Liquid Crystalline Piperazine and Triazacyclononane Derivatives

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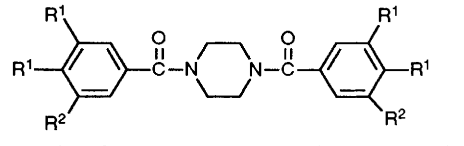
Mesogenic amide and ammonium derivatives of piperazine and triazacyclononane are described.

In the recent past, the mesophase behaviour of azamacrocyclic derivatives has become of considerable interest. Alkoxybenzoyl substituted hexacyclene or larger heterocyclic cores,[1–7] and also cyclam, 1,5,9-triazacyclododecane, and 1,4,7-triazacyclononane derivatives[7,8] have been synthesized. Hexacyclene derivatives with other substituents have also been reported.[6,9]

We wanted to know how the thermal behaviour would be influenced by varying some structural parameters of related molecules and so we synthesized several compounds with rigid benzamide groups. After reduction of selected examples to derivatives with benzylamine moieties, the mesophase behaviour of the corresponding ammonium salts was investigated.

The piperazine derivatives **1a** and **1b** are monotropic liquid crystalline, with a transition from the isotropic melt to the mesophase at 15 °C ($\Delta H = -3.4$ kJ mol^{-1}) and 20 °C ($\Delta H = -3.7$ kJ mol^{-1}) respectively. The melting points of the highest crystalline phases are 60.5 °C ($\Delta H = 98.3$ kJ mol^{-1}) in the case of **1a** and 58.5 °C ($\Delta H = 102.48$ kJ mol^{-1}) in the case of **1b**. No mesophase could be detected for compound **1c**. An elongation of the alkoxy side chains apparently causes the disappearance of the mesophase by the occurrence of a new crystalline phase with increased transition temperatures. The textures of **1a** and **1b**, observed under a polarizing microscope, show pronounced pseudo-focal conics [Fig. 1(*a*)], typical for columnar structures.



1a; $R^1 = R^2 = OC_{10}H_{21}$
b; $R^1 = R^2 = OC_{12}H_{25}$
c; $R^1 = R^2 = OC_{14}H_{29}$

2; $R^1 = OC_{10}H_{21}$, $R^2 = H$

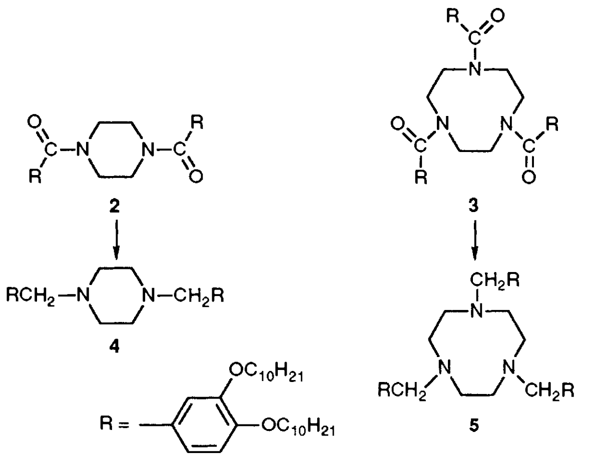
For compound **2**, differential scanning calorimetry (DSC) measurements and polarizing microscopy established a monotropic behaviour too. On cooling from the isotropic melt a mesophase appeared at 44.5 °C ($\Delta H = -3.04$ kJ mol^{-1}). The melting point of the crystalline phase is 102 °C. The texture is mostly homeotropic, indicating a non-columnar but smectic mesophase structure.

X-Ray measurements could not be performed on either group of compounds **1** or **2** because their recrystallization hindered these experiments.

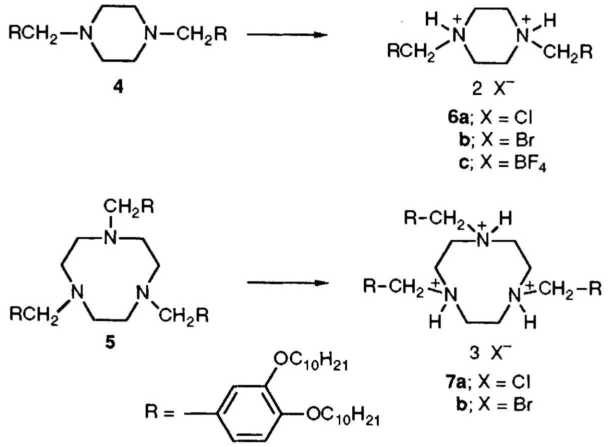
In view of their molecular structure, compounds **1** and **2** seem to belong to the class of polycatenated compounds. To our knowledge, three-ring polycatenated compounds normally do not exhibit mesophases,[9] with the exception of the monotropic nematic behaviour of some bis-imines.[10] As known from phasmidic compounds,[9] the enhanced flexibility of the core, caused by the piperazine ring, seems to favour the columnar structure of the mesophase of compounds **1**.

In order to check the importance of the rigid benzamide group with respect to mesophase formation, we reduced[12] compound **2** and the triazacyclononane ([9]aneN_3) derivative **3** to the corresponding products **4** and **5** (Scheme 1). The consequence was that the monotropic mesophases of **2** and the enantiotropic mesophase of **3**[7] disappeared. Compound **4** exhibited only a melting point at 77 °C ($\Delta H = 102.16$ kJ mol^{-1}), and compound **5** at 41.5 °C ($\Delta H = 69.29$ kJ mol^{-1}).

Some discoidal multivalent cations are known to form lyotropic mesophases in water,[13] whereas thermotropic liquid crystallinity has been reported for several ammonium salts with one larger alkyl chain.[14–16] Therefore, we were interested in



Scheme 1



Scheme 2 *Conditions*: tetrahydrofuran, + conc. HX, 30 min, room temp.

Table 1 Transition temperatures (in °C) of compounds **6a–c** (ΔH in kJ mol^{-1} in parentheses)

Compound	K_1		K_2		K_3		M		I
6a	●	75.5 (10.81)	●	170.5 (54.97)	●	187.0 (24.82)	●	202.5 (2.32)	●
6b	●	67.5 (9.77)	●	143.5 (35.48)	●	178.5 (24.31)	●	193.5 (2.49)	●
6c			●	150.0 (36.78)	●	170.0 (56.54)	●	183.5 (1.55)	●

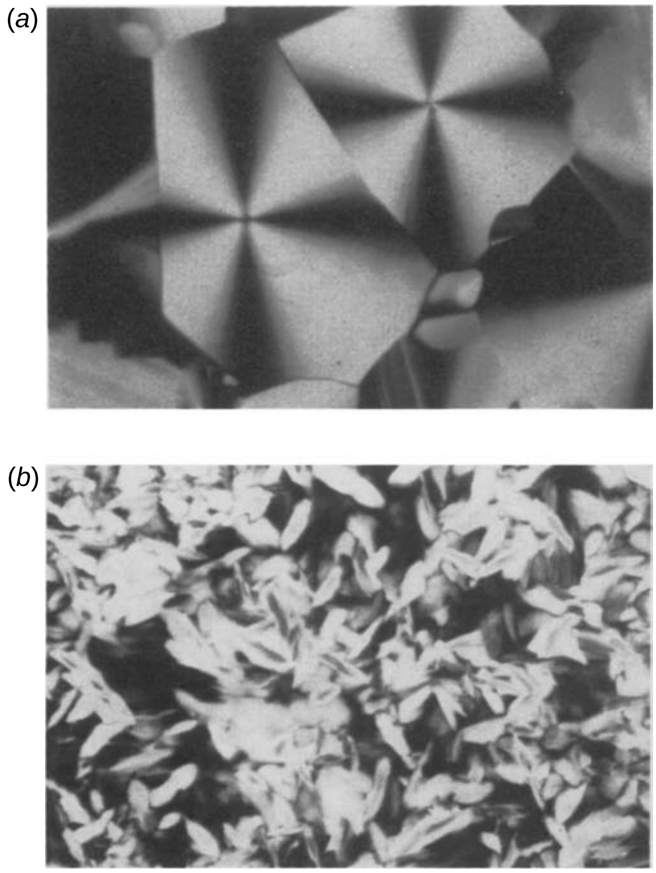


Fig. 1 Optical textures between crossed polarizers: (*a*), **1a** at 25 °C; (*b*) **7a** at 125 °C

obtaining the tertiary ammonium salts of **4** and **5** by adding different inorganic acids, *e.g.* HCl, HBr and HBF_4 (Scheme 2).

The compounds **6a–c** show liquid crystallinity, as revealed by DSC measurements and polarizing microscopy. The main crystalline transitions and the clearing points are summarized in Table 1. The textures under the polarizing microscope can be described as broken focal conics. X-Ray measurements could not elucidate the mesophase structure because of the decomposition of the compounds in the mesophase during the measuring time.

To obtain the trivalent ammonium compound of the [9]aneN_3 derivative, reaction with strong acids is necessary, because of the very different second and third protonation constants of the nitrogen atoms in [9]aneN_3.[17] Product **7a** shows a high glass transition temperature (T_g = 95 °C) without forming a crystalline phase. The clearing temperature (T_c = 154.5 °C) decreases on second and further heating, because of slight decomposition. The texture [broken focal conics, Fig. 1(*b*)] resembles those of the mesophases of the piperazinium salts **6a** and **6b**. X-Ray measurements clearly reveal the hexagonal columnar mesophase with an intercolumnar distance of a = 35.5 Å.

Because of the much higher decomposition rate of **7b**, a mesophase could not be observed.

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