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Vorländer's wheel†

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In this short article, we draw attention to the pioneering studies of Daniel Vorländer, who lived from 1867 to 1941 and worked in Halle, Germany between 1890 and 1935. The number and range of compounds synthesized under his guidance are truly vast, but much of his work is hidden away in Doctoral theses. All of these data are collected in the LiqCryst [1] database and, therefore, now having access to the results of his life's work, we outline some of his achievements and pay tribute to his remarkable contribution to liquid crystal research.

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1. Introduction

It is our opinion that one of the earliest contributors to liquid crystal literature was also one of the greatest. Daniel Vorländer worked in Halle, Germany, for 45 years between 1890 and 1935. He published a large number of papers, supervised many Doctoral theses, and contributed more than 2700 compounds to the literature, about 5% of all mesogenic materials made to date—only Gray and Zaschke have been responsible for more. Truly a remarkable man. In fact, figure 1 plots the number of liquid crystals reported by Vorländer, and the total number, in each year from 1900 to 1950. Note the drop in productivity during the period of the First World War. Although not all of the compounds synthesized by Vorländer and his co-workers were mesomorphic, and while they did not have access to the classification of liquid crystals which was largely developed during the 1960s and 1970s, and which is still evolving, their work was nevertheless remarkable.

It is a sobering thought that of all scientists that have ever worked, most are still alive, and we are all aware of the massive increase in the volume of published literature in science alone. From our point of view as liquid crystal scientists the situation is no different, and figure 2 shows the growth of the number of liquid crystalline materials since the beginning of the century. Thus, while it becomes increasingly troublesome to keep up with the current literature, it is even more difficult to develop a proper appreciation of all that has gone before—in some cases, many years before.

Proper regard for history is a most important aspect of the development of thinking and progress. Societies try to learn the lessons of their past and so, hopefully, do scientists. It is perhaps an indication of the place that history holds, that societies have adopted phrases which counsel us to keep it in mind. Thus, in English we speak of there being 'Nothing new under the sun', while Germans say 'Nichts Neues unter der Sonne'. Another phrase which reminds us of the importance of history, cautions us to beware of 're-inventing the wheel'. What follows is Vorländer's Wheel.

Figure 1. Number of liquid crystal materials reported by Vorländer and in total in each year from 1900 to 1950.

*Authors for correspondence.
† Dedicated to Professor Hans Paulsen on his 75th birthday.

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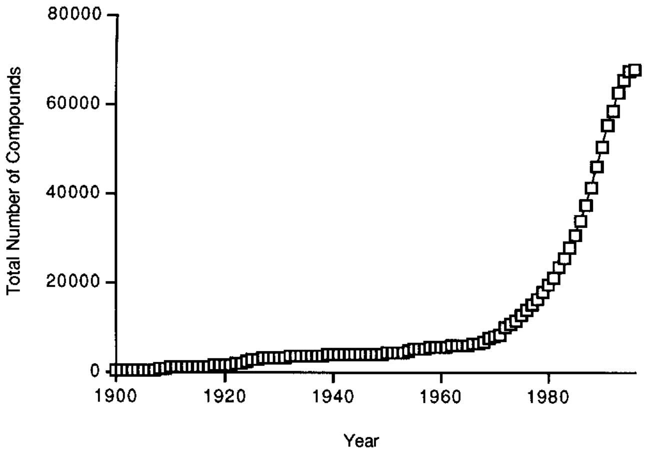

Figure 2. Representation of the total, cumulative number of liquid crystal compounds known by year.

2. Historical background

Although the first discovery of liquid crystals is often ascribed to Reinitzer's work with cholesteryl esters published in 1888 [2], it can in fact be traced back to the 1850s with the observation of birefringent textures in nerve myelin by Virchow [3] and to Heintz's work on magnesium tetradecanoate [4]. Nevertheless, before Vorländer's work began, there was relatively little in the literature about liquid crystals, and certainly nothing particularly systematic.

Vorländer was born on the 11th of June, 1867 in Eupen and died just before his 74th birthday on the 8th of June, 1941, in Halle. He arrived in Halle in 1890 to take his PhD and spent his whole working life there, holding the position of Ordinarius für Chemie from 1908 to 1935. 'Ordinarius' is roughly equivalent to Full Professor, except that there would be one only for chemistry; hence, such people were rather important and not ordinary at all! His interest was in aromatic compounds, and in particular, azo coupling reactions. 4-Azoxyanisole (PAA) had been synthesized by Gattermann and Ritschke [5] in 1890 and had been found to be a liquid crystal material. Vorländer was intrigued by the fact that a molecule so similar to those in which he was interested could be liquid crystalline and in 1902, he found that his own material, azoxybenzoic acid diethyl ester was also mesomorphic. From this point on, liquid crystals became more important in Vorländer's work.

One of us (KH) had Vorländer as his external examiner for his PhD thesis and remembers him well. He was the principal teacher of organic chemistry for all science students in Halle, and held the lecture to be a rather special event, being more than a simple 'service' to the students. Thus, each lecture was accompanied by a demonstration and for example, in a lecture on aromaticity, he would take a flask filled with benzene, add aqueous potassium permanganate and shake. The flask would be 'centre stage' and illuminated with light. Of course, then as now, there was no change in colour in contrast to flasks containing either cyclohexene or aliphatic olefins.

The Leopoldina is an important scientific society in Halle. Once, Professor Emil Abderhalden gave a seminar on the subject of peptides, and Vorländer was asked about possible melting anomalies and mesomorphic behaviour of peptides. Indeed, Abderhalden asked his co-workers wherever possible to record both the temperature of 'Sintern' (meaning the temperature at which shrinking is seen) and the melting point, suggesting that Abderhalden was already considering the possibilities of mesomorphic behaviour in such compounds. Thus, Vorländer was asked about *natural* compounds such as peptides and sugars and we know nowadays that such natural compounds can give rise to liquid crystals. Why then, did Vorländer not check these materials? At this time, all those holding an Ordinarius position had their own field of research. Abderhalden was Ordinarius for physiological chemistry in Halle and it was he who studied peptides and sugars. Vorländer, however, was Ordinarius for chemistry and studied aromatic compounds and liquid crystals, but he never wanted to touch the research area of Abderhalden, a fellow Ordinarius. Thus, biosystems are absent from Vorländer's work. Vorländer similarly felt that others should not encroach on his intellectual territory. Thus, in an article with Selke [6], Vorländer heavily criticized Friedel as a 'physicist introducing new nomenclature', by calling the well-known 'Schlierenphasen' (schlieren phase) 'nematic', and *his* 'Stäbchenphasen' (rod-phases) 'smectic'. He then wrote dismissively, hoping that all those who start in a new area do not all introduce their own nomenclature. For those able to read the original text, the language is rather unequivocal!

3. Vorländer's work

A lot of Vorländer's work concentrated on two-ring mesogens (figure 3) and, for example, he made about

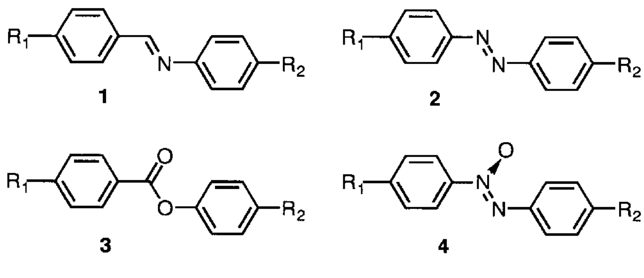

Figure 3. Examples of two-ring mesogens synthesized by Vorländer.

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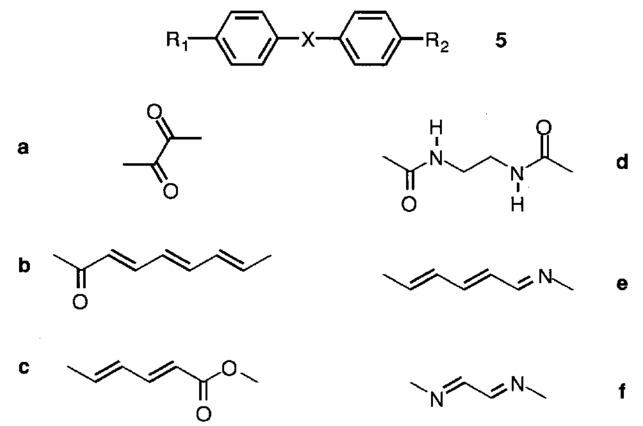


Figure 4. Examples of linking groups used by Vorländer in two-ring mesogens.

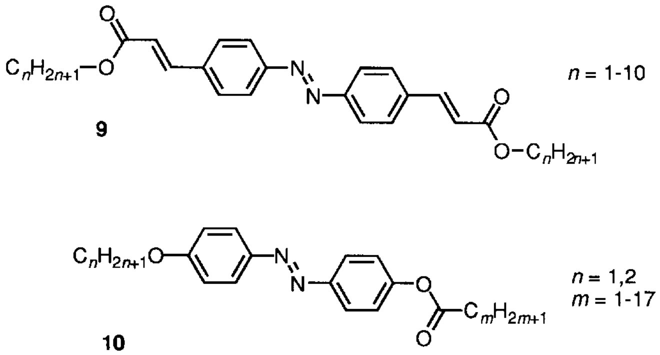


Figure 7. Examples of homologous series.

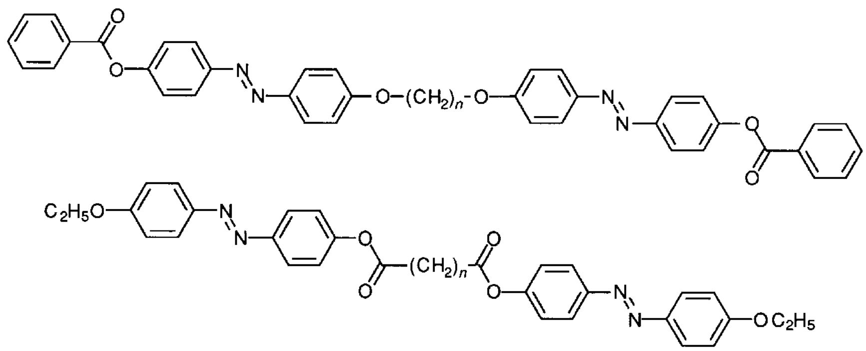
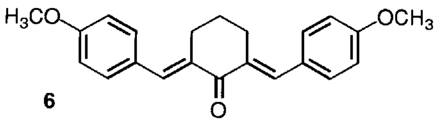


Figure 5. Flexibly linked dimers.



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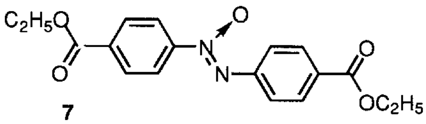
Cr • 160 • X • 173 • I Ref [8a]

Cr • 161 • N • 174 • I Ref [8b]



7

Cr • 114 • X • 124 • I Ref [8c]

Cr • 116 • SmA • 123 • I Ref [8d]

Cr • 173 • N • 269 • I Ref [8e]

Cr • 179 • N • >300 d Ref [8f]

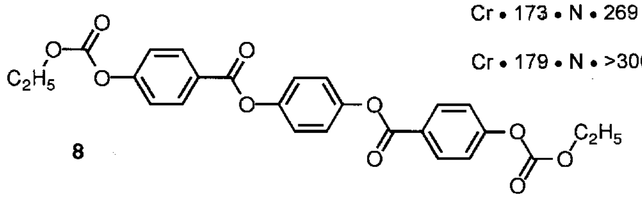


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Figure 6. Examples of transition temperatures and phase sequences determined by Vorländer in different mesogens.

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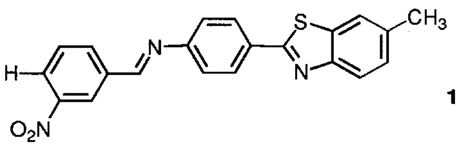

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Cr (• 172 • N) • 200 • I

Figure 8. Example of a heterocyclic mesogen.

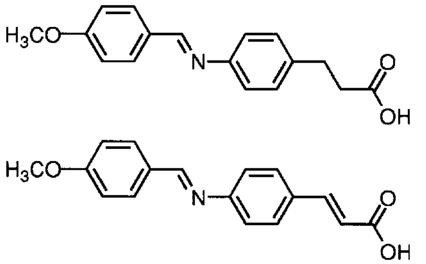

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Figure 9. Examples of hydrogen-bonded mesogens.

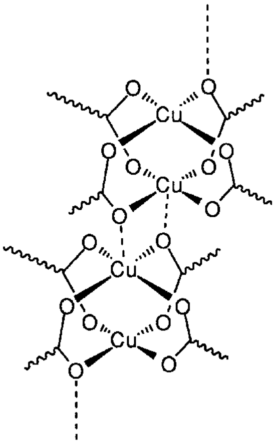
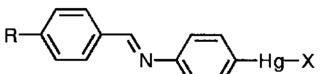


Figure 10. Structure of copper soaps.



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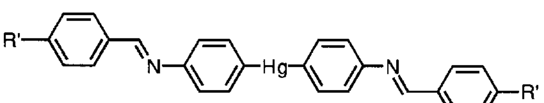
R = H, OMe,

X = Cl, Br, I, OAc



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R' = H, NO_2, Me, MeO, EtO

Figure 11. Mercury-based mesogens.

170 benzylideneanilines (**1**), 150 azobenzenes (**2**), as well as numerous benzoates (**3**) and azoxy compounds (**4**). These short linking groups gave rise to a number of mesomorphic materials, but Vorländer also examined the potential offered by more extended and often esoteric linking groups, as shown by the examples of X groups in figure 4. As part of these studies, he synthesized the earliest examples of flexibly linked dimers, two examples of which are shown in figure 5 [7]. He was also responsible for the first Siamese twin molecules.

What was also remarkable about Vorländer's work was the accuracy of the transition temperatures which he was able to determine, along with smectic-smectic transitions and monotropic phase behaviour. Clearly, the work was carried out with extreme care. A few selected examples are given in figure 6 [8].

In addition, he pioneered the synthesis of homologous series of compounds, for example with the series shown in figure 7. The use of heterocycles was also a feature of Vorländer's work, and in the example in figure 8 there is also a lateral nitro group; other lateral groups were also studied by Vorländer [9] and he reported work on over 150 of these [10].

More than 200 mesogenic, hydrogen-bonded systems were made by Vorländer and co-workers, ranging from the very simple alkoxybenzoic and cinnamic acids [11, 12] to more systematic work on more complex cinnamic acids (figure 9, **12**, **13**) [13, 14]. This area is enjoying something of a renaissance, and has recently been reviewed [15].

Thermotropic ionic mesogens were another feature of Vorländer's work, and he reported work on over 150 of these, from the very simple sodium carboxylate soaps (later studied in depth by Skoulios), through their derivatives with other Group 1 metals and thallium, and again, using the same metals, with structurally more complex carboxylates derived from substituted benzoic and naphthoic acids. Numerous ammonium salts were also studied, as were the first examples of copper soaps (figure 10), later extensively characterized by Giroud-Godquin and collaborators [16]. These, therefore, are early examples of materials forming columnar phases, which are discussed in more detail below.

This use of metals, albeit as simple counter ions in the soaps, signalled some of the first mesogens now

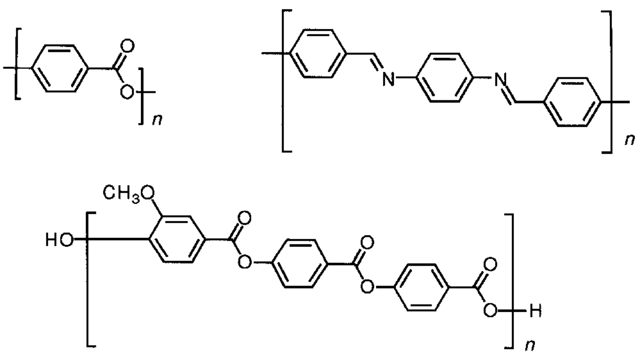

Figure 12. Mesogenic polymers.

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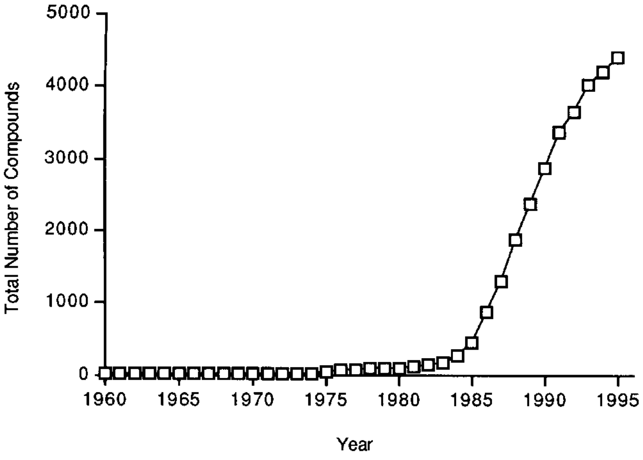

Figure 13. Growth in number of SmC* materials since 1960.

commonly known as *metallomesogens* [17]. In addition to these rather simple derivatives, Vorländer also synthesized a number of mercury compounds, some of which are shown in figure 11 [13, 18].

Although side group liquid crystal polymers are a more recent development [19], main chain systems have been around much longer, and once more Vorländer had a significant contribution to make (figure 12) [20, 21]. Vorländer named the polymers shown in figure 12, 'suprakristallin' or 'unmeltable', because they did not melt. However, one liquid crystal polymer which did melt was found in a PhD thesis [21]. Further, it is noteworthy that Vorländer thought about LC polymers at about the same time that Staudinger was starting polymer science in Freiburg. Vorländer wrote [22]:

> What happens to the molecules if they are elongated further and further? Will the liquid crystalline property

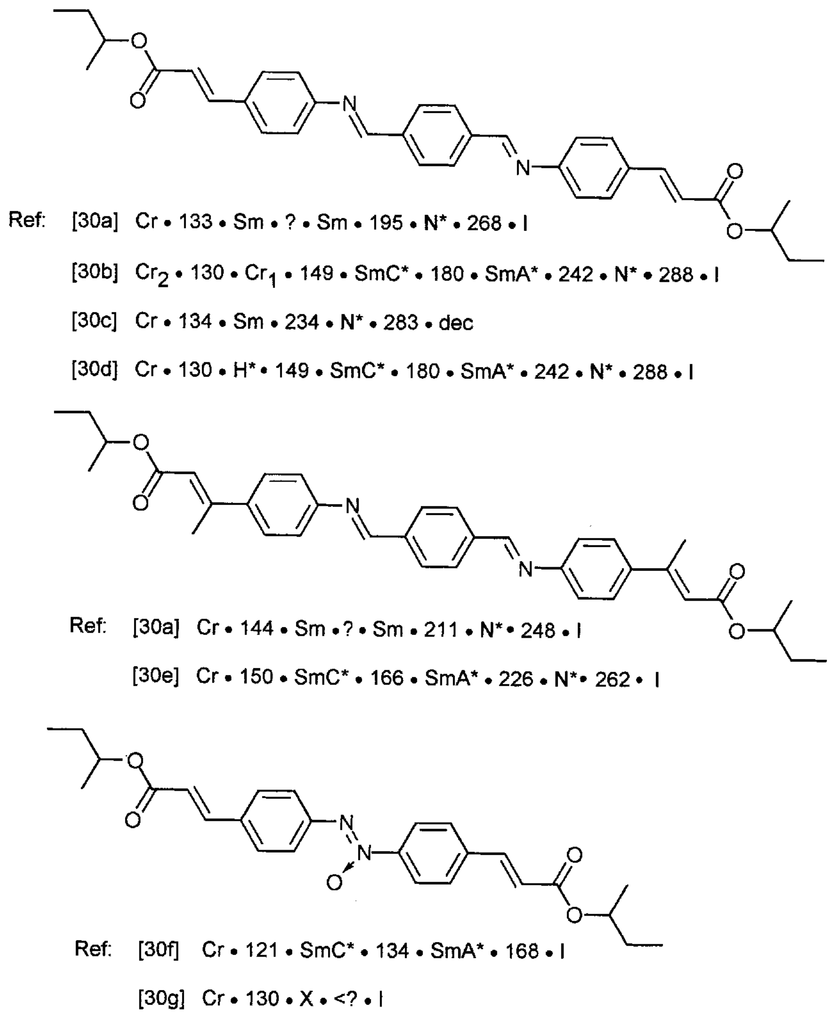

Figure 14. Early ferroelectric materials.

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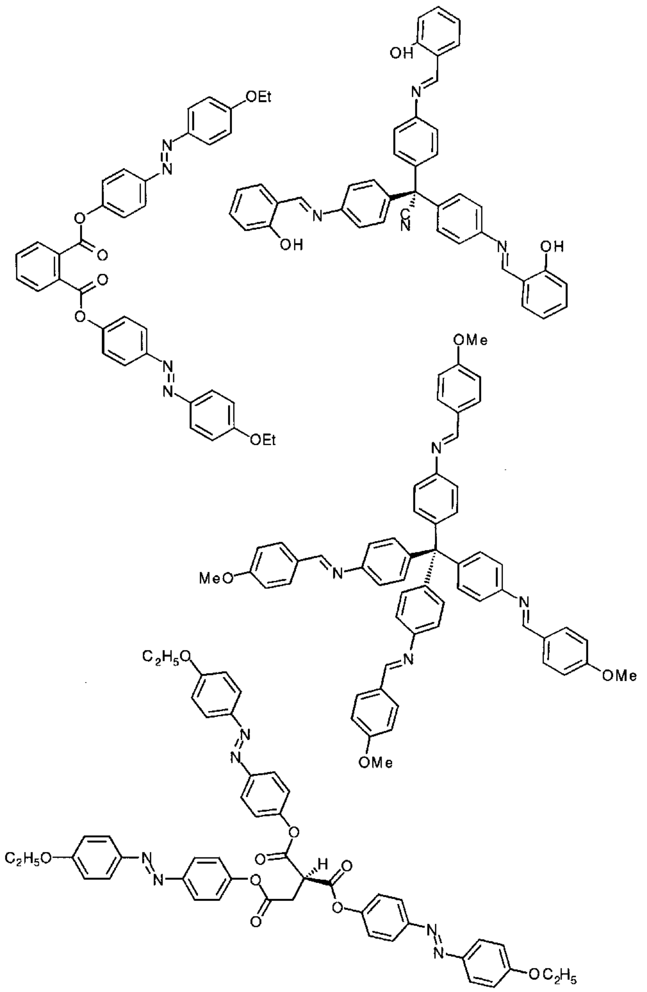

Figure 15. Some unconventionally shaped mesogens synthesized by Vorländer.

eventually disappear? According to my experience, a limit for such a state given by elongation of the chains is not at hand. However, it may happen that the compounds no longer melt without decomposition, or cannot be observed under the microscope. [Was geschieht mit den Molekülen, wenn man sie immer weiter und weiter verlängert? Wird der kr. fl. Zustand schließlich verschwinden? Nach meinen Erfahrungen ist eine Grenze für diesen Zustand bei der Verlägnerung der Ketten nicht vorhanden, es sei den, dass schließlich die Substanzen nicht mehr unzersetzt schmelzen und nicht mehr zu mikroskopieren sind.]

The history of columnar phases is interesting. Clearly, they had been known at least since the 1950s with the work of Skoulios on calcium soaps. However, the phases became more widely recognized in 1977 when Chandrasekhar *et al.* reported [23] the synthesis and mesomorphism of hexa-esters of hexahydroxybenzene. He termed the phase of these molecules 'discotic'. The issue was further complicated by the observation that an entirely different class of mesogen, the polycatenar systems [24], also showed columnar phases, which were labelled ϕ. Clearly, phases ought to be characterized by their symmetry, and hence we might consider all three types of systems as similar, i.e. columnar. And, might we guess who made them first? Vorländer, of course. He reported [25] (essentially correctly) the melting point of triphenylene itself as 196°C (actually 200°C), although he did not find the monotropic columnar phase at 55°C [26]. He also reported mesomorphism in sodium diphenylacetate [27], which was later found to be columnar [28].

Ferroelectric materials have seen increasing importance and interest since the demonstration of a device configuration by Clark and Lagerwall in 1980 [29]. Indeed, figure 13 shows the increase in the number of ferroelectric materials in the literature since 1960. Of course, we should now expect that Vorländer would have been involved somewhere and figure 14 shows his early contributions [30].

Finally, we might marvel at the imagination exercised by Vorländer in the molecular shapes of the compounds synthesized (figure 15). Of particular interest here are those based on a tetrahedral carbon (related derivatives were not synthesized until relatively recently [31]) and those on phthalic acid [32]. These latter complexes are of significance due to the related structures made in hydrogen-bonding systems [33] and by the observation of a ferroelectric effect in non-chiral phthalate derivatives [34].

4. Conclusion

By way of conclusion, we would simply wish to pay tribute to the pioneering work of Vorländer, a scientist of tremendous ability and imagination whose work, in many ways, is only now coming to be recognized. It was Winston Churchill who once said: 'The farther backward you can look, the farther forward you are likely to see'. On this point at least, we can agree with him and cite the work of Daniel Vorländer as a shining example of where this is true.

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