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The first 'banana phase' found in an original Vorländer substance

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D. Vorländer was the leading scientist in liquid crystal chemistry in the first half of the 20th century who discovered many of the building principles for liquid crystalline compounds. It was known that Vorländer also synthesized some compounds with a bent molecular shape. In this paper we show that one of these compounds indeed forms a mesophase (B_6) which is characteristic for the banana-shaped molecular structure.

1. Introduction

In about 1900 Daniel Vorländer, head of the Chemical Department of Halle University, started his pioneering work on the synthesis of liquid crystalline compounds. Up to his retirement in 1937 more than 2000 new mesogenic materials were prepared in his laboratory, representing nearly all of the mesogenic materials known at that time [1–7]. He explored many of the principle inter-connections between chemical structure and liquid crystalline behaviour by systematic variations of chemical structure. He discovered polymorphism in the liquid crystalline state [8–10] and described the first homologous series of liquid crystalline compounds [11, 12]. He and his coworkers synthesized the first liquid crystals with heterocyclic and alicyclic rings [12, 13], the first hydrogen-bonded liquid crystals [14–17] and the first terminal polar nematics [18, 19]. Furthermore, he reported Siamese twins [20] and mesogenic dimers with flexible spacers [12, 16, 21]. Also liquid crystalline metallomesogens [10, 16, 22] and main chain polymers [10, 16, 23, 24] were first reported by Vorländer and his coworkers. It is also remarkable that Vorländer synthesized liquid crystalline compounds in which, much later, ferroelectric SmC* phases [12, 18, 25] or columnar mesophases [26] were detected. In this connection, it should emphasized that Vorländer had written even in 1923: *I can imagine that flat, cross or star-shaped molecules can be packed into kinds of column so that anisotropic building units result* [16].

It is also interesting that Vorländer not only found some general rules for the relations between molecular structure and the occurrence of mesophases, but also reached conclusions from the absence or presence of mesophases about the shapes of molecules [16].

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Banana-shaped mesogens and their liquid crystals have developed into a new fascinating sub-field of liquid crystal research within only a few years. They not only form several new mesophases, but also some of them exhibit unusual properties (ferro/antiferroelectricity or chiral structures) although the individual molecules are achiral [27–29].

The aim of this paper was to find out whether Vorländer was in fact the first who prepared banana-shaped liquid crystal materials which form some of these mesophases. For this reason we investigated three original samples from the collection of Vorländer's materials which is kept in the Institute of Physical Chemistry of the Martin-Luther-Universität Halle.

2. Experimental

The transition temperatures of the compounds studied were determined using a Perkin-Elmer DSC7 differential scanning calorimeter and a Leitz Orthoplan polarizing microscope equipped with a Linkam TH 600 hot stage. X-ray diffraction measurements were performed on powder-like samples using a Guinier goniometer (Huber, Germany) and on samples oriented in a magnetic field using a flat film camera.

3. Results

It was an essential goal of Vorländer's synthetic work to find out which molecular structures favour the formation of mesophases and what the general relationships between chemical structure and mesophase behaviour are. In order to investigate the role of the molecular shape alone, he synthesized isomeric five-ring mesogens where a central aromatic core links two two-ring mesogenic units in the *o*-, *m*- and *p*-positions, respectively. This concept can be seen in the examples of the diesters of dihydric phenols (catechol, resorcinol, hydroquinone)

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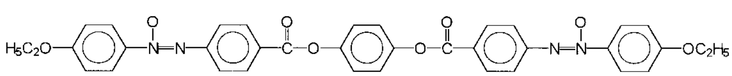
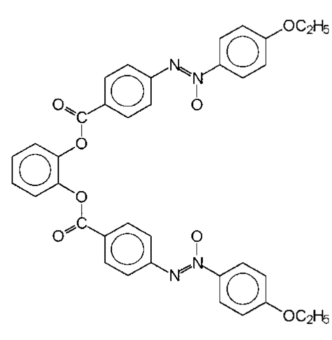
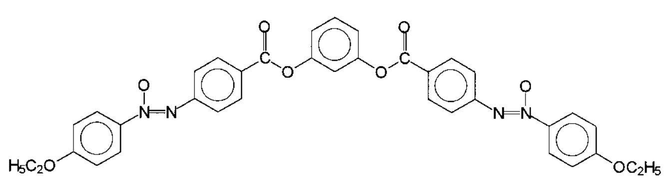
with 4-phenetoleazoxybenzoic acid. Fortunately, the first two of these original Vorländer materials were available and could be used without further purification. The table presents the structural formulae of these compounds and the transition temperatures reported by Vorländer and Apel [30]. For comparison, we determined the phase transitions by calorimetry and polarizing optical microscopy, and the results are included.

Compound **1** with the extended molecular shape was not available in the collection of Vorländer's materials. It is not surprising that this compound possesses the highest melting point of the three isomers. According to [30], a clearing temperature could not be determined because of the strong decomposition above 240°C. From the characterization described in [30], it can be assumed that besides a nematic phase, an unidentified monotropic smectic phase occurs.

In the case of the compounds **2** and **3**, the original samples of Vorländer were available, stored (like all other materials of Vorländer) in cigar boxes, as shown in figure 1. The mesophase of compound **2** could be identified as a nematic phase which could be supercooled to about 140°C. Compound **3** was of particular interest since the structural formula corresponds to a bent molecular shape. Therefore the question arose as to whether the mesophase of this compound is a normal mesophase of calamitic compounds (N, SmA, SmC, etc.) or is a mesophase specific for banana-shaped compounds. On cooling the isotropic liquid, this mesophase forms a SmA-like fan-shaped texture (see figure 2), but a homeotropic texture could never be obtained, only a kind of schlieren texture.

The X-ray pattern of a non-oriented sample of compound **3** shows strong Bragg reflections in the small angle region and diffuse scattering in the wide angle region. This result points to a smectic layer structure without in-plane order. From the small angle reflection, a layer spacing *d* of 1.63 nm was determined. The molecular length of the bent-shaped conformation is about 3.5 nm, assuming a bending angle of 120°. This means, that the layer spacing is a little smaller than half the molecular length. On the basis of these data, we propose a structural model in which the bent molecules are intercalated and, in addition, tilted with respect to the layer normal. Such a structure corresponds to a B_6 phase which is characteristic for a bent molecular shape [29]. This compound is truly the first liquid crystal material reported in the literature which exhibits a mesophase characteristic for a bent molecular shape. In this connection it is interesting that Vorländer described a quite

Table. Transition temperatures (°C) and transition enthalpies (kJ mol^{-1}) of the diesters **1–3**: M: undesignated phase.

Compound	Structure	Phase transitions	Reference
1[a]		Cr 231 M[b]	[30]
2		Cr 164 M 213 I Cr 171 N 219 I (37.6) (0.25)	[30] this work
3		Cr 184 M 218.5 I Cr 186 B_6 224 I (28) (10.9)	[30] this work

[a] This material was not available.
[b] The clearing temperature is not reported.

Figure 1. One of the original cigar boxes in which Vorländer's materials are kept.

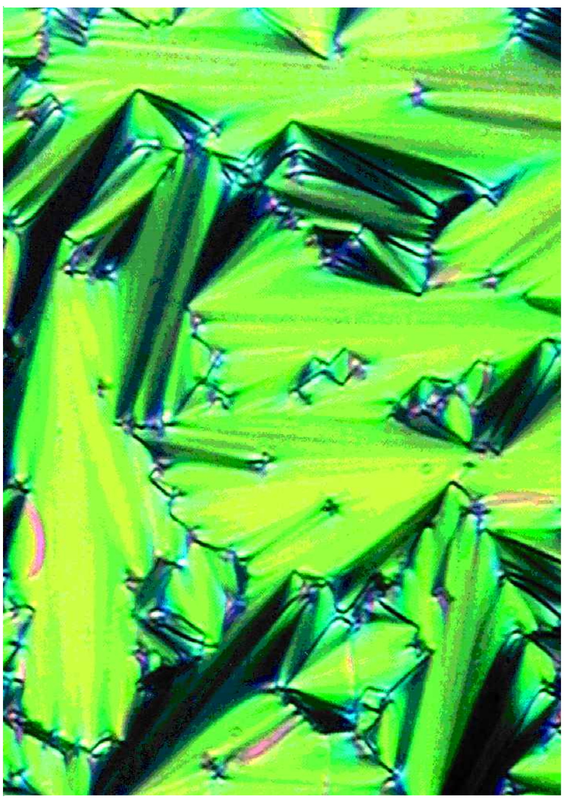
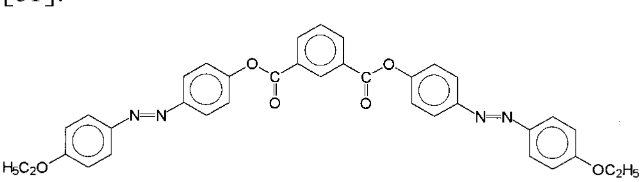


Figure 2. Fan-shaped texture of the B_6 phase of compound **3** obtained on cooling the isotropic liquid.

similar banana-shaped compound even earlier in 1929, the diester of isophthalic acid with 4-phenetole azophenol [31]:



This compound has a considerably higher melting point (261°C) than compound **3**. The anisotropic mesophase described by Vorländer [31] was found to be a nematic phase which immediately crystallizes on supercooling.

It is obvious that Vorländer's results and concepts of synthesis are still important for present day research. With respect to current research on banana-shaped liquid crystal materials and their phases it is interesting that even for this short chained five-ring homologue (compound **3** in the table) the 'banana-specific' B_6 phase could be detected. This is a hint to synthetic chemists not to neglect homologues with very short terminal chains in order to obtain a better insight into the relations between molecular structure and mesophase behaviour for banana-shaped mesogens.

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