheological interests. The excellent fluidity of melts may be present due to the absence of long flexible substituents which may retard the mobility of the molecules in the molten state. Two factors are dominant in promoting the occurrence of a stable mesomorphic phase: asymmetry of the molecular shape and a rigid rod structure with soft anisotropic intermolecular forces [3]. Only a few samples with large axial ratios of the rod-like molecules ($l/d>4$) show liquid crystallinity, even if they have no asymmetry and soft substituents in the molecules, such as poly-*p*-phenylenes $H(C_6H_4)_nH$ with $n=5$–6. However, their solubility is poor and melting temperature are very high, for example, T_m is 388°C for $n=5$ [4]. At such a high temperature the thermal decomposition presents serious difficulties in the conduct of research experiments.

In this paper, BBA in the hydrogen bonded dimer form is symmetric without any soft substituents. It melts at 230°C with good solubility in common organic solvents. Its mixture with 4-acetoxybenzoic acid (Ac-BA) melts at an even lower temperature. The eutectic melting occurs at 175°C.

2. Experimental

2.1. *Synthesis of BBA*

BBA was prepared according to the procedure described in [3] and recrystallized from ethanol. T_m 229–230°C (225°C in [2]). ^{1}H NMR (DMSO) δ: 7·76 (t, 1 H, 1-H), 7·62 (t, 2 H, 2-H), 8·05 (d, 2 H, 3-H), 7·43 (d, 2 H, 4-H), 8·16 (d, 2 H, 5-H).

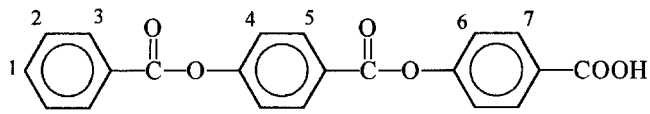


BBA

2.2. *Synthesis of BBBA*

2.2.1. *Preparation of p-benzoxybenzoyl chloride*

p-Benzoxybenzoic acid (2·42 g, 0·01 mol) with 10 ml thionyl chloride in the presence of several drops of DMF as the catalyst were heated at reflux. After removal of the unreacted $SOCl_2$ at 80°C under vacuum, the solid was recrystallized in toluene. A white product 2·2 g (80 percent yield) with $T_m=134·5$–136°C (133–134°C in [3]) was obtained.



BBBA

2.2.2. *Preparation of BBBA*

p-Benzoxybenzoyl chloride (1·6 g, 0·006 mol) in 30 ml dry THF was added in a dropwise manner to the reaction mixture of *p*-hydroxybenzoic acid (4·14 g, 0·03 mol), 25 ml THF and 6 ml pyridine with stirring.

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The temperature was increased to 60°C and stirred for 12 h. The reaction mixture was then poured into 300 ml 10 per cent HCl solution with stirring, and the precipitate was filtered and dried to yield 1·56 g (71·8 per cent) product. The product was washed with hot water to remove the unreacted *p*-hydroxybenzoic acid. After column chromatography separation (2–3 drops of acetic acid in 1000 ml acetone), the product did not melt until 360°C and was identified by ^{1}H NMR in DMSO. ^{1}H NMR (DMSO) δ: 7·79 (t, 1 H, 1-H), 7·66 (t, 2 H, 2-H), 8·05 (d, 2 H, 3-H), 7·29 (d, 2 H, 4-H), 8·26 (d, 2 H, 5-H), 7·57 (d, 2 H, 6-H), 8·19 (d, 2 H, 7-H).

2.3. *Characterization*

Thermoanalysis was performed on a DSC-50 (Schimadzu) at a heating rate of 10°C min^{-1}. FT-IR spectra were performed on a Nicolet Magna-IR 750 FT-IR spectrometer, and NMR spectra on a Varian ARX 400 NMR spectrometer (400 MHz). X-ray diffraction patterns were obtained using a PW 1700 (Philips) diffractometer, and polarizing photomicrographs were taken on a Laborlux 12 Pol Leitz watzlar 350, optical polarizing microscope with hot stage.

3. Results and discussion

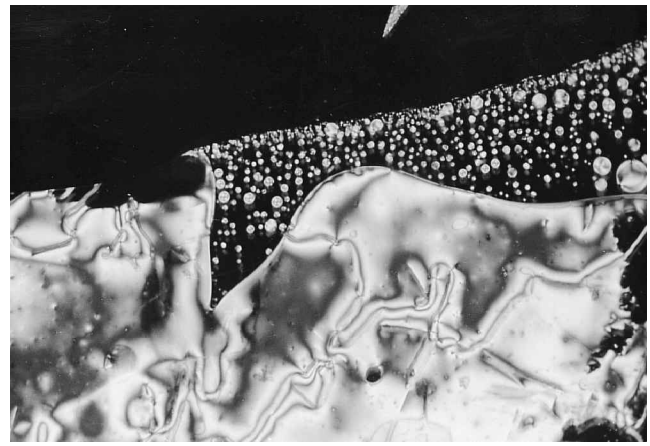
3.1. *Mesomorphic behaviour of BBA*

BBA has a melting point at 230°C, above which the melt flows excellently, and the nematic schlieren texture could be observed under the polarizing microscope (see figure 1(*a*)). Figure 2 shows the diffraction patterns of BBA at temperatures lower and higher than the melting temperature. The sample at 235°C showed only diffuse haloes in the wide angle region, and no crystalline peaks could be observed. The optical anisotropy of the melt is therefore only due to the liquid crystalline behaviour. The central position of the diffuse halo is located at about $2\theta = 20°$, which is in accordance with the lateral packing of nematic liquid crystalline chains.

The mesophase of BBA freshly obtained by recrystallization from absolute ethanol was stable at 240°C at least for one hour. However, for prolonged heating or increased temperature, such as up to 270°C for 20 min, crystallization occurred and the melt solidified. The DSC thermogram shows only an endothermic transition at 230°C, which corresponds with the Cr–N transition temperature observed under microscopy. T_{N-I} could not be observed either by microscopy or DSC. Above 243°C, the DSC trace curves slightly upwards, denoting the occurrence of some side reactions with an exothermic effect.

In order to interpret the side reaction, we heated 0·1 g BBA in a salt bath at 270°C for 20 min and collected the sublimated product. Its IR spectrum was in good agreement with that of benzoic acid. Furthermore, there

(*a*)



(*b*)

Figure 1. Optical polarizing micrographs (320×) of melts (*a*) BBA at 240°C and (*b*) a mixture of BBA and Ac-BA (30:70 by wt) at 184°C.

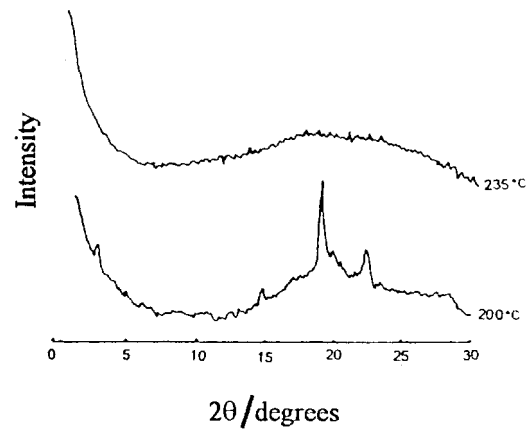
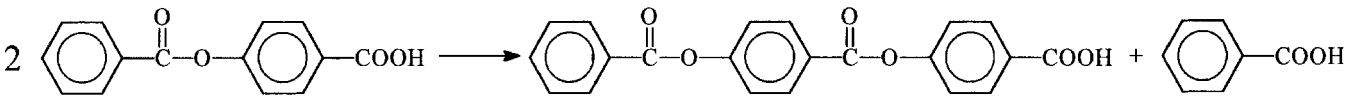


Figure 2. X-ray diffraction patterns of BBA at 200 and 235°C.

was no decrease in the melting point when the product was mixed with an equal amount of benzoic acid. Thus, the sublimated product was verified to be the benzoic acid. As regards the solid residue, it did not melt until 360°C, and the ^{1}H NMR spectrum (in DMSO) was in agreement with that of BBBA (see § 2.2). Therefore, we concluded that the side reaction is mainly a *trans*-esterification reaction as follows:



3.2. *Hydrogen-bond association and structural axial ratio of BBA molecules*

Dimer formation through hydrogen-bond association of the carboxyl groups has been studied for a wide variety of 4-substituted benzoic acids [5]. The hydrogen-bonded dimer of BBA could be verified by FT-IR spectrum (see figure 3). The bands at 2553 and 2673 cm^{-1} for the dimer are considered to be Fermi resonances [6,7]; the broad O–H band centred at 3000 cm^{-1} and the carbonyl band at 1682 cm^{-1} are due to the dimer formation of the carboxylic acid [7].

In order to estimate the axial ratio of the dimer of BBA, we used 6·18 Å for the extension of the length of phenyl carboxyl group and 1·3 Å for the length attributable to the hydrogen atom according to the structural data given in [3] (see figure 4). The length of single bond O–Ph is 1·41 Å [8]. Then the length of the next PhCOO moiety is 6·18–1·41=4·77 Å. The length between two oxygen atoms in two hydrogen-bonded carboxyl groups was estimated to be 2·7 Å [9]. Therefore, the length of the rod-like BBA dimer molecule was calculated to be (1·3+6·18+4·77)×2+2·7=27·2 Å. The mean molecular diameter is 4·7 Å [3]. Thus we obtained the axial ratio (l/d) to be ~5·8, which is large enough to exhibit liquid crystallinity.

When comparing BBA with *p*-*n*-alkoxybenzoic acid, it is interesting to note that the propyloxy to hexyloxybenzoic acids show only the nematic phase, and the heptyloxy to tridecaloxybenzoic acids exhibit both smectic and nematic phases [10]. With regards to BBA, the benzoyloxy substituent groups extend the length of the rod-like dimer of benzoic acid and increase the axial ratio for the appearance of liquid crystallinity. However, its contribution to the permanent dipole as well as the anisotropic intermolecular force perpendicular to the molecular axis are much smaller than alkoxy substituent groups. Thus, while the longer alkoxybenzoic acids show both the nematic and smectic phases, the BBA melt shows only the nematic phase.

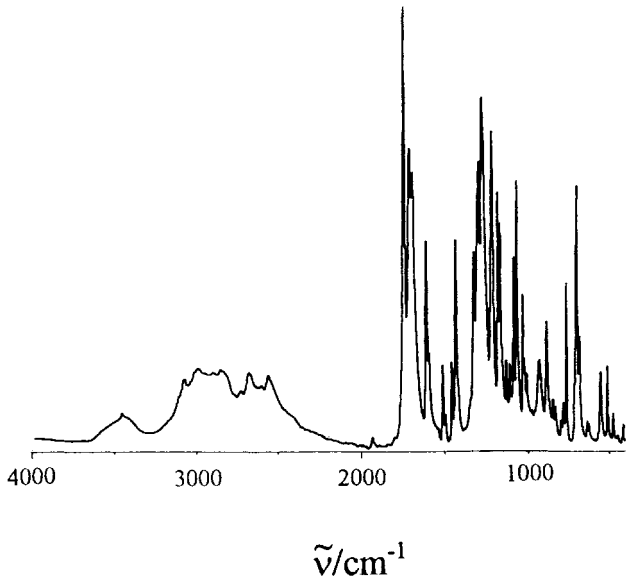


Figure 3. FT-IR spectrum of BBA.

3.3. *Binary mixtures of BBA and Ac-BA and the phase diagram*

The melting curve of the binary eutectic system could be calculated on a thermodynamic basis using the following equation [11]:

$$T_i = \frac{\Delta H_{oi}}{\frac{\Delta H_{oi}}{T_{oi}} - R\,In\,X_i} \qquad (1)$$

where T_i is the temperature at which the mixture melts, ΔH_{oi} is the molar heat of fusion of component i, T_{oi} is the melting point of the pure component i, R is the universal gas constant and X_i is the mole fraction of component i.

We determined the molar heats of fusion by DSC and obtained 26·35 kJ mol^{-1} (6293·0 cal mol^{-1}) for Ac-Ba and 39·67 kJ mol^{-1} (9475·7 cal mol^{-1}) for BBA. Using equation 1, we calculated the theoretical line for the phase diagram (see figure 5) and obtained the theoretical eutectic component to be 30 per cent BBA, which is in agreement with the data determined by DSC. The eutectic temperature is 175°C. The schlieren texture of the nematic mesophase was observed under polarizing microscopy (see figure 1 (*b*)).

4. Conclusions

We have demonstrated that through hydrogen bond association of carboxyl groups BBA molecules exist in

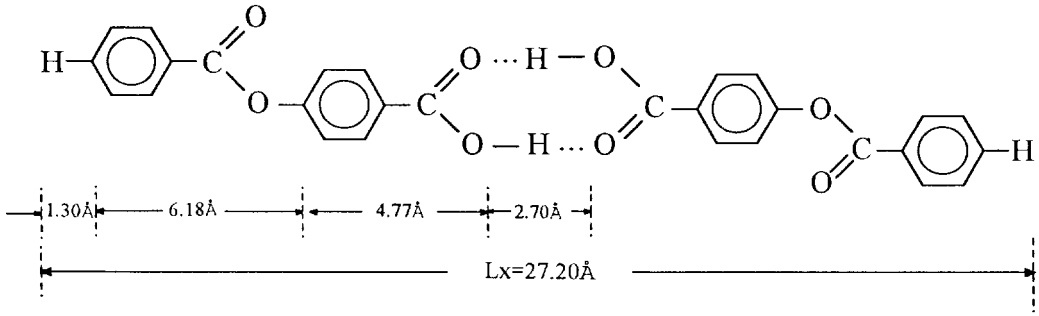


Figure 4. Schematic illustration for calculating the length of dimer molecule.

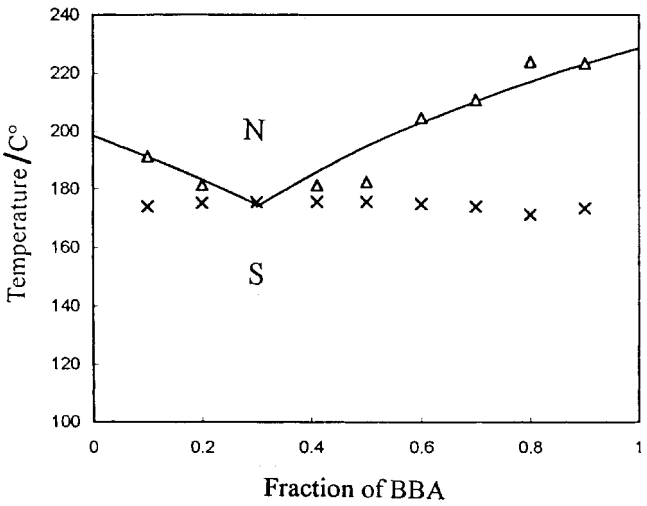


Figure 5. Phase diagram of AcBA-BBA. The full line denotes the theoretical line calculated using equation (1); N denotes the nematic phase and S denotes the solid phase.

the dimer form. The rod-like BBA dimer molecules, without any assistance of asymmetry and soft substituents, exhibit a nematic mesophase which is stable for at least one hour at 240°C. The structural axial ratio was calculated to be 5·8, which is large enough to exhibit liquid crystallinity. On continued heating at 240°C or increased temperature (up to 270°C), a side reaction, which was verified to be mainly a *trans*-esterification reaction between the molecules of BBA with the formation of BBBA and benzoic acid, occurred. When BBA was mixed with Ac-BA, the T_{Cr-N} could be further decreased. The eutectic component of the binary mixture of Ac-BA/BBA was 70/30. The eutectic temperature was 175°C.

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