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Berichte der Deutschen Chemischen Gesellschaft **40**, 1970–72 (1907)

266. D. Vorländer: Einfluß der molekularen Gestalt auf den krystallinisch-flüssigen Zustand.

[Mitteilung aus dem chem. Institut der Universität Halle.]

(Eingegangen am 18. April 1907.)

Obgleich die zahlreichen krystallinisch-festen und krystallinisch-flüssigen Isomeren sich einstweilen nicht den verschiedenen Arten von Stereoisomerie und Strukturisomerie unterordnen lassen, so ist doch die molekulare Struktur neben anderen Faktoren von Bedeutung für den krystallinisch-flüssigen Zustand. Die bisher erhaltenen Resultate[1]) deuten darauf hin, daß der krystallinisch-flüssige Zustand durch eine **möglichst lineare Struktur des Moleküls** hervorgerufen wird.

1. Von den Benzolderivaten haben nur die Para-Disubstitutionsprodukte eine geradlinige Struktur. Man findet dementsprechend die krystallinisch-flüssigen Substanzen bei diesen und nicht bei den *m*- und *o*-Derivaten, wo die Substituenten mit Bezug auf den Mittelpunkt des regulären Benzolsechsecks einen spitzen oder stumpfen Winkel bilden.

2. Sobald zu den beiden Para-Substituenten ein dritter Substituent hinzutritt, wird die Gerade geknickt bezw. verzweigt und der krystallinisch-flüssige Zustand damit verhindert. Die auffallendste Regelmäßigkeit dieser Art fand ich bei den Aldehydderivaten: nur die des **Para-Oxybenzaldehyds** sind krystallinisch-flüssig, und wenn ein zweites OR hinzukommt, so hört der krystallinisch-flüssige Zustand auf. Auch die **Furfurolverbindungen** sind trotz des Sauerstoffgehaltes, der starken Färbung und großen chemischen Aktivität nicht krystallinisch-flüssig. Die Beziehungen gelten in der Reihe der **Azine** aus Anisaldehyd, Piperonal, Veratrylaldehyd, Furfurol ebenso wie bei den Arylidenaminen, Zimtsäuren und den ungesättigten Ketonen aus denselben Aldehyden, sind also keinesfalls zufällige. Durch Methyl in Kresolderivaten und durch Einführung von Naphthalin an die Stelle des Benzols wird der krystallinisch-flüssige Zustand gehindert, doch nicht ganz aufgehoben.

3. Je mehr die Struktur nach der Länge des Moleküls ausgedehnt wird, um so günstiger ist sie für den krystallinisch-flüssigen Zustand. Die Verbindungen $RO.C_6H_4.N:N.C_6H_4.OR$ oder $RO.C_6H_4.CH:N.C_6H_4.COOH$ u. a. sind im Gegensatz zu den kürzeren $RO.C_6H_4.N:N.C_6H_5$ und $RO.C_6H_4.CH:N.C_6H_5$ krystallinisch-flüssig. Befindet sich eine der endständigen Gruppen OR in *m*- oder

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[1]) Diese Berichte 40, 1415 [1907]; 39, 803 [1906].

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INFLUENCE OF MOLECULAR CONFIGURATION ON THE CRYSTALLINE-LIQUID STATE

D. Vorländer
[Contribution from the Institute of Chemistry of the University of Halle]
(Accepted 13 April 1907)

The numerous crystalline-solid and crystalline-liquid isomers cannot at the moment be classified in terms of different types of stereoisomerism and structural isomerism. However, it is certain that the molecular structure, in addition to other factors, is extremely important to the crystalline-liquid state. All results obtained so far[1] suggest that the crystalline-liquid state results from a molecular structure which is as linear as possible.

1. Amongst the benzene derivatives only *para* disubstitution products possess a linear structure. Accordingly one only finds crystalline-liquid substances in these cases and not with *meta*- and *ortho*-derivatives, for which the substituents form an acute or obtuse angle with respect to the centre of the regular benzene hexagon.
2. Whenever a third substituent is added to both *para*-substituents the straight line will be kinked or branched, and so the crystalline-liquid state prevented. I found the most striking regularity of this kind in the case of aldehyde derivatives: only the *para*-oxybenzaldehydes are crystalline-liquid, and if a second OR is added the crystalline-liquid state is prevented. Furthermore the fufuryl compounds are not crystalline-liquid despite the oxygen content, the strong coloration and the large chemical activity. These relationships are valid for the series of azines of anisaldehyde, heliotropin, veratryl aldehyde and fufural, in the same way as the arylidene amines, cinnamic acids and the unsaturated ketones of the same aldehydes. They are thus by no means fortuitous. As a result of the methyl group in cresol derivatives and by the

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[1] This journal **40**, 1415 (1907); **39**, 803 (1906).

introduction of naphthalene instead of benzene, the crystalline-liquid state will be hindered but not totally excluded.

3. The more the structure is extended with respect to the length of the molecule the more the crystalline-liquid state will be favoured. The compounds $RO.C_6H_4.N:N.C_6H_4.OR$ or $RO.C_6H_4.CH:N.C_6H_4.COOH$ and others are crystalline-liquid in contrast to the shorter compounds $RO.C_6H_4.N:N.C_6H_5$ and $RO.C_6H_4.CH:N.C_6H_5$. If one of the terminal OR groups is located in the *m*- or *o*-position, the crystalline-liquid phase will be destroyed (cf. 1). These relations could be attributed also to an unsymmetrical energy distribution.[1]
4. As a result of branching of the carbon skeleton, the α-substitution products of *p*-methoxycinnamic acid[2] are not themselves crystalline-liquid, whereas the acid, according to van Romburgh,[3] exhibits an enantiotropic crystalline-liquid phase. The liquid-crystalline properties are absent in the case of α-bromo-,[4] methyl-, ethyl-, phenyl- and even for α-oxyethyl-*p*-methoxycinnamic acid (m. p. 115 °C; prepared from anisaldehyde and ethoxy ethyl acetate).
5. Comparing normal valeryl- with isovaleryl-cholesterol, F. M. Jäger[5] has found that the range of existence of the crystalline-liquid phase is very small in the case of the branched isovaleryl but large for normal valeryl. Such an effect of branching, however, is not always observable, in which case perhaps it is of less influence in comparison with the predominantly linear shape of the other molecular parts (e.g. acyloxybenzalazine).
6. No crystalline-liquid phases exist in the case of compounds with free hydroxyphenol. Due to tautomerism or a shift and transposition of a hydrogen atom, an uncertainty exists with respect to the energy distribution, which allows the molecules to adopt any arbitrary position with respect to each other, and hence no definite direction. Elimination of the tautomeric hydrogen by alpha-substitution or acylation allows the molecules to achieve the stability necessary for the formation of the crystalline-liquid phase. Amongst all the alpha-substituents, ethyl exhibits the longest linear structure and it also possesses in comparison with other radicals a particularly favourable liquid-crystalline effect (e.g. with azoxybenzoate). However, one has scarcely any idea about the different influence of aryls and the various acyls.

The chemical investigations in this field are consistent with opinions which O. Lehmann advocated for many years.[6] According to Lehmann the origin of the

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[1] Ann. d. Chem. **341**, 1 (1905).

[2] cf. the preceding paper (Ber. Dt. Chem. Ges. **40**, 1415 [1907]) (*ed.*).

[3] Verhandl. Akad. d. Wissenchaften, Amsterdam **1900**.

[4] By removing hydrogen bromide from methoxycinnamic acid dibromide with sodium alcoholate, John Hulme obtained two monobromided methoxycinnamic acids, one of which was crystalline-liquid.

[5] Rec. Trav. Chim. **25**, 344 (1906).

[6] Wied. Ann. d. Physik **40**, 410, 412, 422 (1890); ibid. (4) **8**, 917 (1902); **20**, 77 and **21**, 383 (1906). Kosmos **1907**, 9.

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existence of the crystalline-solid and crystalline-liquid modifications does not depend on the nature of molecular aggregation, but on the constitution of the molecules themselves, and hence on their structural modifications. The birefringence of the crystalline-liquid state is caused by the anisotropy of the molecule. He compares the molecules of crystalline liquids with pieces of wire or lamellae which all orient themselves in parallel direction on shaking, whereas the molecules of amorphous isotropic liquids are spherical.

The results given above indeed seem to me to contain experimental evidence for his theory. From the linear shape of the molecules follows their parallel orientation and hence the anisotropy of the liquid. However, if the shape is jagged, as in the case of *m*- and *o*-derivatives, or branched in another way, then the molecules will rotate. They will then adopt arbitrary positions with respect to each other or become spherical in some other way, and then appear to be isotropic. The anisotropy of the molecule will be illustrated to a certain extent by the structural formula of the crystalline-liquid substances.

The chemical structure must be as uniaxial as possible. In the case of crystal drops, the uniaxiality of liquid crystals follows from the well-known investigations of Lehmann,[1] and from the appearance of pseudoisotropy, first observed by Lehmann,[1] in mixtures of superheated substances.[2] According to Lehmann, pseudoisotropy in liquid crystals is analogous to solid crystal plates, which have been cut in a plane perpendicular to their optical axis, and then viewed in the direction of the axis. The uniaxiality of crystalline-liquid rods follows from my detection of liquid crystals,[3] probably tetragonal , with straight edges and angles.

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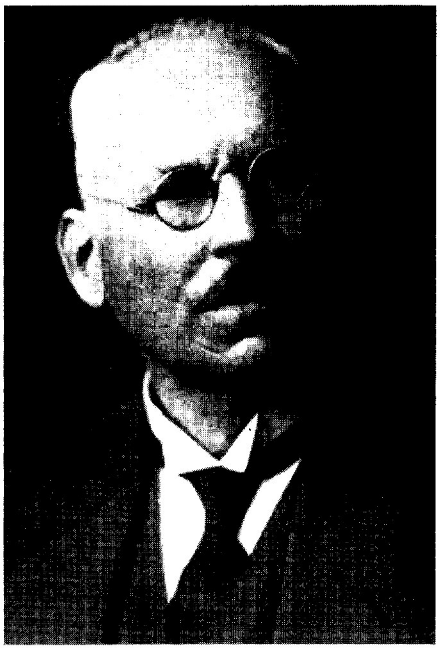
[1] O. Lehmann. Flüssige Kristalle, Leipzig (1904).

[2] Pseudoisotropy of pure homogeneous compounds: Vorländer, Ztscr. physik. Chem. **57**, 360 (1906).

[3] ibid., p. 363.



Daniel Vorländer was born in Eupen, near Aachen in Germany in 1867. His father owned a dyeworks but was in addition a keen amateur linguist. Daniel attended school in Dresden, where the family lived after 1871. He began university study in chemistry in Kiel in 1886, moved to Munich in 1887, and graduated in Berlin, specialising in organic chemistry, in 1890. He then obtained a graduate post at the University of Halle, obtaining his Habilitation degree in 1896. He was then successively promoted in Halle, until in 1908 he became a full professor and director of the Chemical Institute. He also saw active service in the 1914–18 war before returning to Halle in 1917. He directed the studies of a very large number of doctoral students, the most famous being the Nobel prize winner Hermann Staudinger. Vorländer served as Vice-President of the Deutsche Akademie der Naturforscher Leopoldina, the oldest academy in the world. He retired in 1935.

In all he published 214 academic papers, on a wide variety of subjects ranging from inorganic chemistry to natural product chemistry. However, after 1906 and until the end of his career, liquid crystals were his primary interest. By the time of Vorländer's death in 1941, the 35 liquid crystalline compounds known at the start of his liquid crystal work had grown to 1050 whose properties had been catalogued, with the number observed considerably higher. A collection of his liquid crystalline samples remain stored in the Institute of Physical Chemistry in Halle.