

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Some remarks on the evolution of research into the structures of mesogens and mesophases

Jean Billard

Online publication date: 06 August 2010

To cite this Article Billard, Jean(1998) 'Some remarks on the evolution of research into the structures of mesogens and mesophases', *Liquid Crystals*, 24: 1, 99 – 104

To link to this Article: DOI: 10.1080/026782998207622

URL: <http://dx.doi.org/10.1080/026782998207622>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Some remarks on the evolution of research into the structures of mesogens and mesophases

by JEAN BILLARD

Laboratoire de Physique de la Matière Condensée, Collège de France,
Place Marcelin Berthelot, 75005 Paris, France

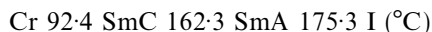
*Presented at the Capri Symposium in Honour of George W. Gray, FRS held at the
Hotel Palatium, Capri, 11–14 September 1996*

Research on mesogens and mesophases began with the surprising observation of a fluid and birefringent phase formed by a pure compound having a calamitic (rod-like) molecule. The structures of the smectic A, nematic and cholesteric phases which emerged after this discovery were elucidated essentially by observations with a polarizing microscope. Smectic polymorphism was also established by microscopic observations. The main historical results on the structures of the different smectic mesophases are listed here. The discotic mesophase, previously predicted theoretically, was then obtained and its polymorphism observed. A further type of purposely designed mesophase was the pyramidal type, also exhibiting a rich polymorphism. Research on mesogens and mesophases is a field in continuous expansion.

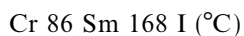
1. The beginnings

In many textbooks, following Aristotle, only three states of matter—solid, liquid and gas—are distinguished. But in 1888, Reinitzer [1] observed [2] a surprising fluid and birefringent phase in a pure compound, cholesteryl benzoate. Lehmann [1, 3, 4] studied this phase, as well as the birefringent and fluid phase of *p*-azoxyanisole, synthesized by Gattermann [1, 5], and another birefringent and fluid phase with a clearly different texture, namely that of ethyl *p*-azoxybenzoate synthesized by Meyer and Dahlen [6]. Vorländer [1] remarked that all the compounds exhibiting such fluid and birefringent phases had elongated molecules [7], now called calamitic molecules from *χαλαμοζ* (*reed*) [8].

The structures of the nematic, smectic A and cholesteric mesophases were elucidated by Friedel [1] in 1922, essentially from observations made with a polarizing microscope [9]. A remark may be made that Friedel used in his studies *n*-octyl *p*-azoxycinnamate [10], first synthesized by Vorländer [11] in 1906 and found later to exhibit smectic polymorphism [12]:



But Georges Friedel, who did not take smectic polymorphism into account, possibly confused the smectic–smectic transition with texture changes within a single phase. For the sample used, the temperatures indicated by Friedel were:



and another possibility was that this sample was too impure to exhibit the two smectic mesophases.

In the developing history of intermediate phases between the solid and the liquid, it is noted that in 1938 Timmermanns [13] found new mesophases, named plastic crystals, exhibited by compounds having globular molecules.

2. Smectic polymorphism

After a long silence, resulting from World War II, a new era for research on mesogens and mesophases began. Organic chemists, particularly George Gray, elaborated many new mesogens. The Halle School, directed by Sackmann [1], established clearly the occurrence of smectic polymorphism, formulated the miscibility rules and used the method of isobaric phase diagrams for binary mixtures (constructed from microscopic observations) to identify different mesophases [14]. With two compounds synthesized by George's team [15], the Halle group also discovered the optically isotropic mesophase named at that time the smectic D modification [16] and now cubic A (CubA) [17]. Chemical rules were then progressively elaborated to obtain mesogens having particular properties.

The structures of the polymorphic smectic mesophases were progressively obtained (see the table): SmC in 1969 by Chistyakov and Chaikowsky [18], SmB in 1971 [19] and, in 1972, the crystal G [20] and E phases [21]. The structures of crystal H [22] and SmI [23] were found in 1974 and of the above mentioned cubic A phase in 1976 [24]. This last mesophase is one of the four non-chiral cubic thermotropic mesophases [17] known today. The structure of the smectic F mesophase was

Table. History of the elucidation of the structures of the smectic mesophases.

Year	Smectic	Authors	Ref.
1922	A	G. Friedel	[9]
1969	C	I. G. Chistyakov, W. M. Chaikowsky	[18]
1971	B	A. M. Levelut, M. Lambert	[19]
1972	G	A. de Vries, D. L. Fishel	[20]
1972	E	S. Diele, P. Brand, H. Sackmann	[21]
1974	H	J. Doucet, A. M. Levelut, M. Lambert	[22]
1974	I	A. M. Levelut, J. Doucet, M. Lambert	[23]
1976	D	A. Tardieu, J. Billard	[24]
1978	F	J. Doucet, P. Keller, A. M. Levelut, P. Porquet	[25]
1983	J, K	P. A. C. Gane, A. J. Leadbetter, P. G. Wrighton, J. W. Goodby, G. W. Gray, A. R. Tajbakhsh	[26]
1983	O, Q	A. M. Levelut, C. Germain, P. Keller, L. Liebert, J. Billard	[27]

obtained in 1978 [25]. In 1983 two laboratories, including George's, discovered the structures of the crystal J and K phases [26]. Also in 1983 the structures of the smectic O and Q mesophases [27] were elucidated.

It is noted here that at the time of their discovery, the crystal G, E, H, J and K phases were classified as smectic, but because of their three-dimensional order, they are now accepted (IUPAC recommendations) as soft crystal phases, closely related to the true smectics.

3. The first non-accidentally obtained mesophases

After the successes obtained with calamitic and with globular molecules, theoretical considerations predicted that another sort of mesophase with molecules having a different form could be obtained. The most simple form after the elongated ellipsoid and the sphere is the flat ellipsoid. With hexahydroxybenzene-*n*-alkanoates (figure 1) Chandrasekhar's team obtained, in 1977, mesophases with short temperature ranges where the molecules were stacked in columns having a hexagonal packing [28]. A French group then synthesized two hexa-alkoxy derivatives of triphenylene (figure 1) exhibiting more stable mesophases, named at the time discotic from $\delta\iota\sigma\chi\omicron\zeta$ (*quoit*). Similarly to the smectic A phase, the structure in the columns of this discophase was established from microscopic observations [29]. These compounds were synthesized with the primary objective of obtaining discophases. After these successes we might observe [8] that hexahydroxybenzene heptanoate had been previously synthesized in 1937 [30], but the mesophase was not detected. Also it should be remembered that di-isobutylsilandiol, first prepared in 1952 [31], has

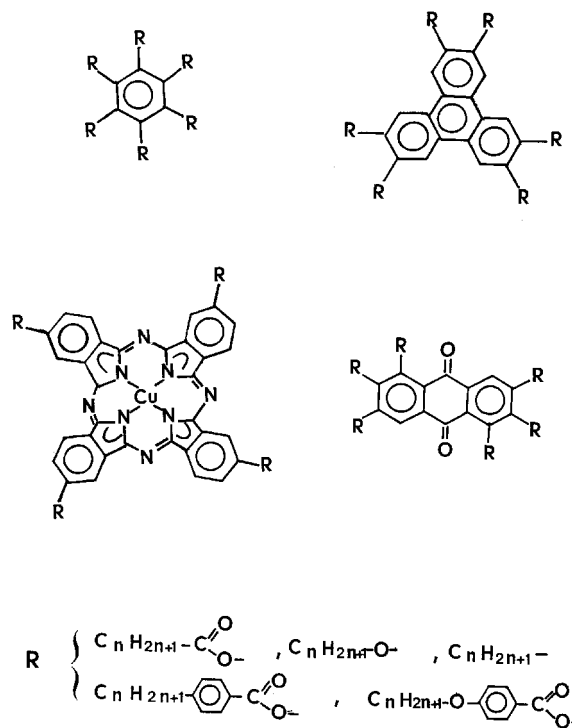


Figure 1. Some central cores of discogens having hexagonal, trigonal, tetragonal and binary symmetries. Hexagonal and trigonal symmetries are represented here by hexahydroxybenzene and triphenylene derivatives, respectively.

a mesophase which was studied in 1955 [32], but identified as discotic only in 1980 by George's group [33].

Contrary to the calamitic mesogens, it is possible for discogens to have a more diversified symmetry (figure 1) of the molecules: for example hexagonal, trigonal, tetragonal or binary. These possibilities were rapidly exploited and a rich discotic polymorphism was obtained [34, 35], including a discophase where the order is only the average parallelism of the molecular planes (figure 2) [36]. By X-ray diffraction observations, the structures of the different columnar organizations were established more precisely. However by microscopic observations alone, new data can often be obtained. For example, discogens with two-fold symmetry can exhibit a layered structure of columns and, consequently, the appearance of Grandjean's [37, 38] terraces [39]. The molecules are assembled (figure 3) in columns with two-fold symmetry; the axes of the columns are perpendicular to the plane of the figure. The ellipses represent the central cores of the molecules and the wavy lines represent the aliphatic chains. These two regions are then stratified.

More sophisticated discophases have also been obtained, for example with molecules having two disc



Figure 2. Washers used as models for the molecules of a fluid discophase. In this phase the molecular order is only the average parallelism of the molecular planes.

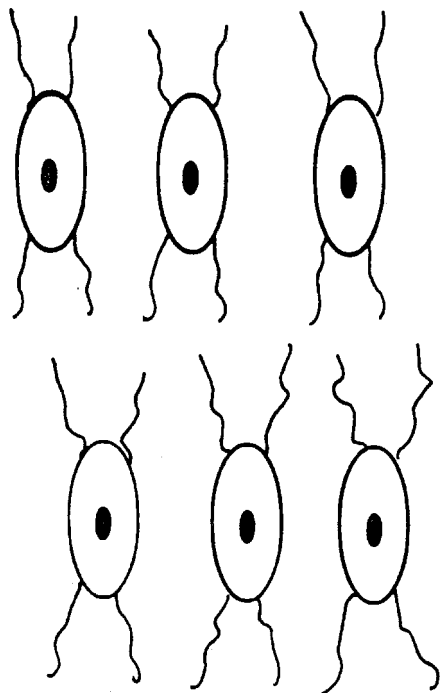
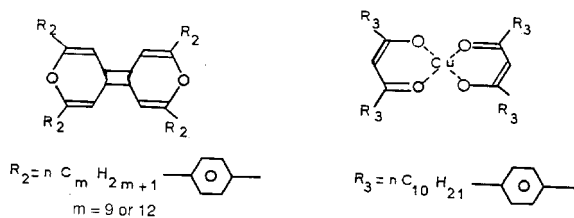


Figure 3. At the top are the structures of two discogens with two-fold symmetry which exhibit mesophases with a columnar and layered structure. The flat molecules with two-fold symmetry assemble in columns with binary symmetry; the axes of the columns are perpendicular to the plane of the figure. The ellipses represent the central cores of the molecules and the wavy lines represent the aliphatic chains. These two parts are stratified [39].

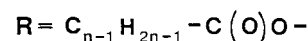
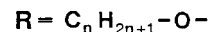
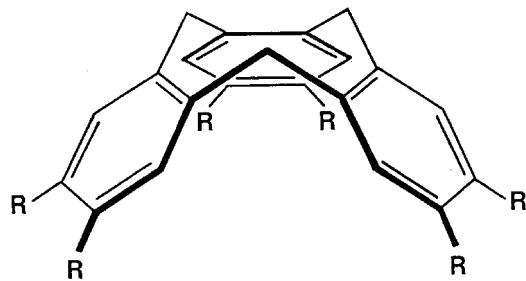


Figure 4. Non-planar molecules with a pyramid-like central core.

shaped units at the ends of an elongated structure: phasmidic mesophases [40].

4. The second type of mesophase obtained by rational design

To obtain by design another type of mesophase, molecules having a more complex general form (figure 4) were synthesized. These molecules, with aliphatic side chains, are not flat and have a pyramidal central core with a trigonal symmetry. With these compounds, mesophases where the molecules are stacked in columns are again obtained. With only two chemical series, a rich

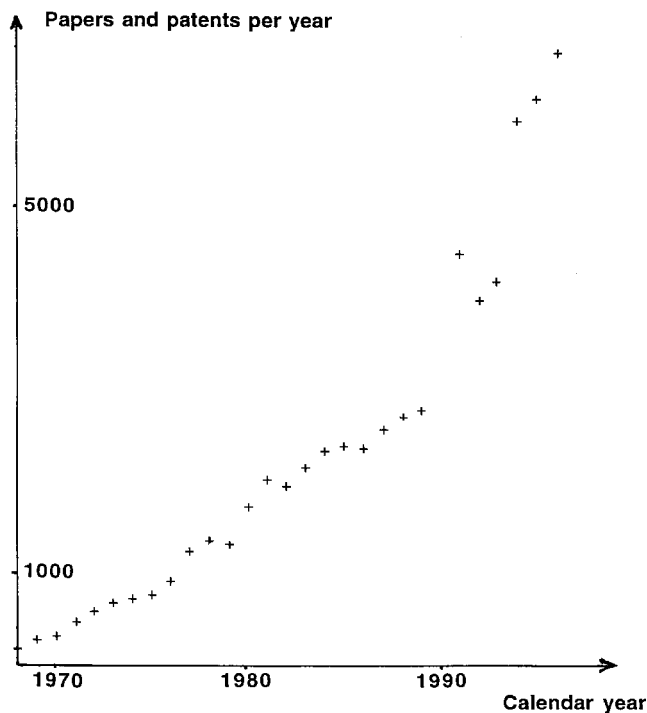


Figure 5. Numbers of papers and patents devoted to mesogens and mesophases per year since 1968.

polymorphism has been observed: five types of these mesophases, named pyramidic from $\pi\nu\rho\alpha\mu\iota\zeta$ (*pyramid*) [41], are known.

5. Conclusion

From the surprising discovery of a fluid and birefringent phase, studies of mesogens and mesophases have evolved strongly: from facts observed by chance, through structure/property rules and on to predictive science.

In the last three decades this field is seen to be increasing in both size and relative importance. The numbers of papers per year has increased continuously since 1968 (figure 5). Can this fact simply be a consequence of the enlargement of the publishing activity of scientists in general? A comparison with the numbers of papers analysed by *Physics Abstracts* (figure 6) establishes however that the proportion of papers on mesomorphism is growing and such papers now represent about 4% of all those published in physics.

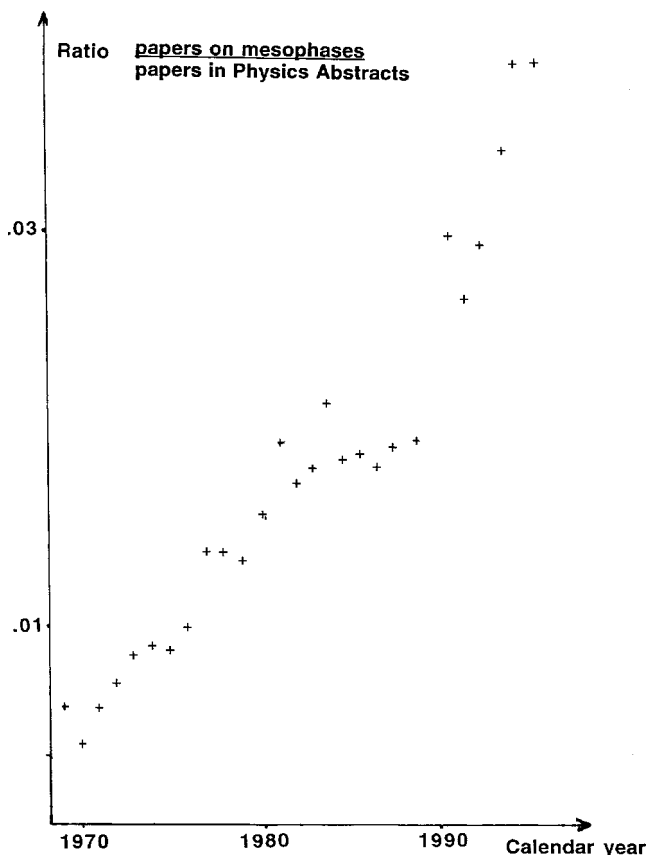


Figure 6. Proportion of papers devoted to mesomorphism. The ratios given here since 1968 are the numbers of publications on liquid crystals selected by *Chemical Abstracts* over the numbers of publications analysed by *Physics Abstracts*.

I thank Professor George Gray for interesting remarks and suggestions.

References

- [1] Portraits of F. Reinitzer and O. Lehmann are in KELKER, H., and KNOLL, P. M., 1989, *Liq. Cryst.*, **5**, 19; of L. Gattermann in KELKER, H., 1988, *Mol. Cryst.*, **165**, 1; of D. Vorländer in KELKER, H., 1973, *Mol. Cryst.*, **21**, 1; of G. Friedel in FRIEDEL, J., 1994, *Graine de Mandarin* (Paris: Odile Jacob) and of H. Sackmann in 1994, *Liquid Crystals Today*, **4**, 1.
- [2] REINITZER, F., 1888, *Monatsh. Chem.*, **9**, 421.
- [3] LEHMANN, O., 1889, *Z. phys. Chem.*, **4**, 462.
- [4] LEHMANN, O., 1904, *Flüssige Kristalle* (Leipzig: Engelmann).
- [5] GATTERMANN, L., and RITSCHKE, A., 1890, *Ber.*, **23**, 1738.
- [6] MEYER, F., and DAHLEN, K., 1903, *Ann. Chem.*, **326**, 331.
- [7] VORLÄNDER, D., 1908, *Kristallinisch flüssige Substanzen* (Stuttgart: Enke).
- [8] BILLARD, J., 1980, *Liquid Crystals of One- and Two-Dimensional Order*, Springer Series in Chemical Physics, part 11, pp. 383–395.
- [9] FRIEDEL, G., 1922, *Ann. de Phys.*, **18**, 273.
- [10] FRIEDEL, G., 1922, *Ann. de Phys.*, **18**, 452.
- [11] VORLÄNDER, D., 1906, *Ber.*, **39**, 803.
- [12] PELZL, G., DEMUS, D., and SACKMANN, H., 1968, *Z. phys. Chem.*, **228**, 23.
- [13] TIMMERMANN, J., 1938, *J. Chim. Phys.*, **35**, 331.
- [14] ARNOLD, H., and SACKMANN, H., 1959, *Z. Elektrochem.*, **63**, 1171.
- [15] GRAY, G. W., JONES, B., and MARSON, F., 1957, *J. chem. Soc.*, 393.
- [16] DEMUS, D., KUNICKE, G., NEELSEN, J., and SACKMANN, H., 1968, *Z. Naturforsch.*, **23a**, 84.
- [17] BILLARD, J., 1987, *C. R. Acad. Sci. Paris II*, **305**, 843.
- [18] CHISTYAKOV, I. G., and CHAIKOWSKY, W. M., 1969, *Mol. Cryst.*, **7**, 269.
- [19] LEVELUT, A. M., and LAMBERT, M., 1971, *C. R. Acad. Sci. Paris B*, **272**, 1018.
- [20] DE VRIES, A., and FISHEL, D. L., 1972, *Mol. Cryst. liq. Cryst.*, **16**, 311.
- [21] DIELE, S., BRAND, P., and SACKMANN, H., 1972, *Mol. Cryst. liq. Cryst.*, **17**, 163.
- [22] DOUCET, J., LEVELUT, A. M., and LAMBERT, M., 1974, *Phys. Rev. Lett.*, **32**, 301.
- [23] LEVELUT, A. M., DOUCET, J., and LAMBERT, M., 1974, *J. de Phys.*, **35**, 773.
- [24] TARDIEU, A., and BILLARD, J., 1976, *J. de Phys.*, **37 C 3**, 79.
- [25] DOUCET, J., KELLER, P., LEVELUT, A. M., and PORQUET, P., 1978, *J. de Phys.*, **39**, 548.
- [26] GANE, P. A. C., LEADBETTER, A. J., WRIGHTON, P. G., GOODBY, J. W., GRAY, G. W., and TAJBAKHSH, A. R., 1983, *Mol. Cryst. liq. Cryst.*, **100**, 67.
- [27] LEVELUT, A. M., GERMAIN, C., KELLER, P., LIEBERT, L., and BILLARD, J., 1983, *J. de Phys.*, **44**, 623.
- [28] CHANDRASEKHAR, S., SADASHIVA, B. K., and SURESH, K. A., 1977, *Pramana*, **9**, 471.
- [29] BILLARD, J., DUBOIS, J. C., NGUYEN HUU TINH, and ZANN, A., 1978, *Nouv. J. de Chim.*, **2**, 535.
- [30] BACKER, H. J., and VAN DER BAAN, S. J., 1937, *Rec. Trav. Chim. Pays-Bas*, **56**, 1161.
- [31] EABORN, C., 1952, *J. chem. Soc.*, 2840.

- [32] EABORN, C., and HARTSHORNE, H., 1955, *J. chem. Soc.*, 549.
- [33] BUNNING, J. D., GOODBY, J. W., and GRAY, G. W., 1980, *Liquid Crystals of One- and Two-Dimensional Order*, Springer Series in Chemical Physics, part 11, pp. 397–402.
- [34] DESTRADE, C., MONDON, M. C., and MALTHÈTE, J., 1979, *J. de Phys.*, **40 C 3**, 17.
- [35] DESTRADE, C., MONDON-BERNAUD, M. C., and NGUYEN, H. T., 1979, *Mol. Cryst. liq. Cryst.*, **49**, 169.
- [36] NGUYEN, H. T., DESTRADE, C., and GASPAROUX, H., 1979, *Phys. Lett. A*, **72**, 251.
- [37] GRANDJEAN, F., 1916, *Bull. Soc. Fr. Min.*, **39**, 164.
- [38] GRANDJEAN, F., 1918, *C. R. Acad. Sci. Paris*, **166**, 165.
- [39] BILLARD, J., 1984, *C. R. Acad. Sci. Paris II*, **299**, 905.
- [40] NGUYEN, H. T., DESTRADE, C., LEVELUT, A. M., and MALTHÈTE, J., 1986, *J. de Phys.*, **47**, 553.
- [41] ZIMMERMANN, H., POUPKO, R., LUZ, Z., and BILLARD, J., 1984, *Z. Naturforsch.*, **40a**, 149.

