

## NEW LIQUID CRYSTALLINE STATES

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SCIENTISTS have discovered a new class of liquid crystalline materials that are solid-like in two dimensions and liquid-like in the third. Since the first observation of liquid crystallinity by Reinitzer in 1888, several thousands of pure compounds have been found to show mesophases. The single characteristic feature common to all these compounds is the rod-like shape of the molecule<sup>1</sup>. The new result that has been established recently is that pure materials composed of relatively simple disc-like molecules may also be mesomorphic. It has formed a major topic of discussion at all International Liquid Crystal Conferences held in the last three years.

The first instance of this new type of mesomorphism was reported in 1977 by scientists of the Raman Research Institute, Bangalore<sup>2</sup>. They prepared a few simple disc-shaped molecules, the hexa-substituted esters of benzene, and looked for their mesomorphic properties. Three of the compounds showed intermediate phases, but the question was: is the intermediate phase a birefringent plastic crystal (a phase that has rotational disorder in two dimensions and a very low plastic yield stress) or is it a true liquid crystal? From detailed thermodynamic, optical and x-ray studies

they concluded that the mesophase is indeed a liquid crystal, but quite different from the classical nematic or smectic types that have been investigated for over 90 years: the discs are stacked aperiodically one on top of the other to form liquid-like columns, the different columns forming a hexagonal array (Fig. 1 *a*). Thus the structure has quantized symmetry translations in two dimensions but not in the third. Sir Charles Frank, University of Bristol, UK, has named this mesophase 'canonic' (Greek *κατων* = rod), Prof. W. Helfrich, Freie Universitat, Berlin, has suggested the term 'columnar', while Prof. J. Billard, College de France, Paris, has proposed the word 'discotic' to describe the molecules as well as the mesophases formed by them.

A number of other discotic systems, *e.g.*, the hexa-substituted esters or ethers of triphenylene<sup>3-5</sup>, were found soon afterwards, notably by the groups working in the laboratories of Thomson-CSF, Orsay (France), College de France and Centre de Recherche Paul Pascal, Talence (France). The basic canonic or columnar structure proposed by the Bangalore group has been confirmed by the very precise x-ray studies of Madame

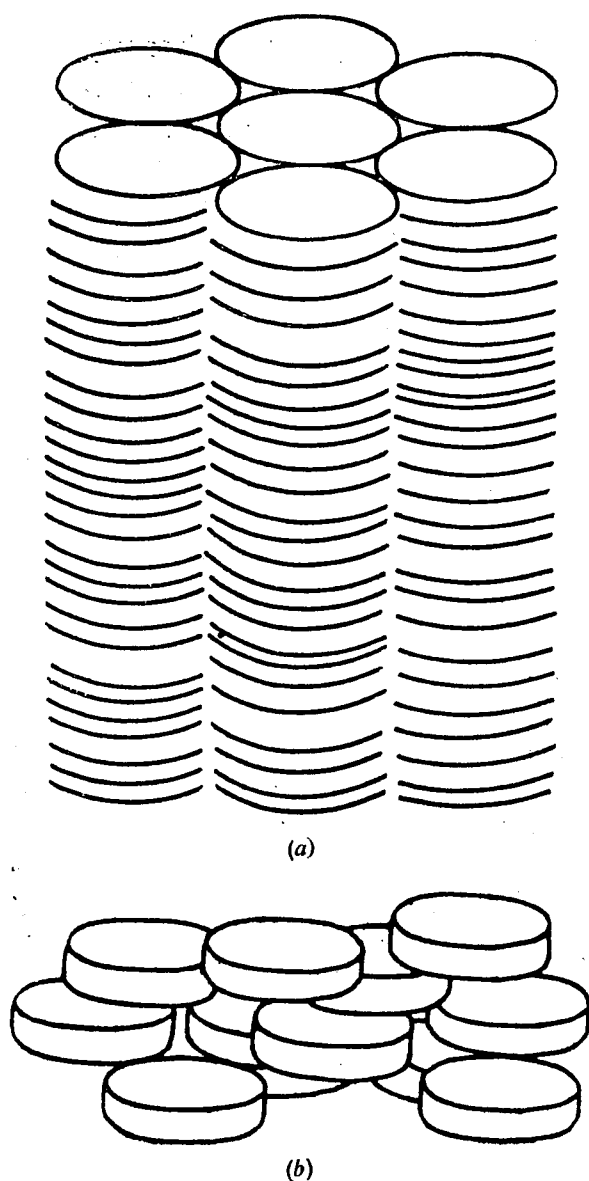


FIG. 1. (a) Columnar and (b) nematic-like mesophases of disc-shaped molecules.

A. M. Levelut<sup>6,7</sup> of the University of Paris-Sud. A few variants of this structure have been established<sup>7-9</sup>—a pseudo-hexagonal or rectangular array of columns, or a tilted columnar arrangement—and polymorphism has been observed, the same compound exhibiting more than one type of columnar phase. The case of hexa-*n*-alkoxy or alkyl benzoate of triphenylene is of special significance<sup>9</sup>: a transition occurs from a columnar to a

nematic-like phase, the structure of which is illustrated in Fig. 1 *b*.

The canonic or columnar phase is the first example in nature of a system 'melted' in one dimension<sup>10</sup>. Although the possibility was envisaged in general terms by Landau, it was considered improbable. For instance, in his famous 1958 paper 'On the Theory of Liquid Crystals' Frank wrote 'It is very unlikely that translational order in two dimensions, and not in the third, can occur as an equilibrium situation.' The discovery has therefore opened up new vistas for the physicist. The hydrodynamical properties of this phase may be expected to be quite different from those of the lamellar liquid crystal (e.g., smectic A). Permeation should take place in two dimensions (whereas in a layered structure it occurs in only one dimension). In smectic A there exists in addition to the usual longitudinal wave a second phonon branch (called *second sound* in analogy with a similar phonon branch in superfluids) associated with fluctuations in the phase of a complex order parameter. It turns out that in the canonic phase there should be a *third sound*<sup>11</sup>.

The fact that the liquid-like rods can be bent *at constant density* preserving equispacing gives rise to a whole new category of defects, which are just beginning to be explored<sup>12</sup>. In smectic A the layers are two-dimensional liquids and can take any shape at constant density and thickness. The geometrical problem of classifying these textures and describing the curvature defects is well known since the monumental work of Friedel and Grandjean: the solution consists of 'co-focal' domains. In the canonic phase the solution consists of 'developable domains', a concept introduced by Kleman and by Bouligand. One of the structures predicted by Kleman is a spiral arrangement of the columns and such a structure has indeed been observed<sup>13</sup>. It is a question of time before other configurations are identified and analyzed.

Scientists have realised that the discovery of liquid crystals of simple disc-like molecules will have important technological applications<sup>14,15</sup>. It is known that there is a mesophase transformation during the carbonization of graphitizable organic materials, such as petroleum and coal tar pitches, at temperatures between about 400–550° C. This mesophase, called the carbonaceous phase, is believed to be composed of large plate-like molecules of a range of molecular weights (around 2000) formed by the reactions of thermal cracking and aromatic polymerization. The occurrence of this mesophase has proved to be of great industrial importance since the mechanical properties of carbon fibres spun from the 'ordered fluid' state are far superior to those produced by the conventional method of spinning from the isotropic melt. The carbonaceous phase is a highly complex multi-component system and moreover its life-time is limited by its hardening into semi-coke. Not surprisingly therefore little is understood about its structure and physical properties. However, evidence seems to be fairly conclusive that the nematic-like phase exhibited by simple discotic systems is closely similar to the carbonaceous phase. The single-component systems are obviously much easier to study experimentally and the results will no doubt throw light on the role of molecular order in the thermal graphitizability of the pyrolysis product and in the production of ultra-high strength carbon fibres.

1. See, for example, Chandrasekhar, S., *Liquid Crystals*, Cambridge University Press, 1977.

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3. Billard, J., Dubois, J. C., Nguyen Huu Tinh and Zann, A., *Nouveau J. Chimie*, 1978, 2, 535.
4. Destrade, C., Mondon, M. C. and Malthete, J., Seventh International Liquid Crystal Conference, Bordeaux, 1978, *J. Physique*, 1979, 40, C3-17.
5. For an up-to-date review, see Chandrasekhar, S., "Liquid Crystals of Disc-like Molecules", invited lecture, Eighth International Liquid Crystal Conference, Kyoto, 1980, *Mol. Cryst. Liquid Cryst.* (in press).
6. Levelut, A. M., Seventh International Liquid Crystal Conference, Bordeaux, 1978, *J. Physique*, 1979, 40, L81.
7. —, *Proceedings of the International Liquid Crystals Conference*, Bangalore, 1979, ed. S. Chandrasekhar, Heyden, London, 1980, p. 21.
8. Frank, F. C. and Chandrasekhar, S., *J. Physique*, 1980, 41, 1285.
9. Destrade, C., Bernaud, M. C., Gasparoux, H., Levelut, A. M. and Nguyen Huu Tinh, *Proceedings of the International Liquid Crystals Conference*, Bangalore, 1979, ed. S. Chandrasekhar, Heyden, London, 1980, p. 29.
10. Helfrich, W., *Ibid.*, 1980, p. 7.
11. Prost, J. and Clark, N. A., *Ibid.*, 1980, p. 53.
12. Kleman, M., *Proceedings of the Conference on Liquid Crystals of One and Two-Dimensional Order*, Garmisch-Partenkirchen, West Germany, 1980, eds. W. Helfrich and G. Heppke, Springer-Verlag, 1980, p. 97.
13. Chandrasekhar, S., Sadashiva, B. K., Suresh, K. A., Madhusudana, N. V., Kumar, S., Shashidhar, R. and Venkatesh, G., Seventh International Liquid Crystal Conference, Bordeaux, 1978, *J. Physique*, 1979, 40, C3-120.
14. Dubois, J. C., *La Recherche*, 1979, 10, 284.
15. Gasparoux, H., *Proceedings of the Conference on Liquid Crystals of One and Two-Dimensional Order*, Garmisch-Partenkirchen, West Germany, 1980, eds. W. Helfrich, and G. Heppke, Springer-Verlag, 1980, p. 373.

#### R. D. BIRLA MEMORIAL AWARD

Prof. Abdus Salam, last year's Nobel Laureate in Physics from Pakistan and Director, International Centre for Theoretical Physics, Trieste, Italy, has been awarded the first R. D. Birla Memorial Award of the

Indian Physics Association. The award is given in recognition of Prof. Salam's contributions towards "The understanding of the basic structure of the matter and forces that underlie the physical world".

*[India is in the midst of an oil crisis. Many long-term solutions have been suggested. The question that is being asked is : Can something be done immediately? Prof. A. K. N. Reddy, who leads the group on the Application of Science and Technology to Rural Areas at the Indian Institute of Science, has come up with a simple solution which appears to be well within our present technological capability. At our request Prof. Reddy has written a brief article for "Current Science" on this novel idea. The idea is so unorthodox and provocative that it merits discussion. We hope to publish comments of our readers on this article in a later issue.]*