Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Volkmar Vill

Online publication date: 06 August 2010

To cite this Article Vill, Volkmar(1998) 'Grey levels in the history of liquid crystals', Liquid Crystals, 24: 1, 21 — 24
To link to this Article: DOI: 10.1080/026782998207541
URL: http://dx.doi.org/10.1080/026782998207541

Liquid Crystals, 1998, Vol. 24, No. 1, 21–24

Grey levels in the history of liquid crystals

by VOLKMAR VILL
Institute of Organic Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

Presented at the Capri Symposium in Honour of George W. Gray, FRS held at the Hotel Palatium, Capri, 11–14 *September* 1996

History is not always straightforward—not a simple black and white picture. Therefore a description including the grey levels is given of the history of the chemistry of liquid crystals. Daniel Vorländer had the biggest impact following the discovery of liquid crystals in the first part of the 20th century. George Gray dominates the second part of the 20th century.

The history of research on liquid crystals has been recorded by Kelker [1], and the new database LiqCryst [2] affords a view of the history of liquid crystalline compounds and the researchers behind them. This history of the compounds [3] is dominated by the work of Daniel Vorländer [4] and of George Gray.

Historical reflections can however be a little bit tricky. Huth [5], for example, prepared the first ferroelectric liquid crystal materials (figure 1). He observed the transitions between the smectic C* and the smectic A phases and made comments on the microscopic textures, but of course, at this time nobody knew the arrangements of the molecules in the SmC* phase and nobody noticed the ferroelectric properties. Did Huth discover the first ferroelectric compound? The answer is not simple—neither white nor black—and such a situation can only be described by a grey scale with various levels.

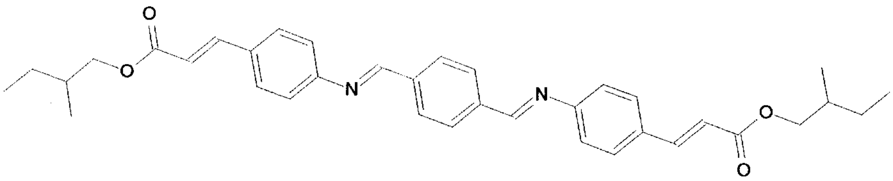
Today, we are interested in Huth's and Vorländer's work, *after* the discovery of ferroelectric liquid crystals. Huth's compounds were unimportant at the time of their discovery without the knowledge of ferroelectrics, and therefore Vorländer never published on Huth's compounds. Thus, the history of liquid crystals is a view from today. It is a story combining milestones in research, lost chances and forgotten results.

Another grey level in the history can be found in the case of carbohydrate liquid crystals, which started seriously only in the last few years [6]. On the other hand, carbohydrate chemists reported the liquid crystalline properties of their compounds many years ago, but liquid crystal researchers took no notice. For example, Fischer and Helferich [7] reported in 1911 the two melting temperatures of hexadecyl-β-D-glucopyranoside, **1** (figure 2). Did they discover the first carbohydrate liquid crystal? Some people argue that they did not use the term 'liquid crystal' and therefore other scientists did not take notice of this report; thus, Fischer and Helferich's paper is not considered of relevance to liquid crystals. But, the molecular theory of liquid crystals was not very well developed in the year 1911 and a big part of the current research was concerned with phenomenological descriptions of mesomorphic compounds. Fischer and Helferich however gave a very precise description of the melting process, with exact values for the temperatures. Some researchers did notice this report and Salway [8] verified Fischer and Helferich's observations in 1913. Hori and Ikegami studied this compound again in 1959 [9]. They did use the term 'liquid crystal', but their paper appeared in a Japanese journal and the Chemical Abstract Service did not apparently believe in the results. The word 'liquid crystal' was removed from the abstract. Most researchers outside of Japan referred only to the abstract and so the important findings of Hori and Ikegami remained hidden away.

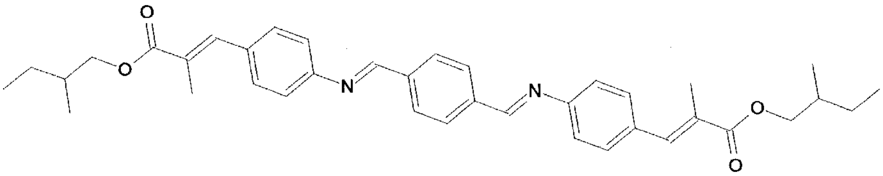
Another instance is provided by agaric acid, a thermotropic liquid crystal material with an amphiphilic structure comparable to glycolipids, and studied by Gaubert [10] in 1919. This paper was exclusively focused on the liquid crystalline properties of the material, but the structure of the molecule was too unusual for the established theories of liquid crystals. This report appears to have been 'banned' from reviews and data collections, effectively decreeing that the discovery of liquid crystalline carbohydrates occurred just in *our* time.

In 1888, Reinitzer [11] and Lehmann [12] reported cholesteryl benzoate and cholesteryl acetate as the first thermotropic liquid crystal materials. Research in the following years was dominated by the physicist O. Lehmann, and only a few more chemical substances with liquid crystalline properties were discovered in this period, e.g. PAA (**2**) [13], *p*-methoxybenzylideneazine (**3**) [14] and a few other compounds (figure 2). *p*-Methoxycinnamic acid (figure 3) was the first example of a hydrogen-bonded liquid crystal material. Perkin

Figure 1. The first ferroelectric liquid crystals: transition points in °C.

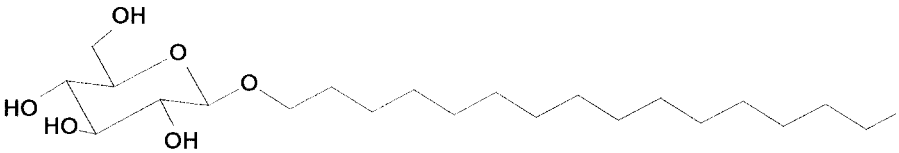


Cr 133 Sm ? Sm 195 Ch 268 I
Huth, M. E., (Vorländer. D), 1909, PhD thesis, Halle.
Cr_2 130 Cr_1 149 SmC* 180 SmA 242 Ch 288 I
Urbach, W. Z., and Billard, J., 1972, *C. R. Acad. Sci.*, **B274**, 1287.
Cr 134 Sm 234 Ch 283 I
Coates, D., Harrison, K. J., and Gray, G. W., 1973, *Mol. Cryst. liq. Cryst.*, **22**, 99.
Cr 130 H 149 SmC 180 SmA 242 Ch 288 I
Vilfan, M., Blinc, R., Selinger, J., and Zagar, V., 1980, *Ferroelectrics,* **24,** 211.

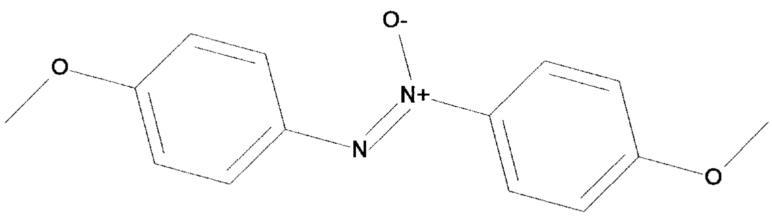


Cr 144 S ? S 211 Ch 248 I
Huth, M.E. (Vorländer, D.), 1909, PhD thesis, Halle.
Cr 150 SmC 166 SmA 226 Ch 262 I
Keller, P., Liebert, L., and Strzelecki, L., 1976, *J. Phys. (Paris), Suppl 37,* **C3,** 27.

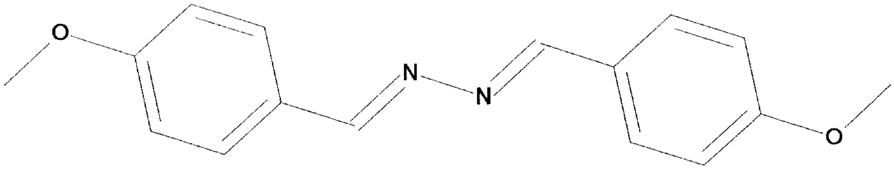
Figure 2. Some early liquid crystal materials.



1: Hexadecyl-β-D-glucopyranoside



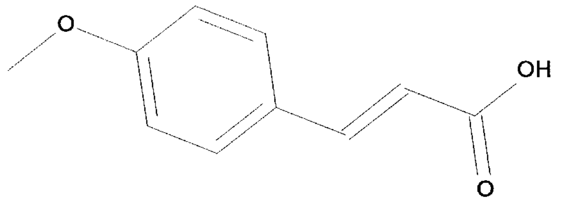
2: PAA=*p*-Azoxy-anisole



3: *p*-Methoxybenzylidene-azine

and Einhorn *et al.* lost their opportunity to discover the *first* thermotropic liquid crystal by failing to note the unusual melting behaviour of the acid, but de Kock in 1904 finally discovered the liquid crystalline properties. Some earlier reports about unusual melting of compounds are given in the literature, e.g. magnesium

Figure 3. Thermotropic properties of *p*-methoxy-cinnamic acid.



Cr 171 I Perkin, W. H., 1877, *J. chem. Soc.*, 388.
Cr 171 I Einhorn, A, Grabfield, J. P., 1888, *Liebigs Ann. Chem.*, **243**, 362.
Cr 170·6 X 185·5 I De Kock, A. C., 1904, *Z. Phys. Chem.*, **48**, 129.
Density versus temp. Eichwald, E., 1905, PhD thesis, Marburg.
Cr 170 X 185 I Rotarski, T., 1908, *Ber. Dtsch. Chem. Ges.*, **41**, 1994.
Cr 170 X 186 I Vorländer, D., 1908, *Ber. Dtsch. Chem Ges.*, **41**, 2033.
Cr 170 X 185 I Stoermer, R., 1911, *Ber. Dtsch. Chem. Ges.*, **44**, 637.
Cr 170 N 183 I Friedel, M. G., 1922, *Ann. Physique*, **18**, 273.
Cr 171 X 187 I Walter, R., 1925, *Ber. Dtsch. Chem. Ges.*, **58**, 2303.
Cr 170 X 186 I Wasum, L.-W. (Vorländer, D.), 1928 PhD thesis, Halle.
Cr 173·5 N 190 I Gray, G. W., and Jones, B., 1954, *J. chem. Soc.,* 1467.

myristate in 1855 by Heintz [15] and cholesterylamine in 1878 by Loebisch [16]. They describe most probably the thermotropic properties of these compounds without using the term 'liquid crystals' but their findings have never again been verified. The reader may decide for himself which was the first liquid crystal, but obviously the writer's point that the history of liquid crystals is not one of black and white situations is clearly made.

Figure 4 shows the development of new liquid crystal materials in the 20th century. Vorländer started work on the synthesis of liquid crystalline compounds around 1905 and the name of the chemist Vorländer dominates the liquid crystal research scenario for the next 30 years. Nearly all the new liquid crystals discovered were prepared in his laboratory. His results are still important for present day research, because even in these early times he describes the first metallomesogens, polymer mesogens, banana-shaped mesogens, mesogenic twins etc. [4]. His work was of course disrupted by the First World War: he reported about 300 compounds in 1910 and 550 compounds in 1925, but nothing in 1916 and 1917.

In his life's work, Vorländer reported considerably more than 2000 new mesogenic compounds, but in fact the biggest number of new liquid crystals has been reported by George Gray. He dominates in the quantity and quality of the synthesis of mesomorphic compounds

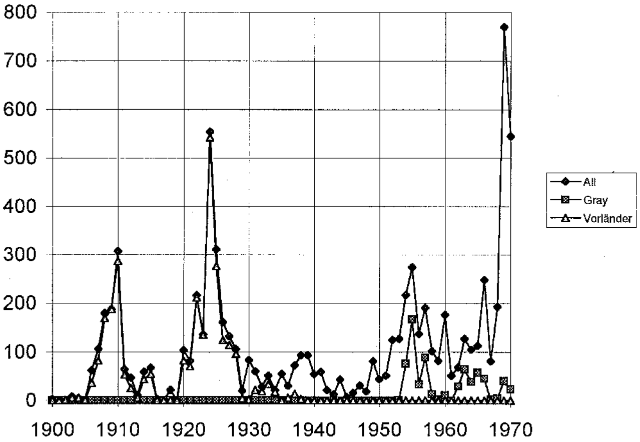


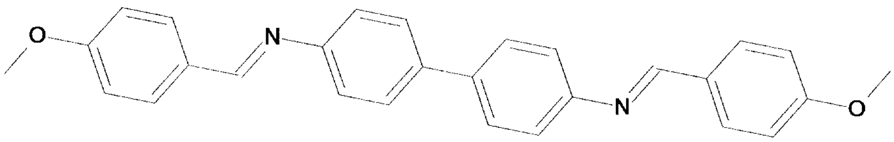
Figure 4. Annual numbers of new mesogenic compounds reported between the years 1900 and 1970. These numbers also include non-mesomorphic compounds, which have typically mesogenic structures.

in the first part of his career between the years 1953 and 1968. Then in 1968 industrial research on liquid crystals began giving an explosive growth in the number of new materials [17], and Gray's newest materials, including the cyanobiphenyls [18] were the most important compounds for research and applications. Vorländer was the leading chemist in a period when only one chemist was working on liquid crystals. Gray, is the leading chemist in a period up to the early 1990s when many chemists have been working on this topic.

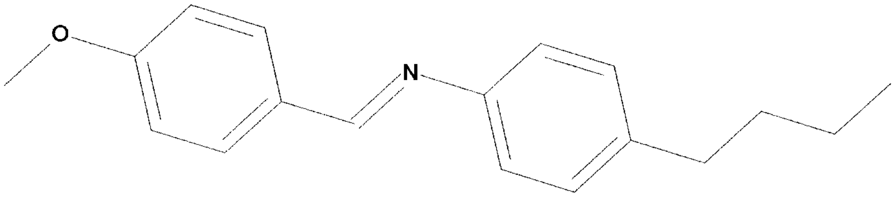
Figure 5 gives another view on the history of liquid crystals. The discovery of materials with new properties activates the synthesis of similar molecules in order to analyse structure/property relationships. Thus, single molecules can be regarded as guidelines or initiators for the synthesis of new materials. Vorländer explored many of the principle structure/property relationships of liquid crystals by a systematic variation of the chemical structure of **4**. Today, 63 compounds are known which are just simple modifications of **4**, e.g. just one functional group has been replaced in the chemical structure. Kelker discovered MBBA (**5**) as the first room temperature nematic liquid crystal. Now some 70 molecules are closely related to MBBA. Gray first reported the synthesis of 5CB (**6**), a nematic liquid crystal with a high positive dielectric anisotropy, and today 124 compounds can be viewed as structural modifications of his invention. Fukuda's group reported the first antiferroelectric liquid crystal material MHPOBC (**7**), and since then 30 compounds have been prepared as simple variations of MHPOBC to analyse structure/property relationships of antiferroelectrics.

Finally, liquid crystal displays (LCDs) may be only one aspect of liquid crystal research, but perhaps they

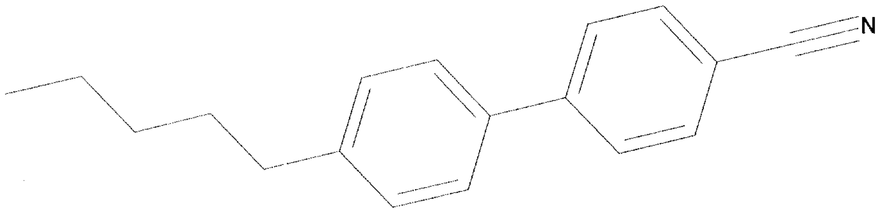
Figure 5. Liquid crystalline compounds as guidelines for the synthesis of new materials. Structure, name, basic researcher and number of structural modifications found in the database LiqCryst 2.1.



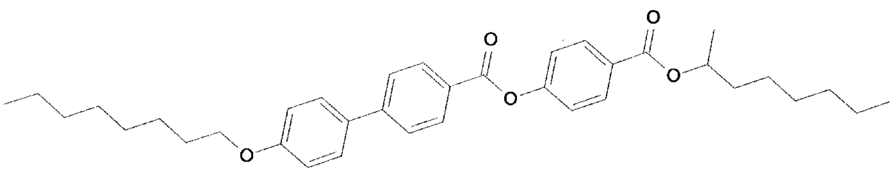
4: Bis-*p*-methoxybenzylidene-benzidine, by Vorl nder, 63 modifications



5: MBBA, by Kelker, 70 modifications



6: 5CB, by Gray, 124 modifications



7: MHPOBC, by Fukuda, 30 modifications

are the most stimulating reason for the industrial interest in new mesogens. The requirement for the first LCDs was a good black and white contrast. Modern LCDs require a good set of grey levels to give realistic pictures. Thus, the grey scale remains a challenge for liquid crystal research in the present and the future.

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