Mixed-dimer formation in binary systems of 4-substituted benzoic acids and structure considerations[1]

Maren Roman, Annett Kaeding-Koppers, and Peter Zugenmaier

Abstract: The phase behavior of binary systems of 4-substituted benzoic acids is governed by the formation of mixed dimers. This study was conducted to determine the effect of the components' structural difference on mixed-dimer formation in crystalline and liquid-crystalline phases. The phase diagrams of two systems, with 4-[(*S*)-(–)-2-methylbutoxy]benzoic acid (MBOBA) as one component and 4-(hex-5-enoxy)benzoic acid (HOBA) and 4-(dec-9-enoxy)benzoic acid (DOBA), respectively, as the second component, were determined by differential scanning calorimetry, polarized-light microscopy, and X-ray diffraction. The MBOBA-HOBA system exhibited a cholesteric phase, two solid solutions, and above 58 °C for compositions between 40 and 80 mol% HOBA a crystalline phase of mixed dimers. The MBOBA-DOBA system showed a crystalline phase of mixed dimers at all compositions, a cholesteric phase, and a twisted smectic C phase, which was dominated by mixed dimers at 60 and 70 mol% DOBA. We conclude that liquid-crystalline phases are generally dominated by mixed dimers, but in crystalline phases the formation of mixed dimers is promoted by a greater difference in molecular structure. The crystal structure of two of the pure compounds MBOBA and DOBA and comparable compounds have been determined for an evaluation of the arrangements of the molecules in the crystal and liquid-crystalline state.

Key words: benzoic acid, crystal arrangement, phase diagrams, liquid crystal.

Résumé : Le comportement de phase des systèmes binaires d'acides benzoïques substitués en position 4 est régi par la formation de dimères mixtes. On a réalisé cette étude dans le but de déterminer les effets des différences de structure des composants sur la formation de dimères mixtes dans les phases cristallines et à cristaux liquides. Les diagrammes de phase de deux systèmes dans lesquels ont retrouve d'une part, dans tous les deux, de l'acide 4[(*S*)-(–)-2-méthylbutoxy]benzoïque (AMBOB) et, d'autre part, respectivement de l'acide 4-(hex-5-énoxy)benzoïque (AHOB) et de l'acide 4-(dec-9-énoxy)benzoïque (ADOB) en faisant appel à la calorimétrie à balayage différentiel, à la microscopie à lumière polarisée et la diffraction des rayons X. Le système AMBOB/AHOB, on observe une phase cholestérique, deux solutions solides et, au-dessus de 58 °C, pour les compositions entre 40 et 80 mol% d'AHOB, on observe aussi une phase cristalline des dimères mixtes. Le système AMBOB/ADOB, présente une phase cristalline de dimères mixtes pour toutes les compositions, une phase cholestérique et une phase smectique C décalée qui était dominée par les dimères mixtes pour les compositions allant de 60 à 70 mol% d'ADOB. On en conclut que les phases à cristaux liquides sont généralement par les dimères mixtes, but que dans les phases cristallines la formation de dimères mixtes est facilitée par une plus grande différence dans les structures moléculaires. On a déterminé les structures cristallines des composés AMBOB et ADOB et de composés apparentés afin d'évaluer les arrangements des molécules dans le cristal et dans l'état à cristal liquide.

Mots-clés : acide benzoïque, arrangement cristallin, diagrammes de phase, cristal liquide.

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Introduction

Molecules of benzoic acid and its derivatives generally pair through intermolecular hydrogen bonds and form dimers. The bonding is so strong that, on heating, the dimers persist from the crystalline state through to the isotropic state (1). A dimer has a larger aspect ratio and twice the number of polarizable aromatic rings and carbonyl groups

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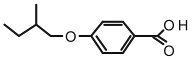
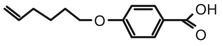
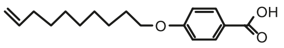
Table 1. Properties of the pure components.

Compound	Molecular structure	Molecule/Dimer length[a] (Å)	d Value[b] (Å)	Phase transition temperatures (°C) (above arrow) and enthalpies (kJ·mol^{-1}) (below arrow)
MBOBA		12.2/24.2	8.7–9.0 14.6–14.5	$C^{\alpha} \xrightarrow[6.1]{105.8} C^{\beta} \xrightarrow[11.5]{110.5} I$
HOBA		15.2/30.2	16.2–16.0	$C \xrightarrow[15.8]{99.5} N \xrightarrow[1.4]{140.0} I$
DOBA		16.7/32.8	24.1–25.0 25.2–26.0 28.1–29.7	$C^{\alpha} \xrightarrow[12.4]{\leq 80} C^{\beta} \xrightarrow[16.3]{78.4} S_C \xrightarrow[1.2]{115.4} N \xrightarrow[2.1]{137.0} I$

[a] Determined by the lengths of the molecules in the crystal structure; for HOBA by adding the lengths of appropriate segments.
[b] Change of d values upon increase of temperature.

with respect to a single molecule. However, due to the formation of dimers by hydrogen bonding by the carbonyl groups, the dipoles are compensated and an antiparallel arrangement of the molecules is favored. For this reason, most of the 4-substituted benzoic acids with linear substituent groups are liquid-crystalline (2). When 4-substituted benzoic acids are mixed, dimers containing two different molecules can be formed. In studies of binary systems of 4-substituted benzoic acids (3, 4), a number of systems showed deviation from eutectic phase behavior. Mixed-dimer formation is thought to be the reason for the high melting points in these systems.

In this study, crystalline and liquid-crystalline phases of these systems have been investigated with a focus on the formation of mixed dimers. To determine the effect of the difference in molecular structure of the components on mixed-dimer formation, we studied two systems that have one common component and whose second components differ only in the length of the substituent groups. In the first system, the molecular structures of the components are fairly similar so that mutual solubility is expected. In the second system, the molecular structures of the components are distinctly different, which can result in eutectization. The component that both systems have in common is the chiral 4-[(*S*)-(–)-2-methylbutoxy]benzoic acid (MBOBA). This compound is not liquid-crystalline but a tendency to form a mesophase is anticipated because 4-butoxybenzoic acid is mesomorphic. Because of its asymmetric carbon atom, MBOBA is further expected to twist the molecular arrangements in the mesophases of the second components, which are 4-(Hex-5-enoxy)benzoic acid (HOBA) and 4-(Dec-9-enoxy)benzoic acid (DOBA). Further clues for the formation of chiral phases can be provided by consideration of the unusual arrangement of the pure compounds.

Experimental

Materials

MBOBA was synthesized by brominating (*S*)-(–)-2-methylbutan-1-ol (5, 6) with phosphorus tribromide (7, 8) and subsequently reacting the obtained (*S*)-(–)-2-methyl-1-bomobutane with 4-hydroxybenzoic acid. The different alkenoxy benzoic acids used in this study were prepared as described in ref. (9). The properties of the pure components (Table 1) were determined as described in the methods section below. For MBOBA, no liquid-crystallinity was observed; it showed two crystalline phases, C^{α} and C^{β}. HOBA, consisting of longer molecules, exhibited a nematic mesophase. DOBA showed a nematic and a smectic C mesophase. A crystalline phase transition was observed below 80 °C in X-ray measurements. The transition was very slow, which we attributed to impurities (10). As a consequence, the crystalline phase transition of the DOBA was only indirectly revealed by differential scanning calorimetry (DSC): the enthalpy of melting upon cooling was lesser by 12.4 kJ/mol than upon first heating. This decrease implied that in the heating run the crystalline phase transition occurred at the melting temperature and was supercooled below 0 °C in the cooling run. The transition did not occur during the second heating, as the enthalpy of melting was in good agreement with the one for cooling.

Methods

Eleven mixtures were prepared for the MBOBA–HOBA system and nine for the MBOBA–DOBA system by codissolving various amounts of the components in warm ethanol. The solvent was allowed to evaporate over a period of one to two weeks after the solutions had cooled to room temperature.

Transition temperatures were determined with a PerkinElmer DSC7. Samples were prepared by weighing 4–6 mg of a mixture into an aluminum pan and then sealing it. Every sample was heated, cooled, and heated again at a rate of 5° min^{-1}.

Mesophases were identified using an Olympus BH-2 polarized-light microscope with a Linkam THM600 hot stage. The crystalline regions were investigated with an Anton Paar Kratky Compact Small Angle System with a KH-R sample heater. Samples were prepared by melting a small amount (about 2 mg) of a mixture on a microscope slide and driving it by capillary action into a quartz capillary, where it recrystallized on cooling.

Crystals of the mixture 65 mol% HOBA in MBOBA, as obtained from solution, were investigated with an in-house flat-film camera equipped with an FP82-Mettler hot stage.

Single crystals suitable for X-ray investigations were obtained by slow crystallization. The data collections was performed on a CAD4 single-crystal diffractometer with Mo K α radiation and the MolEN package (Enraf Nonius, Delft) (11), and (or) the Shelxl-93 program (12) was used for data processing and refinement. The starting models were obtained by SIR97 (13). Here, we concentrate on the conformation and packing arrangement of the molecules only. A full description and discussion of the data will be published elsewhere. The drawings were obtained with SCHAKAL-92 (14).

Results and discussion

Crystal structures

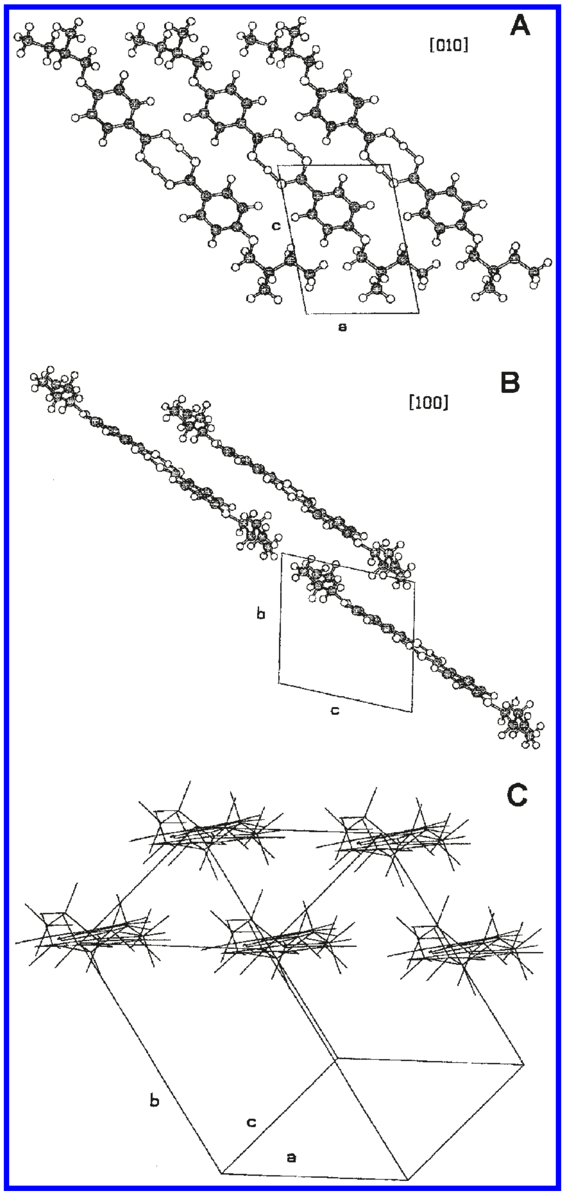
Almost all benzoic acids, composed of single non-chiral compounds and forming dimers by hydrogen bonds, crystallize in centric space groups with an inversion center between the carbonyl groups (15, 16). However, a 1:1 mixture of two different benzoic acids is devoid of the inversion center and an acentric space group can describe the crystal structure (16) with consequences for the chirality of the liquid-crystalline phases (17).

MBOBA and four benzoic acids with a linear group attached in 4-position of the benzyl ring, namely 4-(but-3-enoxy)benzoic acid (BOBA), 4-(pent-4-enoxy)benzoic acid (POBA), 4-(dec-9-enoxy)benzoic acid (DOBA), and 4-(undec-10-enoxy)benzoic acid (UOBA), have been investigated by single crystal analysis to get insight into the conformation and packing arrangements of these molecules, which are important for a discussion of the liquid crystal phases observed. All five compounds are arranged in antiparallel fashion to compensate the strong dipoles of the molecules and form dimers. They have in common a similar distance of the two C–O bonds of the carbonyl group of which both oxygens are involved in hydrogen bonds and a gauche position of the alkoxy segment of the linear substituent.

The chiral MBOBA crystallizes in the enantiomorphous space group *P*1 and projections representing the conformation and packing arrangement are shown in Fig. 1. The dimer formations are revealed. Both molecules forming the asymmetric unit have similar conformations. The carbon atom of the methyl branch of the substituent lies in plane with the preceding carbon atoms and oxygen, while the alkoxy segment of the linear group is placed in gauche position involving the oxygen attached to the benzene ring. The molecules are placed in a tilted direction in the unit cell, which means that the length of the molecule, which amounts to 12.2 Å, does not agree with the longest unit-cell axis of *c* = 9.4 Å. The molecules pack in planes with the benzene rings lying flat in these planes and they are staggered (Figs. 1A, 1B, 1C).

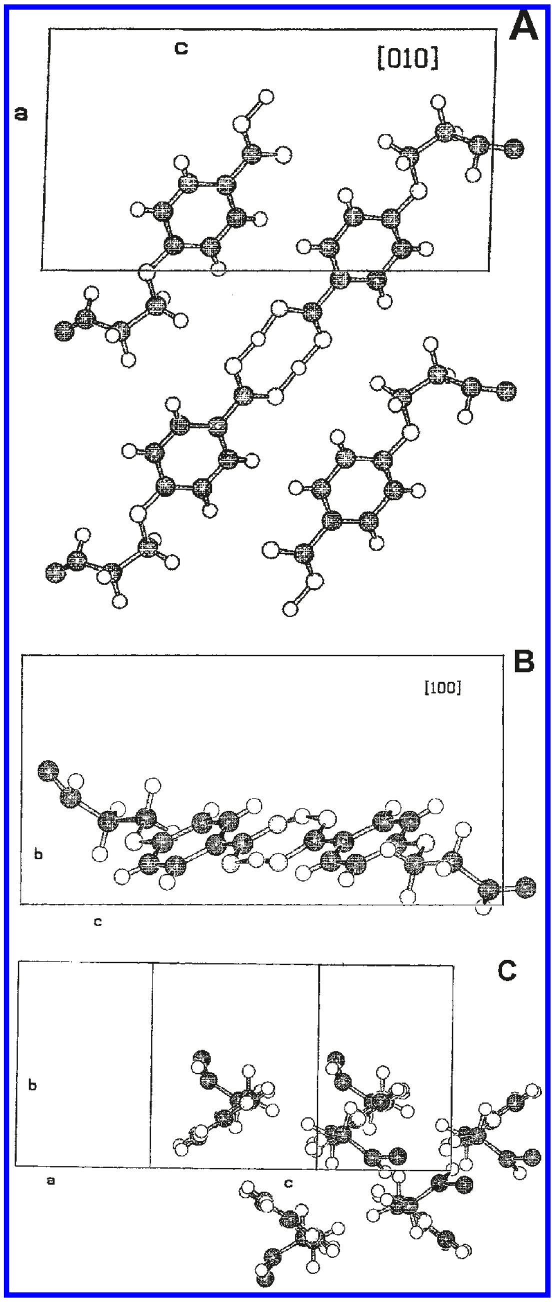
BOBA crystallizes in the acentric space group *Pa* with two antiparallel molecules in the asymmetric unit, unique axis *b* (Fig. 2). Although the torsion angles of the alkoxy segment have reversed signs, as expected for centrosymmetric arrangements, the torsion angle of the terminal atom does not follow this reversal, and two distinct different molecules form the dimer and cannot crystallize in a centric space group with an inversion center between the carboxyl groups of the dimers. Here, the dimer is tilted in the *a*–*c* plane, and the length of the dimer of ~20 Å is also longer compared with the largest unit-cell parameter *c* = 14.9 Å. According to our experience, the centric or acentric packing of molecules in the crystalline state may also lead to different kinds of arrangement in the liquid-crystalline state.

Fig. 1. Representation of 4-[(*S*)-(–)-2-methylbutoxy]benzoic acid (MBOBA), which crystallizes in the triclinic two-molecule acentric space group *P*1 in three projections. (A) Projection in [010] direction on the *a*–*c* plane showing the formation of dimers through hydrogen bonding. (B) Projection in [100] direction on the *b*–c plane showing the continuous rod formation. (C) Projection along the continuous rods showing the relative packing arrangement of the molecules.



Surprisingly, the space group of crystalline POBA is $P2_1$, unique axis *b*, which belongs to the optically active space groups and the ones, which may exhibit second-order nonlinear properties. The packing arrangement of the dimers formed is represented in Fig. 3 in two projections. Two antiparallel molecules form the asymmetric unit, which by application of a 2_1 screw axis lead to the four molecules within the unit cell. The molecular axes are placed almost perpendicular to the screw axis *b* in contrast to DOBA, to be discussed. The overall arrangement of POBA resembles the one of BOBA. The length of the dimers amounts to 26.8 Å and is much longer than the *c* parameter of the unit cell with 15.4 Å. Here, a the tilt is observed in the *a*–*c* plane. If mesophases are formed, they are expected to be chiral.

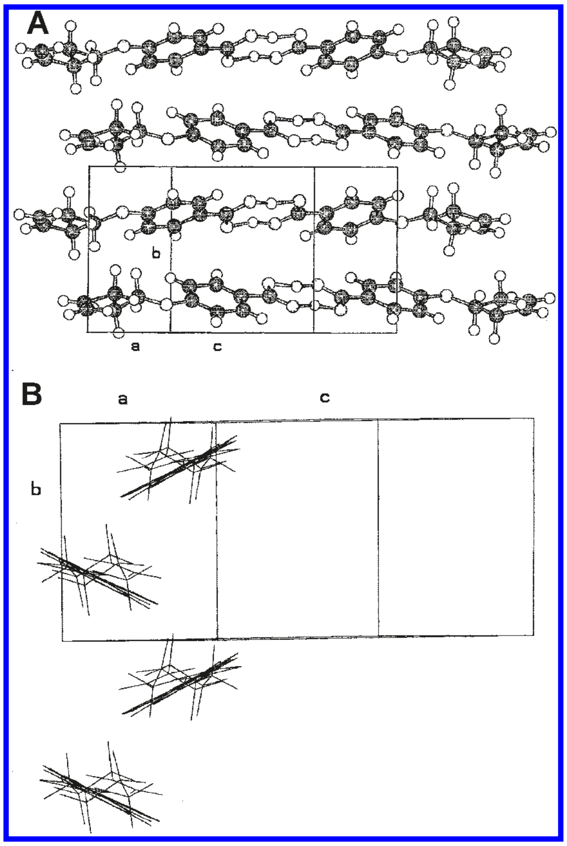
Fig. 2. Representation of 4-(but-3-enoxy)benzoic acid (BOBA), which crystallizes in the monoclinic four-molecule unit cell of the acentric space group *Pa* in three projections. (A) Projection in [010] direction on the *a*–*c* plane showing the formation of dimers through hydrogen bonding. (B) Projection in [100] direction on the *b*–*c* plane showing the overlapping molecules of the plane represented in A. (C) Projection in rod direction showing the lateral packing arrangement of the molecules. The hydrogen atoms at the terminal carbon could not be localized.



In contrast, centric space groups are found for longer linear chains attached in the 4-position on the benzene ring of benzoic acids as DOBA and UOBA. But again the packing arrangement differs for these two compounds.

UOBA crystallizes in the triclinic space group *P*-1. The unit cell contains two molecules, which are connected by an inversion symmetry element, thus forming the expected dimer through hydrogen bonds as in almost all benzoic acids (Fig. 4). The gauche conformation of the alkoxy segment forces a change of direction between the central part of the dimer and the linear chain, which exhibits an almost trans conformation. A chain length is difficult to define and amounts to 39.3 Å between the two terminal groups of the dimer and differs considerably, if this length is calculated with a trans conformation of the alkoxy segment.

Fig. 3. Representation of 4-(pent-4-enoxy)benzoic acid (POBA), which crystallizes in the monoclinic four molecule unit cell of the acentric space group $P2_1$ (*b* unique axis) in two projections. (A) Projection showing the formation of dimers through hydrogen bonding. (B) Projection in rod direction showing the lateral packing arrangement of the molecules.



A similar conformation for the single molecule is found for DOBA as compared to UOBA, but the packing arrangement in the crystalline state differs considerably as shown in Fig. 5. The long dimension *c* is almost doubled due to the centric space group $P2_1/n$, c = 41.51 Å for DOBA and *P*-1 with 22.34 Å for UOBA. The unit cell of DOBA has to accommodate two succeeding molecules related by a 2_1 screw axis, which changes the direction of the central part of the dimer in space. Nevertheless, quite similar dimensions of the unit cell are found for the lateral packing of the molecules for DOBA and UOBA. A single molecule represents the asymmetric unit in both structures. A distance between the terminal hydrogen of 32.8 Å was determined for the dimer of DOBA as compared with 39.3 Å for UOBA, and both lengths deviate from a trans conformation of the alkenoxy substituent.

The crystal and molecular structures of the four homologous achiral benzoic acids show a broad variation of possible

Fig. 4. Representation of 4-(undec-10-enoxy)benzoic acid (UOBA), which crystallizes in the triclinic two-molecule unit cell of the centric space group *P*-1 in two projections. (A) Projection in [100] direction on the *b*–*c* plane showing the formation of dimers through hydrogen bonding. (B) Projection in [010] direction on the *a*–*c* plane showing the relative packing arrangement of the molecules.

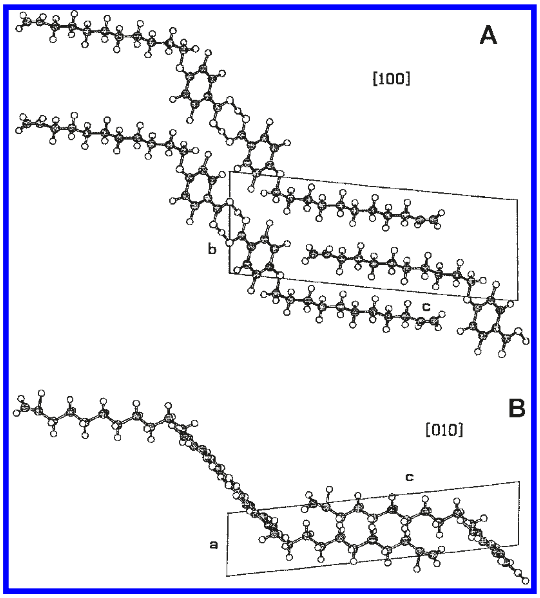


Fig. 5. Representation of 4-(dec-9-enoxy)benzoic acid (DOBA), which crystallizes in the monoclinic four-molecule unit cell of the centric space group $P2_1/n$ (*b* unique axis) in two projections. (A) Projection in [100] direction on the *b*–*c* plane showing the formation of dimers through hydrogen bonding. (B) Projection in [001] direction on the *a*–*b* plane representing the lateral packing arrangement of the molecules.

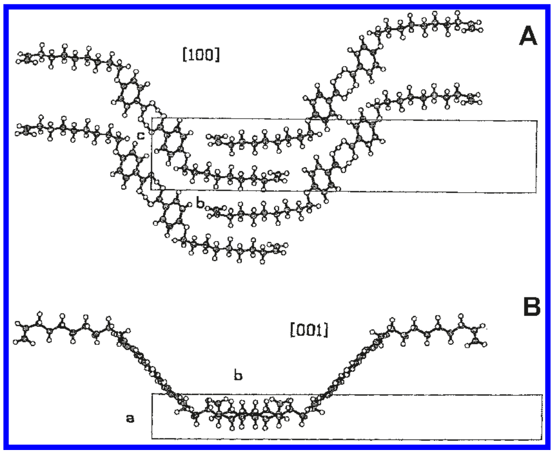
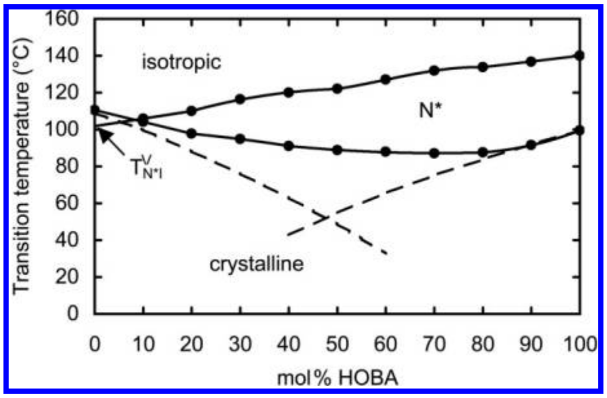


Fig. 6. Crystalline-cholesteric and cholesteric–isotropic transition line for the MBOBA–HOBA system (peak temperatures of the first DSC heating run); T^{V}_{N*I}: virtual cholesteric–isotropic transition temperature (– – –): theoretical melting curves for a eutectic system.



low energy states, which may lead to a variety of arrangements of molecules in the liquid-crystalline state. Moreover, chiral molecules are created when the chiral MBOBA forms dimers with achiral benzoic acid homologues regardless of the conformation of the achiral partner.

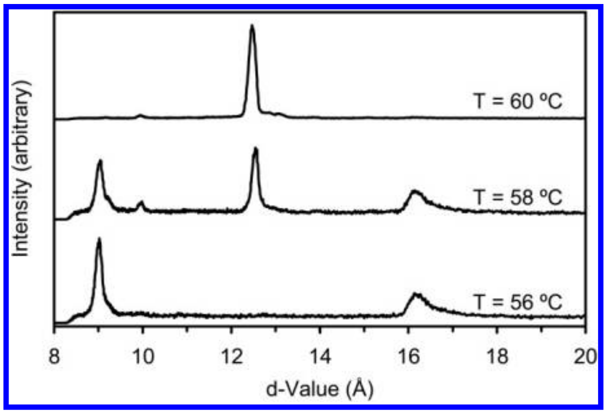
MBOBA–HOBA system

All MBOBA–HOBA mixtures were liquid-crystalline (Fig. 6). The only mesophase upon heating revealed an “oily streak” texture in the polarized-light microscope, which is characteristic of the cholesteric phase. As anticipated, the nematic molecular arrangement was twisted by the chiral MBOBA molecules and became cholesteric. The fact that 10 mol% of HOBA was enough to induce a mesophase indicated the expected tendency of MBOBA to show liquid-crystallinity. In accordance, extrapolation of the cholesteric–isotropic transition line to 100 mol% MBOBA gave a value of 101.8 °C for the acid’s virtual cholesteric–isotropic transition temperature (T^{V}_{N*I}). This value defines how disruptive the non-mesomorphic compound is towards the mesophase (18). Since the value was close to the melting point of 110.5 °C, the disruptive effect of MBOBA, due to the methyl branch of the substituent group, on the nematic molecular arrangement was small.

The melting curve indicated that the MBOBA–HOBA system was not eutectic. To elucidate the deviation from eutectic behavior, we calculated eutectic melting curves (Fig. 6) on a thermodynamic basis using the Schroeder–vanLaar equations (19, 20). The observed melting temperatures were notably higher than the theoretical temperatures for the mixtures with 20 to 70 mol% HOBA, which suggested solid-solubility of the two components or the formation of phases of mixed dimers. To identify the cause for the thermal stability of the crystalline region, we investigated the mixtures at different temperatures below their melting temperatures by X-ray diffraction. Below 58 °C two crystalline phases (C_A^{α} and C_B) were found, represented by different reflections in the diffraction patterns (Fig. 7). The C_A^{α} phase was formed by mixtures containing less than 80 mol% HOBA (Fig. 8). It had a characteristic *d* value equal to the *d* value of MBOBA and was therefore most likely a solid solution of HOBA in MBOBA. The C_B phase was formed by mixtures with more than 65 mol% HOBA and had a *d* value equal to that of HOBA. In this phase, MBOBA molecules or dimers are probably incorporated into the HOBA crystal lattice. In the mixtures with 65 to 80 mol% HOBA, the two phases, C_A^{α} and C_B, coexisted.

The high-temperature crystalline phase of the MBOBA, C_A^{β}, was found only in the mixtures with a HOBA content less than 20 mol%. For the mixtures containing 40 to 80 mol% HOBA an additional phase (C_{AB}) was found above

Fig. 7. X-ray diffraction patterns of 70 mol% HOBA in MBOBA.



58 °C. The characteristic *d* value (d = 12.5 Å) lay between the *d* values of C_A^α and C_B and thus indicated the formation of mixed dimers. The *d* value of MBOBA amounts to ~9 Å that of HOBA to ~16 Å. In the crystalline state, the molecular length of the monomer does not correlate with the *d* spacing obtained by X-ray diffraction due to possible tilted positions within the unit cell. The *d* value of MBOBA is confirmed by the longest *d* spacing derived from the unit cell (d = 9.12 Å). The length of the mixed dimer was calculated to 27.4 Å as opposed to 24.2 and 30.2 Å for the pure MBOBA and HOBA dimers (Table 1). The *d* value increased slightly with increasing temperature to d = 12.6 Å before melting. The phase transition from the two-phase region into the high-temperature phase was clearly evident at 58 °C in X-ray experiments (Fig. 7).

To assure that this high-temperature phase was not a more highly ordered liquid-crystalline phase, we investigated the mixture with 65 mol% HOBA above 70 °C by polarized-light microscopy. We did not observe any fluidity. A flat-film X-ray diffraction pattern of the same mixture, taken at 80 °C, showed discrete Bragg maxima indicating the presence of small crystalline domains. We concluded that this was not a smectic phase of higher order but a fourth crystalline phase dominated by mixed dimers.

The C_A^α–C_{AB} or C_B–C_{AB} phase transitions, respectively, in the mixtures with 40 to 90 mol% HOBA were also revealed in DSC measurements as shown for 50 mol% HOBA in MBOBA in Fig. 9. In most mixtures, the transition occurred just below or at the melting temperature in the first heating run and was strongly supercooled in the cooling run. The shift of the crystalline transition to lower temperatures upon cooling differed for the different mixtures. At 40, 50, and 90 mol% HOBA in MBOBA, the transition was supercooled by about 15 °C, 40 °C (Fig. 9), and 50 °C, respectively. In the mixtures with 60, 70, and 80 mol% HOBA, the transition was supercooled below 0 °C and thus not seen in the cooling trace. It occurred in both directions (exotherm and endotherm) during the second heating run for the mixture with 60 mol% HOBA, but the mixtures with 70 and 80 mol% HOBA did not show the transition upon second heating. The different thermal behavior upon cooling reflected that the transition in the mixtures with 40, 50, 60, and 90 mol% HOBA was into a one-phase region; whereas it was into a two-phase region in the mixtures with 70 and 80 mol%. In the latter case, the molecules had to arrange from one crystal lattice into two different crystal lattices.

Fig. 8. Crystalline phase diagram of the MBOBA–HOBA system (temperatures from X-ray diffraction measurements).

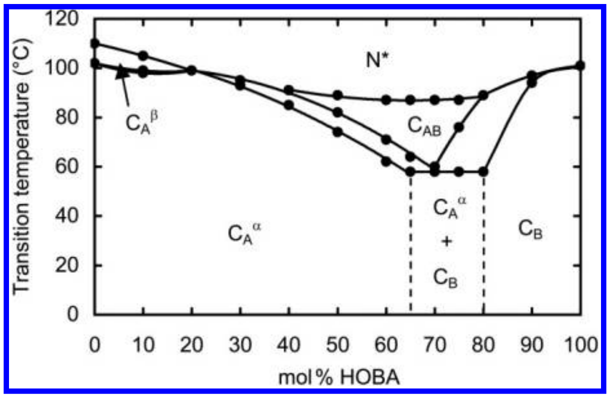
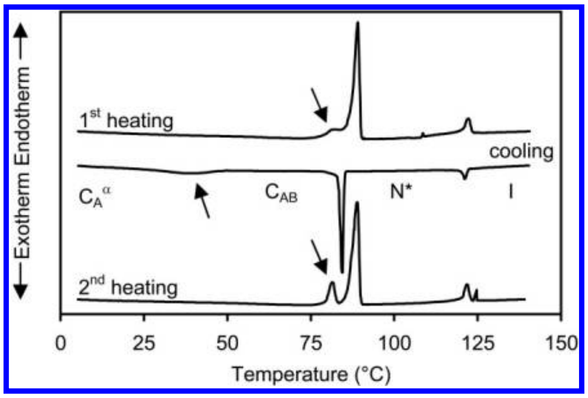


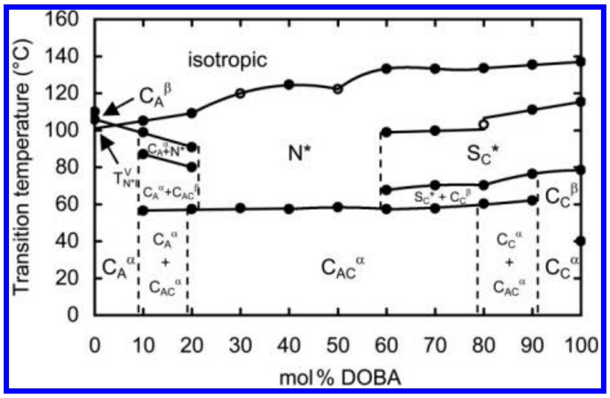
Fig. 9. DSC traces of 50 mol% HOBA in MBOBA; the arrows indicate the C_A^α–C_{AB} phase transition.



MBOBA–DOBA system

As in the MBOBA–HOBA system, all mixtures exhibited a cholesteric mesophase (Fig. 10). The cholesteric–isotropic transition temperature of the mixture 10 mol% DOBA in MBOBA was 105.1 °C as opposed to 105.9 °C for 10 mol% HOBA in MBOBA, reflecting that the molecular arrangement of the cholesteric phase was only weakly affected by the greater difference in molecular lengths of the components. The cholesteric–isotropic transition line, however, was not as smooth as in the case of the MBOBA–HOBA system. It was straight at the extremes of the composition range and had a local minimum at the composition with a one-to-one ratio of the components. The shape of the cholesteric–isotropic transition line indicated that the cholesteric phase at DOBA contents less than 20 and more than 80 mol% was dominated by pure MBOBA or DOBA dimers, respectively, but that mixed dimers dominated at DOBA contents in between. This conclusion was supported by microscopy results: the textures observed for the cholesteric phase on heating were “oily streak” textures for all mixtures; on cooling, the mixtures with a DOBA content less than 70 mol% showed fan textures; whereas the mixtures with 80 and 90 mol% DOBA showed textures of a cholesteric phase with greater pitch.

Fig. 10. Phase diagram of the MBOBA–DOBA system (peak temperatures of the first DSC heating run); DSC transition peak has a shoulder (◦).



The low thermal stability at 50 mol% DOBA in MBOBA was attributed to the structural difference of the substituent groups of the components. The linear decenoxy group of DOBA allowed a narrower molecular arrangement than the branched 2-methylbutoxy group of MBOBA. The DSC thermogram of the mixture 50 mol% DOBA in MBOBA showed a shoulder peak for the cholesteric–isotropic transition, which implied that the cholesteric phase of this mixture is not homogeneous. It might separate into domains with differently tight molecular arrangements.

The mixtures that contained more than 50 mol% DOBA exhibited a twisted smectic C phase. In the polarized-light microscope the phase appeared in form of a fine Schlieren texture.

To determine whether this phase contained mixed dimers, we analyzed the mixtures by X-ray diffraction at temperatures between their melting points and S_C*–N* transition temperatures. The temperature dependence of the *d* value was similar in all mixtures (Fig. 11*a*) and the absolute value increased with increasing DOBA content (Fig. 11*b*). The increase in *d* value was linear with a discontinuity and change in slope at 80 mol% DOBA. In comparison the longest *d* value calculated from the size of the unit cell depicted in Fig. 5 with interdigitated molecules of DOBA amounts to *d* = 20.82 Å. We concluded that similar to the cholesteric phase, the twisted smectic *C* phase at a DOBA content less than 80 mol% was dominated by mixed dimers, but pure DOBA dimers dominated at a DOBA content higher than 80 mol%. This conclusion was supported by DSC results, which revealed a shoulder peak for the S_C*–N* transition at 80 mol% DOBA in MBOBA, indicating that the S_C* phase in this mixture was not homogenous. The mixed dimers with a length of 28.9 Å did not form a smectic phase on their own. The smectic phase in the mixtures with 60 and 70 mol% DOBA was induced by the dimers of excess DOBA molecules.

At 58 °C, the mixtures with 10 and 20 mol% DOBA showed a phase transition into another mixed phase (C^β_{AC}, Fig. 10). This phase must have a slightly different composition (higher DOBA content), since the crystalline phase of the MBOBA is formed simultaneously with it.

Fig. 11. *d* Values of the smectic *C* phases at different MBOBA–DOBA compositions: (*a*) as a function of temperature (numbers indicate DOBA content in mol%), (*b*) at the smectic–nematic transition temperatures.

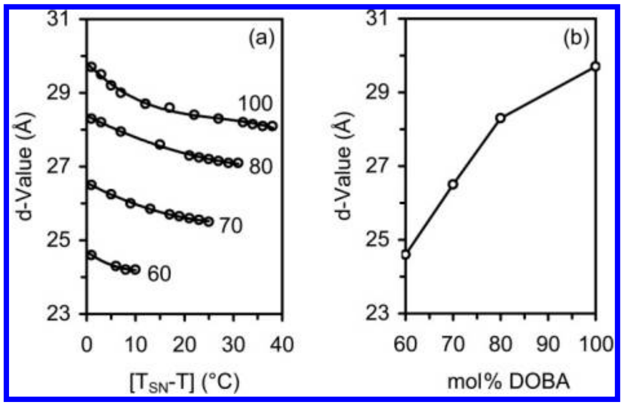


Table 2. *d* Values of the crystalline phases of the MBOBA–DOBA mixtures (at 30 °C for the α-phases and at the temperature of the phase transition for the β-phases).

DOBA content mol%	*d* Value (Å)					
	C^α_A	C^β_A	C^α_{AC}	C^β_{AC}	C^α_C	C^β_C
0	8.7	14.6				
10	8.8		14.6	19.2		
20	8.8[a]		15.1	16.2		
30[b]						
40			17.2			
50			19.8			
60			20.8			25
70			21.7			25.6
80			22.1		23.9	25.9
90[a]						
100					24.1	25.2

[a] Appeared at ~57 °C upon heating.
[b] Values not available.

With respect to the crystalline region, X-ray diffraction gave a variety of *d* values (Table 2). We were able to distinguish at least six different crystalline phases. The two phases at the extremes of the composition range (C_A and C_C, Fig. 10) were most likely the crystalline phases of the pure components with a low- and a high-temperature modification (α and β). The C^α_{AC} phase presumably contained different amounts of mixed dimers in the different mixtures, as the *d* value varied with composition. Most of the mixtures (30 to 90 mol% DOBA in MBOBA) melted at about 58 °C. The mixtures with 60 to 90 mol% DOBA separated above 60 °C into a S_C* phase and the high-temperature crystalline phase of DOBA. On melting, the *d* value of the smectic phase showed a distinct shift to higher values, which reflected increasing incorporation of DOBA molecules into the smectic molecular arrangement.

Conclusions

A variety of shapes and packing arrangements was found for crystalline 4-substituted benzoic acids. Achiral pure compounds with longer substituents attached crystallize in acentric and with shorter substituents in centric crystal structures with dimers formed by hydrogen bonding. The symmetry elements present in the crystalline state also influence the kind of arrangements in liquid crystals.

Regarding the crystalline phases in the mixed systems, the formation of mixed dimers was found to be promoted by a greater difference in molecular structure. The system with the more structurally similar components, the MBOBA–HOBA system, exhibited a crystalline phase of mixed dimers at compositions between 40 and 80 mol% HOBA and temperatures above 58 °C. The system with the greater structural difference in components (the MBOBA–DOBA system) showed crystalline phases containing mixed dimers at room temperature and for all compositions. A greater difference in molecular structure led to a decrease in solubility. Due to the tendency of these systems to form mixed dimers, the region in which mixed dimers were found was enlarged, as opposed to enlarging the region where two crystalline phases coexisted.

The liquid-crystalline phases were found to be dominated by mixed dimers at compositions in the midrange. At the extremes of the composition range, pure dimers dominated the liquid-crystalline phases. Concerning the cholesteric phase, mixed-dimer formation in the composition midrange was indicated by the shape of the cholesteric–isotropic transition line and was more obvious for the system with the more structurally different components. Regarding the twisted smectic *C* phase, the change from mixed-dimer prevalence to pure-dimer prevalence with composition was evident by a discontinuity in the increase of the *d* value with increasing DOBA content.

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