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The Earliest Researches on Liquid Crystals

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ABSTRACT Here it is proposed a discussion concerning the earliest researches on the liquid crystals. The discussion is based on a book published in 1911, written by Alfred Tutton. In this book, we find described the instrument which was fundamental for observing the mesophases of thermotropic liquid crystals, the “crystallisation microscope”, that Otto Lehmann built for his studies on crystals. It consisted of a polarized-light microscope, equipped by heating and cooling systems for the control of temperature. This experimental set-up allowed Lehmann to study the cholesteryl benzoate, the first material that was discovered by Friedrich Reinitzer as exhibiting a mesophase. In the following years, many other materials were prepared for Lehmann’s studies. In the Tutton’s book, among the chemists who prepared the samples, we can find mentioned Ludwig Gattermann and Daniel Vorländer. We can find also the Vorländer’s “recipes” to obtain liquid crystalline materials, those which have rod-like molecules.

Introduction Liquid crystals are materials which possess phases, defined as mesophases, characterized by properties between those pertaining to isotropic liquids and to solid crystals. It means that in a mesophase, the substance can flow like a liquid, but its molecules have an order as in the crystal phase. Today, we have that many different types of mesophases exist, usually distinguished by their optical properties. When observed under a polarized-light microscope, the mesophases are characterized by different textures, produced by the domains in which molecules are oriented in different directions [1,2]. Texture transitions are displaying the changes between different mesophases and the subtle variations within them [3-5].

The liquid crystals are usually divided into thermotropic and lyotropic materials. Thermotropic substances exhibit mesophases as temperature is changed [6], whereas the lyotropic substances exhibit the mesophases driven by concentration [7]. The large part of the liquid crystals consist of organic molecules, but inorganic materials are also known to give mesophases [8]. More recently, the class of metallotropic liquid crystals has been introduced too [9].

The first liquid crystalline material was discovered in 1888, when the Austrian botanist and chemist Friedrich Reinitzer examined the properties of some derivatives of cholesterol [10]. The material was the cholesteryl benzoate, now defined as a cholesteric liquid crystal. However, the history of the early researches on liquid crystals cannot be confined to the discovery of the first material of this family. It deserves a more detailed discussion.

To help us in this study, we have a book written in 1911 by Alfred Tutton. In his book on Crystals [11], Tutton ascribed the discovery of liquid crystals to Otto Lehmann. Then, let us see, what was the history of the first researches on liquid crystals, as depicted by Tutton.

Tutton Alfred Tutton (1864-1938) was an English scientist. He was the only child of James Tutton, a venetian blind manufacturer. Alfred won a scholarship to the Royal College of Science in London, where in 1886 he graduated. In 1889 he became lecturer in chemical analysis. In 1895 he was appointed inspector of technical schools and served successively in the Oxford, London, and Plymouth districts. Tutton retired to Cambridge in 1924 and occasionally lectured for the university. From 1895 until 1931, he maintained a crystallographic laboratory in the various houses where he lived. His principal interests besides crystallography were climbing and glaciology; all three were united in his book *The Natural History of Ice and Snow* (1927) [12].

Tutton's discussion of liquid crystals Book [11] presents a chapter on the liquid crystals, after having discussed the crystals. The chapter begins remembering that a crystal is usually a solid, highly organised in a homogeneous manner, which is in general anisotropic. For this reason, a crystal can exhibit double refraction. "Section plates of it, more or less thin according to the strength of the double refraction, exhibit colours in parallel polarised light, and show the phenomenon of a single optic axis, or of two optic axes, in convergent polarised light." Tutton observed that many of the softer crystallised substances "develop the property of permitting one layer to glide over another by gentle side pressure with a knife blade, when inserted in an edge or face in an attempt to cut the crystal. Calcite and ice, for instance, both possess such planes of gliding of the structural units over one another in layers. There are also the border line cases of crystals so soft as to be readily bent, and many well known viscous substances crystallisable only with great difficulty, some of which form pliable crystals". In his introduction to liquid crystals, Tutton is stressing that it is the polarized light microscopy the method used for studying the slices of anisotropic crystals, due to the birefringence of light which creates coloured domains, when viewed with polarized light. He also mentions a method to study the deformation of crystals and the existence of the soft matter of plastic crystals.

Tutton continues: "But in the year 1876 Lehmann discovered a new property in an already remarkable substance, iodide of silver, AgI, namely, that at temperatures superior to 146 °C, it can flow like a viscous liquid, while exhibiting several of the properties which are characteristic of crystals." Silver iodide is a material which is dimorphous. It exhibits a hexagonal form at the ordinary temperature, which is persisting up to 146 °C. "But during the heating to the latter temperature a regularly accelerating diminution of volume occurs, the feeble expansion in directions perpendicular to the axis being overbalanced by a considerable contraction along the axis, both quantities having been accurately measured so long ago as the year 1867 by Fizeau, by means of his delicate interference dilatometer. This contraction, so unusual an occurrence with increase of temperature, culminates at 146 °C, according to Mallard and Le Chatelier, in a sudden change of condition into a cubic modification, accompanied by absorption of heat"[11]. Lehmann studied therefore this cubic modification of silver iodide, by means of a microscope which he had "devised - specially adapted for observations at temperatures higher than the ordinary, by being supplied with the means of heating the object under observation - found that it was not only plastic, but actually a liquid" [11].

Iodine of silver is the first material discussed in the chapter of [11] on liquid crystals. However, is the iodide of silver the first “flowing crystal”, or, as we say today, the first “liquid crystal”? No, as explained by Georges Friedel in [13], it is simply plastic. However, what is important is the fact that Lehmann had a device suitable for studying the passage from the hexagonal to the cubic phase.

Otto Lehmann (1855 – 1922), a German physicist, was the “father” of liquid crystal, as told in [https://en.wikipedia.org/wiki/Otto_Lehmann_\(physicist\)](https://en.wikipedia.org/wiki/Otto_Lehmann_(physicist)). Otto was the son of Franz Xavier Lehmann, a mathematics teacher in the Baden-Wurtemberg school system, with a strong interest in microscopes. From the father, Otto learned to experiment in microscopy. Between 1872 and 1877, Otto Lehmann studied natural sciences at the University of Strassburg and obtained the Ph.D. under crystallographer Paul Groth. Otto used polarizers in a microscope so that he might watch for birefringence appearing in the process of crystallization. In 1889, he became the head of the Institute of Physics in Karlsruhe. Lehmann was an unsuccessful nominee for a Nobel Prize from 1913 to 1922.

The Crystallisation Microscope In 1876 then, Otto Lehmann was studying the behaviour of the Iodide of Silver, using a polarized light microscope that he had developed in his laboratory. “The form of Lehmann's "Crystallisation Microscope," as now constructed by Zeiss is shown in the Fig.102” of book [11]. Tutton explains that the essential features of the microscope “are that the glass object-plate, which is somewhat wider than the usual microscope 3 by 1 inches slip, is supported by little metallic columns at a height an inch or more above the ordinary stage, and may be heated from below by a miniature Bunsen burner, which is provided with a delicate graduated gas-tap and is adjustable for its position, swinging in or out as desired.”

Besides the Bunsen flame, the microscope was equipped by two cooling blasts, “connected with a gas-holder of air”. The blasts were adjustable “to the most suitable symmetrical positions above the slide for directing the cooling air on the part of the latter where the liquid is situated. These arrangements enable the substance on the slide to be rapidly or slowly heated or cooled at will. Electric connections are also provided, in the event of the observer desiring to study the behaviour of the liquid crystals under the influence of the electric current” [11]. That is, Tutton is giving a precise description of a microscope where the temperature of the sample can be changed and where the liquid crystals can be investigated under the effect of an electric field. Lehmann’s microscope was therefore the first instrument suitable for studying the behaviour of the thermotropic liquid crystals.

As told in [14], “O. Lehmann’s remarkable observations with regard to crystallization phenomena were doubtless due to the fact that he had at his disposal apparatus by means of which he could study his microscopic objects at high temperatures which could be regulated in a very exact manner. This exact regulation was possible because he was able to heat his objects as well as cool them.” In the Lehmann’s microscope, “the condenser had to be eliminated, and the application of a polarizer required special provisions” [14]. After suitable arrangements, the Lehmann’s “crystallization microscope” turned into the most usual supply to the trade.

Let us continue reading [11]. “Considerably later, in the year 1889¹, the attention of Lehmann was called by Reinitzer to another similarly singular substance, cholesteryl benzoate, which appeared to consist of an aggregate of minute crystals which flow as readily as oil, while

1 A mistake or misprint. The year was 1888.

preserving many of the characters of crystals”. As told in [15], referring to [16], Lehmann received a letter from Friedrich Reinitzer asking for confirmation of some unusual observations. As Dunmur and Sluckin (2011) say “It was Lehmann's jealously guarded and increasingly prestigious microscope, not yet available off the shelf, which had attracted Reinitzer's attention. With Reinitzer's peculiar double-melting liquid, a problem in search of a scientist had met a scientist in search of a problem”.

Friedrich Reinitzer (1857 – 1927) was an Austrian botanist and chemist. He was born into a German Bohemian family in Prague. He studied chemistry and in 1883 received the qualification as a private docent. From 1888-1901 he was a professor at Karl-Ferdinands-Universität, then professor at technical university in Graz. During 1909 - 1910 he served as the rector of the university. When he was working at Karl-Ferdinands-Universität in 1888, he discovered the “strange” behaviour in the above mentioned material that today we know as belonging to the family of cholesteric liquid crystals.

This was the beginning. “In the next year, 1890, the substance para-azoxyphenetol, then recently discovered by Gattermann, was observed by Lehmann to form a turbid "melt" on fusion, which consisted of an aggregate of crystals flowing with a mobility equal to that of water” [11]. “In polarised light the drops show dichroism, that is two different colours in different parts or directions” [11]. Under crossed Nicols the drops of the liquid crystal show a black cross.

Ludwig Gattermann (1860 – 1920) was a German chemist, who contributed significantly to both organic and inorganic chemistry, as stressed in the Wikipedia item at en.wikipedia.org/wiki/Ludwig_Gattermann. In the item it is told that his “book about practical work in the laboratory became a standard textbook of organic synthesis at almost every German university. In some universities the organic course is still called "Gattermann".” [17,18].

Another substance, the para-azoxyanisol, was subsequently found to behave similarly, “and forms an excellent substance to use for demonstration” purposes [11]. As told by Tutton, the para-azoxyanisol (today known as PAA) was mixed “with a little para-azoxy-phenetol, oil and resin (colophony)”. At Page 280, of the book [11], it is told that the para-azoxyanisol mixed with resin is a material “which exhibits the phenomenon of rotating drops”.

Lehmann effect of rotating drops In [19], it is told that the para-azoxyphenetol was the material that allowed Lehmann to discover a thermo-mechanical phenomenon. In 1900 [20], Lehmann was working with a cholesteric liquid crystal. He obtained it by dissolving a small quantity of a chiral substance in the nematic para-azoxyphenetol [19]. Otto Lehmann observed that the droplets of the cholesteric phase in the isotropic liquid were rotating when heated from below. In [19], some drawings by Lehmann of the droplets are given, The droplets present a spiralling texture: the texture is rotating at constant velocity under the action of the temperature gradient.

As told before, Lehmann has observed the rotating drops also in the para-azoxyanisol mixed with resin.

The Lehmann effect was explained 68 years later by Leslie [21], who assumed the director experiencing a torque proportional to the temperature gradient. The proportionality constant is called the Lehmann coefficient [19]. As explained in [19], the concept of Lehmann effect was extended by de Gennes to the electric and chemical cases.

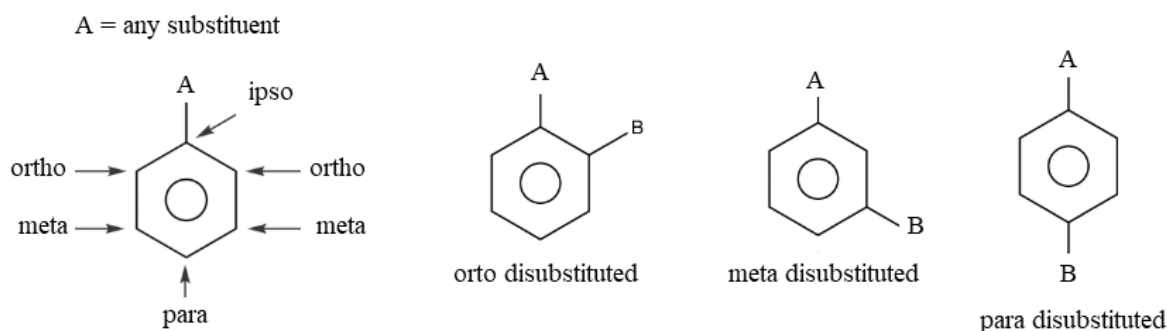
From Tutton's book "The next and possibly most interesting step in this remarkable series of discoveries was made by Lehmann himself in the year 1894. He alighted on the fact that ammonium oleate, crystallised from solution in alcohol, affords a splendid example of flowing crystals, which are sufficiently large to enable their habits to be studied in detail. ... Another substance of a different nature was discovered by Vorländer in the year 1904, namely, the ethyl ester of para-azoxy-benzoic acid. ... Vorländer also prepared the ethyl ester of paraazoxy-cinnamic acid, and Lehmann found it to be similarly interesting." [11].

For what concerns the ammonium oleate, Otto Lehmann observed tubular structures in the lamellar phase of this material when exposed to excess water [22,23].

Daniel Vorländer (1867 – 1941) was a German chemist who synthesized most of the liquid crystals known until his retirement in 1935. Vorländer studied chemistry at Kiel, Munich, and Berlin, after which he became a professor at University of Halle-Wittenberg. Vorländer applied his knowledge of molecular structure to select those exhibiting the crystalline liquid state.

In the benzene ring About the liquid crystalline materials, Tutton notes a very important contribution made by Vorländer (Ber der deutsch. Chem. Oes., 1907, 40, 1970). The contribution is in "the facts regarding the relationship between chemical constitution and the formation of liquid crystals. It must have already struck the reader that most of the substances which exhibit liquid crystals are composed of a large number of chemical atoms, being either long-chain compounds of the fatty acids or complex derivatives of the hydrocarbon benzene, C_6H_6 ; also that many of the latter are "para" compounds, that is, derivatives in which the substitution groups are inserted in the benzene ring of six carbon atoms in the "para" position, which is that at the opposite corner of the hexagon to the carbon atom to which a substitution group has already been attached." [11].

From the link <http://www.ochempal.org/index.php/alphabetical/o-p/ortho-carbon/>, we can learn about the labels we can give to the carbon atoms in benzene, labels used for identification purposes.



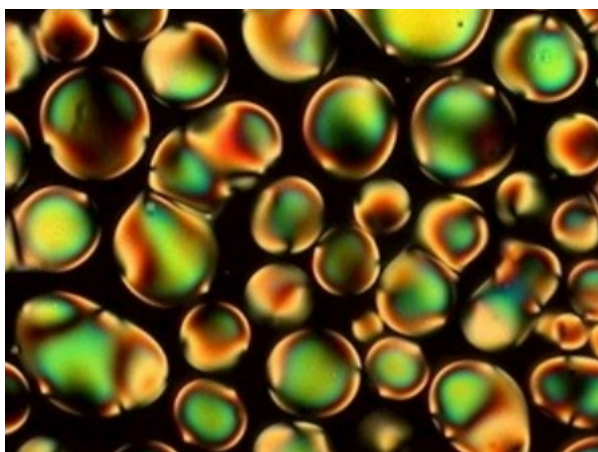
"This renders the para compounds the most extended in a straight line of all the benzene derivatives. Now Vorländer finds that a particularly favourable condition for the production of liquid crystals is a linear structure of the molecule. As the para substitution products of benzene derivatives possess this elongated structure, many of them exhibit the development of liquid crystals. The more linearly extended the structure becomes, that is, the longer the straight chain of atoms is, the more favourable become the conditions." [11] Here Tutton is

mentioning a “recipe” to obtain a liquid crystalline material, that of having rod-like long molecules.

“The advent of a third substitution group, however, which would have the effect of producing a kink in the chain, or of bending it, appears to destroy the possibility of the production of liquid crystals. This interesting observation may afford the key to many of the extraordinary phenomena of liquid crystals which have been described, and is undoubtedly one of prime importance. Further favourable conditions for the formation of liquid crystals, according to Vorländer [Zeitschr. f. Phys. Chemie., 1907, 57, 357], are the aromatic character, and the presence of the doubly-linked carbon and nitrogen groups C : C, C : N, and N : N, which are usually so rich in energy” [11].

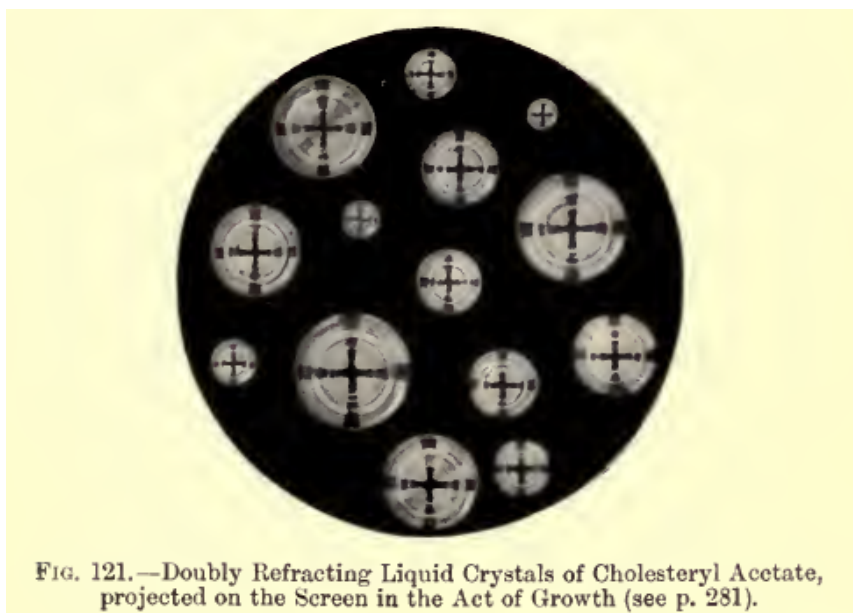
Bent-core liquid crystals Materials with rod-like molecules constitute the vast majority of the investigated liquid crystals. However, also disc-like molecules can create materials possessing mesophases, such as the discotic nematic and a variety of columnar phases. “Such discotic liquid crystals have been reasonably widely investigated” and applications have been provided in areas of films of negative birefringence [24]. The bent-core and banana-shaped liquid crystals became, around fifteen years ago, a fashionable field of research. However, as told in [24], some materials “with bent-core molecular architectures have been known for many years, dating back to the early 1900s and the work of Vorländer”. At the time, the bent-core materials were rare; moreover it soon became well-known that mesophases were more easily generated through by rod-like molecules [24]. And this is the framework that we have to consider, when we read Tutton’s words on the shape of molecules.

Projection “The phenomena of "liquid crystals" lend themselves admirably to screen demonstration, for which purpose an excellent improved form of the crystallisation microscope of Lehmann ... is constructed by Zeiss, and its actual use in the projection, with the aid of the well-known Zeiss electric lantern, but specially fitted for the purpose, is shown in Fig. 120.” [11]. It was clear, from the first studies on liquid crystals, that the colours and the textures observed by means of the polarized light microscope were very fascinating, in particular the growth of coloured droplets in the black background of the isotropic phase.



Transition from the isotropic liquid into the nematic phase, viewed by means of a polarized light microscope with crossed polarizers. The liquid is black in the image; the nematic phase appears as coloured bubbles. The liquid crystal is 12OBAC alkyloxybenzoic acid [25].

“The following substances lend themselves particularly well to projection purposes. Para-azoxyanisol with resin, which exhibits the phenomenon of rotating drops; cholesteryl acetate, which affords a fine example of spherical liquid crystals; para-azoxy-phenetol with resin, which gives beautiful interference colours; and the acetyl ester of para-azoxybenzoic acid with resin, which shows the uniting of crystals to form larger and larger individuals. Perhaps the most interesting and beautiful of all is cholesteryl acetate, a characteristic field of which is shown in Fig. 121 on Plate XVI., facing page 208” [11]. Here we find mentioned the Lehmann’s effect of the rotating drops in a PAA-based mixture, as previously told.



At the web site <https://www.olympus-lifescience.com/en/microscope-resource/micd/galleries/moviegallery/chemicalcrystals/cholesterylacetate/cholesterol1/>, we find a contribution by Omar Alvarado, Thomas J. Fellers and Michael W. Davidson, of the National High Magnetic Field Laboratory, at the Florida State University, Tallahassee, Florida, which is showing the textures of the Cholesteryl Acetate.

Tutton’s conclusions The book by Tutton ends with some considerations. “It is thus obvious that we have now arrived at a stage in the history of crystallography when more experimental data, and many more measurements of the most carefully conducted character, on pure materials and excellently developed crystals, are most urgently needed” [11]. In the study of crystals and liquid crystals, Tutton sees a “rapidly growing branch of science, the importance of which to chemistry and physics is increasing every day”. It is a field “ripe for the harvesters”, with promising opportunities.

In fact, at the time, we were at the beginning of the researches on liquid crystals, and to this new research contributed the new instrumental set-up prepared by Otto Lehmann for sure. The beginning of the study of the liquid crystals was in 1888, when Reinitzer found that the cholesteryl benzoate has two melting points; at 145.5 it melts into a cloudy liquid, and at 178.5 °C it melts again into a clear liquid (clearing point). “Seeking help from a physicist, on

March 14, 1888, he wrote to Otto Lehmann, ... They exchanged letters and samples. Lehmann examined the intermediate cloudy fluid, and reported seeing crystallites.” [10]. In the Tutton’s book too we find, as we have previously reported, that the cholesteryl benzoate “appeared to consist of an aggregate of minute crystals which flow as readily as oil”. Also Victor Leopold Ritter von Zepharovich, in Vienna, indicated the intermediate phase as crystalline [10].

“The exchange of letters with Lehmann ended on April as 24, with many questions unanswered. - continues Wikipedia - Reinitzer presented his results, with credits to Lehmann and von Zepharovich, at a meeting of the Vienna Chemical Society on May 3, 1888.” [10,26] Reinitzer had discovered and described the following remarkable properties of the material: the existence of two melting points, and therefore the presence of a mesophase, the reflection of circularly polarized light, and the rotation of the polarization of light. “After his accidental discovery, Reinitzer did not pursue studying liquid crystals further.” The research was continued by Lehmann, who realized that he had encountered a new phenomenon, different from those observed in crystals. He was in the proper position to investigate the new family of materials, being an experimental physicist specialized in the polarized light microscopy. Lehman named the new materials as “fliessende Krystalle”, that is “flowing crystals” [27].

“Lehmann's work was continued and significantly expanded by the German chemist Daniel Vorländer, who from the beginning of 20th century until his retirement in 1935, had synthesized most of the liquid crystals known. However, liquid crystals were not popular among scientists and the material remained a pure scientific curiosity for about 80 years”, as told in [10,28]. That is, the liquid crystals became “ripe for the harvesters”, when they became useful for displays, that is, when a suitable electronic set-up able to control them was available and combined with a twisted nematic cell. And this happened around 1970, when James Ferguson, Wolfgang Helfrich and Martin Schadt developed and patented the TN-LCD displays [29].

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