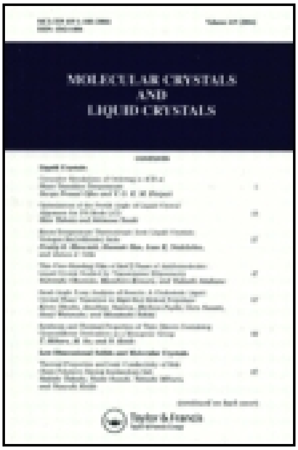

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Liquid Crystalline Primary Benzamides†

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Several alkoxybenzamides are synthesized and characterized by spectroscopic and chromatographic methods. 3,4,5-Tris(alkoxy)benzamides have been found to exhibit a mesophase of a columnar or stack-like type.

Keywords: liquid crystals, columnar phases, 3,4,5-Tris(alkoxylbenzamides, primary benzamides, hydrogen bonding

INTRODUCTION

Intermolecular hydrogen bonding is known to play an important role in the formation of liquid crystalline phases of carboxylic acids and of a large number of amphiphilic polyhydroxy compounds.[1–9] Mesogens, containing secondary and tertiary amide groups have been known for a long time.[10–17] Until now, primary mesogenic benzamides have not been described in the literature.

Simple benzamides are able to form networks of hydrogen bonds.[18–20] Their crystalline phases are stabilized to such an extent that the appearance of mesophases is not possible. However, it is known, that terminal substituents, e.g., alkoxy chains can create liquid crystal formation.[21] Therefore, it seemed possible to find new mesogens by attaching alkoxy chains to the aromatic core of benzamide.

SYNTHESIZED COMPOUNDS

Different alkoxybenzamides, Figure 1, were synthesized by adding aqueous ammonia (**I–VI**), or aqueous methylamine (**VII**) to a solution of the corresponding carbonic acid chlorides[22] in 1,4-dioxane. The products were purified by recrystallization twice from ethanol and subsequent column chromatography (silica gel, hexane/ethyl acetate). The characterization was performed by means of IR, NMR, MS, GPC and elemental analysis.

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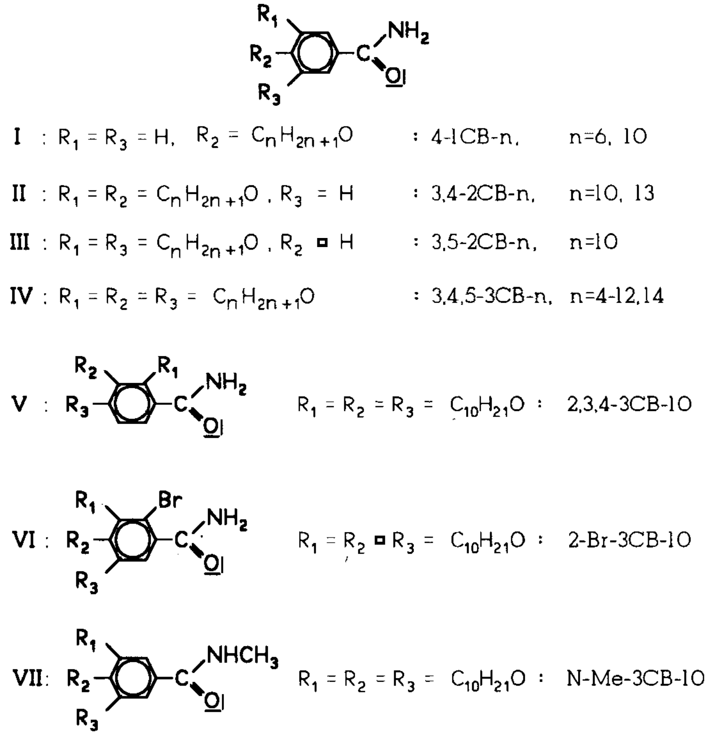

I : $R_1 = R_3 = H$, $R_2 = C_nH_{2n+1}O$: 4-1CB-n, n=6, 10

II : $R_1 = R_2 = C_nH_{2n+1}O$, $R_3 = H$: 3,4-2CB-n, n=10, 13

III : $R_1 = R_3 = C_nH_{2n+1}O$, R_2 □ H : 3,5-2CB-n, n=10

IV : $R_1 = R_2 = R_3 = C_nH_{2n+1}O$: 3,4,5-3CB-n, n=4-12,14

V : $R_1 = R_2 = R_3 = C_{10}H_{21}O$: 2,3,4-3CB-10

VI : $R_1 = R_2$ □ $R_3 = C_{10}H_{21}O$: 2-Br-3CB-10

VII: $R_1 = R_2 = R_3 = C_{10}H_{21}O$: N-Me-3CB-10

FIGURE 1 Synthesized alkoxybenzamides.

THERMAL INVESTIGATIONS

The thermal behaviour of all compounds was investigated by polarizing microscopy and that of the mesogens additionally by DSC measurements.

I (*n* = 6, 10), **II** (*n* = 10, 13), **IV** (*n* = 4), **V** (*n* = 10), **VI** (*n* = 10) and **VII** (*n* = 10) do not show liquid crystalline properties. **III** (*n* = 10) and **IV** (*n* = 5–6) exhibit a monotropic, **IV** (*n* = 7–12, 14) an enantiotropic mesophase. The mesophases of **III** and **IV** are identical, as can be verified by miscibility experiments.

The transition temperatures and transition enthalpies of **I–III** and **V–VII** are summarized in Table I, the corresponding values for **IV** ("three chain benzamides," 3CB-n) are given in Table II.

The clearing enthalpy and entropy values of compounds **IV** (Table II) are rather high (ΔH_c = 4.9–6.9 kJ/mol, ΔS_c = 13.6–20.0 J/Kmol). This indicates a highly ordered mesophase type, probably containing aggregated species. The compounds with chain length *n* = 7 and *n* = 8 show the highest values for both the clearing temperatures and the clearing enthalpy.

OPTICAL TEXTURES OF THE MESOPHASE

The "three chain benzamides," 3CB-n with short chains (*n* = 5–9) show spherolithic (pseudo focal conic) textures, while 3CB-n with long chains exhibit broken textures (Figure 2).

TABLE I

Transition temperatures and transition enthalpies of compounds **I**, **II**, **III**, **V**, **VI** and **VII**

	Compound	K		M		I
I	4-1CB-6	●	153 (32.5)			●
	4-1CB-10	●	149 (37.2)			●
II	3,4-2CB-10	●	154 ---(a)			●
	3,4-2CB-13	●	152 (72.1)			●
III	3,5-2CB-10	●	86 (61.5)	●	[67 (1.8)]	●
V	2,3,4-3CB-10	●	45 (63.7)			●
VI	2-Br-3CB-10	●	134 (38.0)			●
VII	N-Me-3CB-10	●	63 (38.0)			●

Values in brackets: transition enthalpy in kJ/mol; transition temperatures in °C; [···] monotropic phase; heating rate: 10 K/min. (a) not determined

TABLE II

Transition temperatures and transition enthalpies of 3,4,5-tris(alkoxy)benzamides (3CB-n)

3CB-n	K		M		I
4	●	117 (20.2)			●
5	●	90 (26.9)	●	[88 (4.4)]	●
6	●	94 (28.1)	●	[87 (4.9)]	●
7	●	80 (17.9)(a)	●	89 (6.1)	●
8	●	82 (43)(a)	●	89 (6.8)	●
9	●	81 (37.9)(a)	●	88 (6.6)	●
10	●	58 (9.8)	●	85 (6.1)	●
11	●	57 (14.3)	●	81 (6.0)	●
12	●	58 (26.4)	●	81 (5.7)	●
14	●	79 (14.2)	●	80 (5.7)	●

Values in brackets: transition enthalpy in kJ/mol; transition temperatures in °C; [···] monotropic phase; heating rate: 10 K/min; (a) only on first heating

From these textures, a mesophase of a columnar or stack-like type can be deduced.

X-ray investigations on the mesophase structure are in progress and will be described in a subsequent paper.

According to the crystal structure of benzamide[18] it seems evident that the mesogenic unities are formed by dimerization via hydrogen bonding (Figure 3).

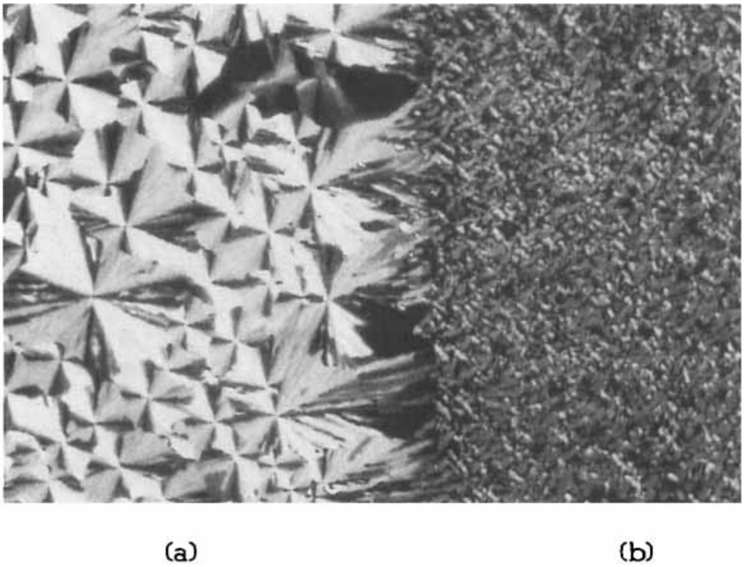

FIGURE 2 Optical textures of 3CB-n (contact preparation of 3CB-7 and 3CB-10 at 79°C). (a) 3CB-7: spherolithic texture and (b) 3CB-10: broken texture. See Color Plate XI.

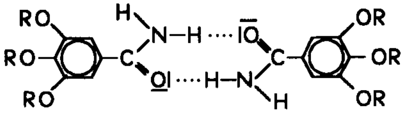

FIGURE 3 Hydrogen bonded cyclic 3CB-dimer.

Furthermore, since amide groups are known to be tilted against the plane of the aromatic core,[20] not only *intra*dimeric but also *inter*dimeric hydrogen bonding occurs, stabilizing the columnar order. The existence of interdimeric hydrogen bonding is supported by the following experimental results:

The intensity of the N-H stretching vibrations at 3360 cm^{-1}, $\nu_{as}(NH_2)$, and 3195 cm^{-1}, $\nu_{sy}(NH_2)$, decreases drastically at the clearing temperature, indicating the loss of ca. 50% of the hydrogen bonds. Presumably, the columns disintegrate into their dimeric components, which dissociate to the single amide molecules only at much higher temperatures.

The "three chain benzamides" are very sensitive towards variations of the environment of the amidic head group. Bromination in the aromatic 2-position (**VI**) or synthesis of the isomeric 2,3,4-tris (alkoxy)benzamides (**V**) results in the loss of mesomorphism, apparently due to steric hindrance of the interdimeric hydrogen bonding. The same can be observed after N-methylation of 3CB (**VII**).

The proposed system of hydrogen bonds in the mesophase of "three chain benzamides" is similar to the crystal structure of benzamide itself. There, the molecules are connected by two sorts of N—H···O type hydrogen bonds, the first set joining pairs of molecules to form dimers, and the second set joining such dimers into endless chains extended along one crystallographic axis.[18]

The necessity of interdimeric interaction to produce stable columns is shown by the phase behaviour of the analogous alkoxybenzoic acids: 3,4,5-tris(alkoxy)benzoic acids do not exhibit any mesomorphism despite their ability to form dimers.

CONCLUSION

Monoalkyl substituted benzoic acids are denominated as the "most simple liquid crystalline compounds" with respect to calamitic structures.[23] Likewise the described primary benzamides are the *most simple molecules, which form columnar or stack-like mesophases.*

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