

The Mesomorphism of Diisobutylsilanediol.

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Diisobutylsilanediol exists as a mesophase between 89.5° and the m. p., 101.5° (both $\pm 1^\circ$). The properties of the mesophase, which is optically negative, cannot be classified unequivocally as smectic, nematic, or cholesteric.

EABORN (*J.*, 1952, 2840) had observed that diisobutylsilanediol, $\text{Bu}_2\text{Si}(\text{OH})_2$, displayed behaviour near its melting point which might indicate a liquid-crystal phase, and we have now confirmed that the substance exists as a mesophase between 89.5° and the melting point, 101.5° (both $\pm 1^\circ$). Melting is accompanied by formation of a liquid decomposition product, presumably a siloxane, but the presence of this does not appear to have much effect on these transition temperatures. The properties of the mesophase do not allow it to be classified unequivocally as smectic, nematic, or cholesteric, if the characteristics of these groups are as defined and described by Friedel (*Ann. Phys.*, 1922, 13, 273). Thus, although it shows some optical phenomena which superficially resemble those associated by Friedel with smectic phases, it is optically negative, and this, according to his classification, should place it at once in the cholesteric group. It shows, however, none of the other characteristic properties of cholesteric phases, such as optical rotatory power, and the display of iridescent colours. The molecular structure of diisobutylsilanediol would not lead one to expect a mesophase, whether nematic, smectic, or cholesteric, according to generalisations based on mesomorphic substances previously described (see, *e.g.*, Bernal and Crowfoot, *Trans. Faraday Soc.*, 1933, 29, 1032).

The diisobutyl compound is apparently alone among reported dialkylsilanediols in giving a mesophase. Di-*n*-propyl-, di-*n*-butyl-, di-*tert*-butyl-, di(trimethylsilylmethyl)-, diallyl-, dibenzyl-, diethyl-, diisopropyl-, and dicyclohexyl-silanediols, for example, are all reported as showing normal behaviour on melting (George, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1953, 75, 1585; Sommer and Tyler, *ibid.*, 1954, 76, 1030; Okawara, Hashitani, and Watase, *Bull. Chem. Soc. Japan*, 1953, 26, 279; Robison and Kipping, *J.*, 1912, 101, 2142; Eaborn, *loc. cit.*), and we have confirmed that the last three substances, and also di-*o*-tolylsilanediol, do not exhibit mesomorphism. Several silanediols containing aryl groups have also been reported without mention of unusual behaviour on melting (see, *e.g.*, Robison and Kipping, *loc. cit.*; Cusa and Kipping, *J.*, 1932, 1040; Gilman and Dunn, *J. Amer. Chem. Soc.*, 1951, 73, 5077; Eaborn, *loc. cit.*). Dimethylsilanediol is described by Kantor (*J. Amer. Chem. Soc.*, 1953, 75, 2712) as melting at 100–101° after previous shrinkage at 96°, behaviour which might suggest formation of a mesophase but may simply arise from the volatility of this diol, or its instability to heat, and we have been unable to detect any positive evidence of mesomorphism in this compound. (However, when the crystal is heated there is an interesting development, meriting closer study, of what are apparently retreating growth steps on the crystal surface.) *tert*-Butylhexadecasilanediol, although stable, is reported as melting over a range of 40–45° (Sommer and Tyler, *loc. cit.*).

EXPERIMENTAL

For the study of the mesophase, the electrically heated stage already described by one of us (N. H. H.), and fitted to a Swift "Lapidex" polarising microscope, was used (Hartshorne and Roberts, *J.*, 1951, 1101). This stage permits interference figures of the heated specimen to be obtained. Photomicrographs were taken with a Leitz "Makam" camera attachment.

Much of the optical crystallographic work on the crystalline phase was done on single crystals mounted on a single-axis rotation apparatus (to be described elsewhere), a mounting technique being used based on that of Wood and Ayliffe (*J. Sci. Instr.*, 1935, 12, 194). In this way different sections of the crystal could be readily brought perpendicular to the axis of the microscope, while the crystal was immersed in a liquid of known refractive index. The rotation apparatus was fitted to a Cooke "Research" polarising microscope.

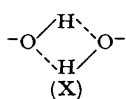
Diisobutylsilanediol.—The preparation of this substance has been described by Eaborn (*loc. cit.*). *X*-Ray examination and most of the optical work were carried out on samples crystallised from light petroleum, but the larger crystals examined were obtained by slow evaporation of a solution in methanol.

Cryoscopic measurements show that the association factor in benzene is 1.6 (molal concentration, 0.017), and in naphthalene 1.15 and 1.2 (molal concentrations, 0.035 and 0.088, respectively), so that, although the diol shows a strong tendency to associate, it exists substantially in the monomeric form in naphthalene.

The stability of dialkylsilanediols has recently been discussed by Sommer and Tyler (*loc. cit.*); the *diisobutyl* compound is distinctly more stable than diethylsilanediol since it can be recrystallised satisfactorily from high-boiling solvents (*e.g.*, water or nitromethane), or precipitated unchanged by acid from its alkaline solutions, but it is less stable than *diisopropyl*- and *dicyclohexyl*-silanediols since it decomposes fairly readily when melted.

The Crystalline Phase.—*Diisobutylsilanediol* crystallises from solution in light petroleum or methanol, and from the mesophase between a slide and cover slip, as fine bladed needles with a negative sign of elongation, *i.e.*, the axis of elongation is the "fast" direction of vibration. The growth from the mesophase is usually spherulitic and the radiating bundles of needles often show marked curvature (Fig. 1). The needles have a very pronounced cleavage parallel to the needle axis (Fig. 8), and possibly also an imperfect transverse cleavage, since when pressure is applied to them they break readily along lines of fracture which are often nearly straight and at right angles to the needle axis, in addition to cleaving into numerous individuals parallel to this axis: $\alpha = 1.476$, $\beta = 1.487$, $\gamma = 1.489$, and the dispersion to within 0.001 is negligible; $2V = 43^\circ \pm 2^\circ$ and the sign is negative; α is nearly parallel (within *ca.* 2°) to the needle axis.

We are indebted to Professor J. D. Bernal, F.R.S., Dr. H. Carlisle, and Miss Abd el Rahim, of the Birkbeck College Crystallography Laboratory, for a preliminary *X*-ray examination of the crystals. They find that the symmetry is triclinic, with $a = 14.79$ (or possibly a multiple), $b = 5.06$, $c = 28.82$ Å, and interaxial angles $\alpha \approx 90^\circ$, $\beta \approx 121^\circ$, and $\gamma \approx 96^\circ$ (b = the needle axis). A "sharpened" Paterson projection suggests that the *isobutyl* chains are lying approximately parallel to the γ vibration direction, *i.e.*, perpendicular to the needle axis. This could mean that the molecules are arranged in chains, $\cdots \text{HO}-\text{Si}-\text{OH} \cdots \text{HO}-\text{Si}-\text{OH} \cdots$, which are parallel to the needle axis, and this is supported by the fact that the b spacing is very near to that given by Kakudo and Watase for the monoclinic diethylsilanediol [$b = 4.97$ Å; *Technol. Reports Osaka Univ.*, 1952, 2, (50), 247] in which they find that chains as above and parallel to the b axis occur. Moreover, Kakudo, Kasai, and Watase (*J. Chem. Phys.*, 1953, 21, 1894) report a similar b spacing (4.95 Å) and a similar molecular arrangement for diallylsilanediol. These authors consider that the $\text{OH} \cdots \text{HO}$ linkages are due to interaction between the opposed OH dipoles, (X).



Kakudo and Watase (*loc. cit.*) find that the silicon-hydroxyl chains in diethylsilanediol are packed side by side in such a way as to form layers which are parallel to the ab plane, and consist essentially of planes of oxygen atoms sandwiched between planes of silicon atoms and, outside these, planes of ethyl groups. The Paterson projection for this compound and that obtained for *diisobutylsilanediol* show similarities which are consistent with (though they do not prove) the existence of analogous layers in the latter compound, *i.e.*, layers parallel to the silicon-hydroxyl chains, and the outer "surfaces" of which consist of *isobutyl* groups. This would make the direction normal to the layers the γ vibration direction (see above).

Kakudo and Watase also report the optical properties of diethylsilanediol: the sign is negative as for the *diisobutyl* compound, but the vibration directions corresponding to the two largest principal refraction indices, β and γ , lie in the ab plane instead of in a plane normal or nearly normal to b as in *diisobutylsilanediol*. This indicates that the arrangement of the molecules into layers parallel to the ab plane in the diethyl compound is its dominant structural feature optically. In *diisobutylsilanediol*, on the other hand, if we assume that its structure is essentially the same, the different optic orientation shows that the dominant structural feature is the presence of the large *isobutyl* side groups on the silicon-hydroxyl chains, which makes the polarisability for light vibrating normally to the chains greater than that for light vibrating parallel thereto. A similar effect is found in fully acetylated or nitrated cellulose.

Optical properties for diethylsilanediol have also been reported in a later paper by George, Sommer, and Whitmore, the optical examination having been carried out by M. L. Willard (*J. Amer. Chem. Soc.*, 1953, 75, 1585). These authors appear to have been unaware of the

FIG. 1. Spherulite of crystalline phase.
Crossed Nicols. $\times 25$.

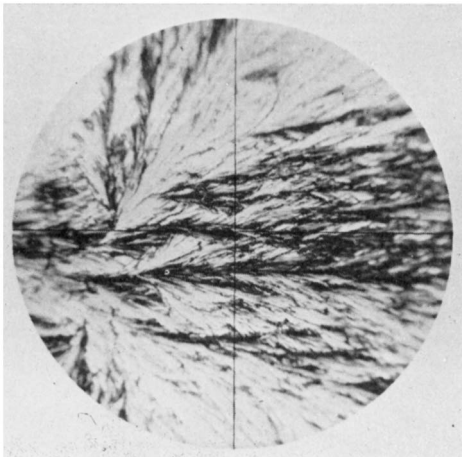


FIG. 2. Striated band structures obtained by heating spherulite in Fig. 1.
Crossed Nicols. $\times 25$.

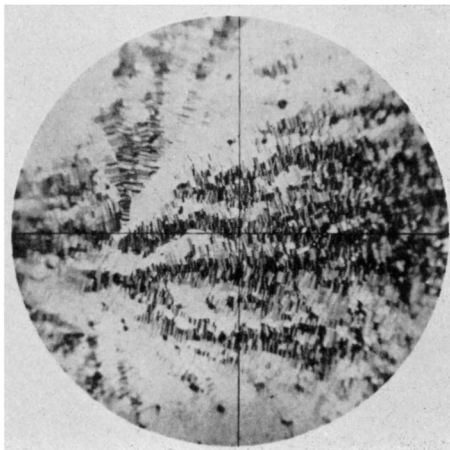


FIG. 3 Striated band structures.
Crossed Nicols. $\times 115$.

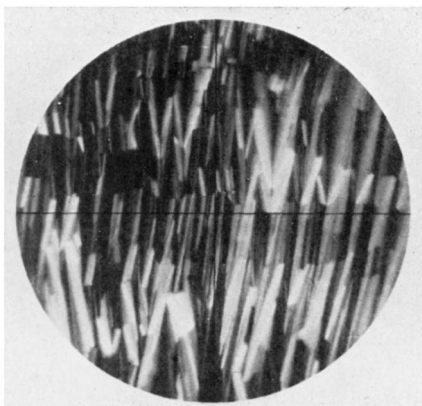


FIG. 4. Striated band structures.
Crossed Nicols. $\times 174$.

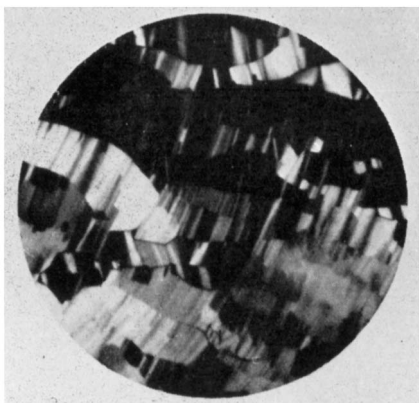


FIG. 5. Bâtonnets.
Crossed Nicols. $\times 25$

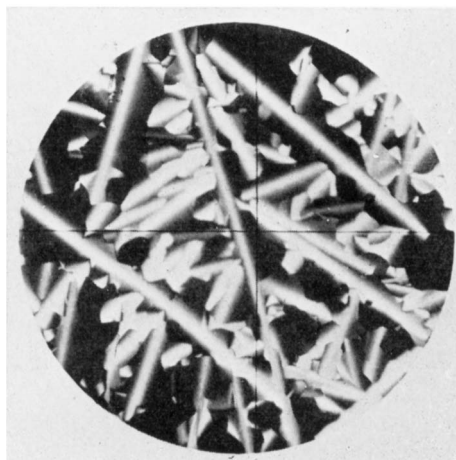


FIG. 6. *Bâtonnets*.
Crossed Nicols $\times 115$.

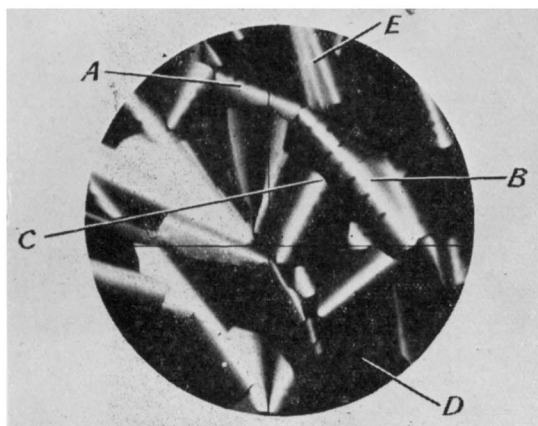


FIG. 7. *Bâtonnets* in Fig. 6.
Polarised light. $\times 115$.

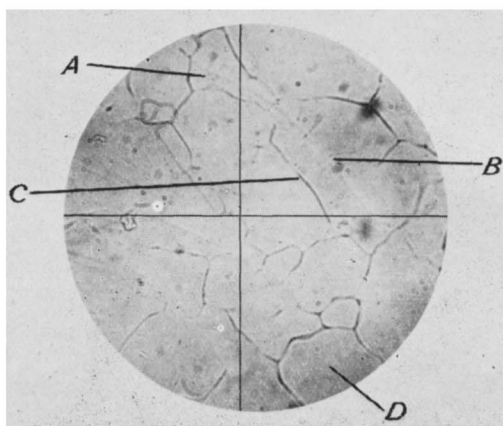


FIG. 8. *Large single crystal showing longitudinal cleavage.*
Crossed Nicols. $\times 25$.

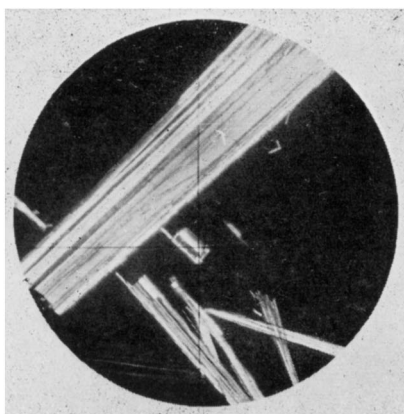


FIG. 9. *Striated band formed from crystal in Fig. 8.*
Crossed Nicols. $\times 25$.

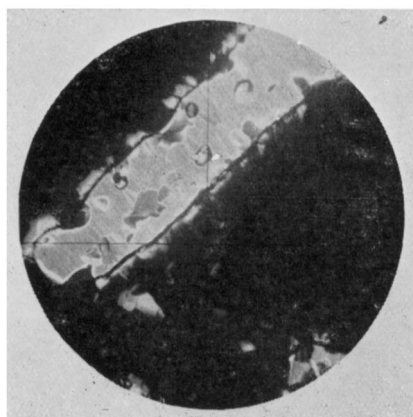
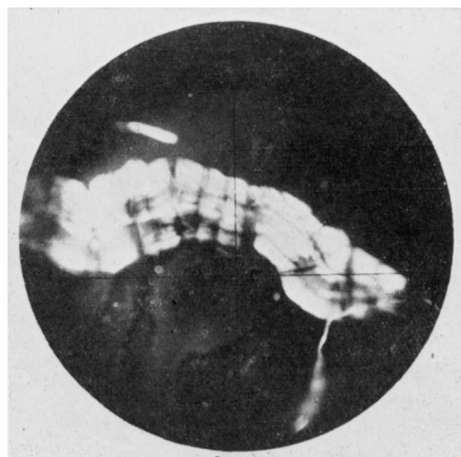


FIG. 10. *"Scalloped" structure.*
Crossed Nicols. $\times 25$.



work of Kakudo and Watase. There are considerable discrepancies between their values for the α and γ indices and for $2V$ and those of Kakudo and Watase, and the symmetry is given as orthorhombic. However, they, too, find the sign to be negative and, after allowance for a different choice of axes, the same optic orientation.

The Mesophase.—Fig. 1 is a photomicrograph taken between crossed Nicols of a typical spherulite of crystalline diisobutylsilanediol prepared by melting the substance between a slide and cover-slip and allowing it to cool. The mesophase first appears as “bâtonnets” (see below), and on further cooling a spherulitic growth of the crystalline phase occurs. Fig. 2 shows the mesophase obtained from this spherulite by raising the temperature to the mesomorphic region. It will be seen that the original pattern of the spherulite is broadly preserved, but that the acicular crystals give place to bands which between crossed Nicols appear to be transversely striated, and to which we shall refer in the sequel as the “striated band structure.” Figs. 3 and 4 show examples of this structure at greater magnification. The striated appearance is due to variations in the extinction directions of successive small portions of the bands. These variations are mostly within the range of a few degrees, and the “fast” direction is always the one parallel or more nearly parallel to the direction of elongation of the bands, so that the latter as a whole have a negative sign of elongation like the crystals from which they were formed. It will be observed that the bands do not maintain a constant width, and in this they differ from the “stries huileuses,” described by Friedel (*loc. cit.*) and first observed by Lehmann, with which they might at first have been identified for these too are striated and have a “fast” length. (“Stries huileuses” are birefringent bands sometimes produced when the focal conic structure in a smectic phase between a slide and cover-slip is broken up by agitating the cover-slip.) However, Friedel states that under a sufficiently high magnification, “stries huileuses” can be seen to contain chains of minute focal conic structures, and we have always failed to find any definite evidence in the form of unmistakable ellipses and hyperbolæ of the existence of such structures either in the striated bands or in any other mesomorphic preparation of diisobutylsilanediol. Some parts of the structures in Fig. 3 do, however, recall the “eventail” type of smectic structure described by Friedel (*loc. cit.*).

When diisobutylsilanediol is completely melted between a slide and cover-slip and allowed to cool, the mesophase appears in a dendritic form which at first sight might be mistaken for a dendritic habit of a truly crystalline phase, since the branches are quite straight. Further examination shows, however, that the angles between the branches vary widely whereas they would have a constant value in a crystalline dendrite; secondly, that the branches are apparently rounded in section with no sign of plane faces; and lastly, that when pressure is applied to the cover-slip the structure flows and takes up new forms. Figs. 5 and 6 show examples of this structure at different magnifications. For convenience, and by analogy with the elongated objects which separate from the liquid phase on cooling in the case of ordinary smectic substances, we shall refer to the branches of this structure as “bâtonnets.” The extinction along the “spine” of a bâtonnet is usually sharp and straight, and this is the “slow” direction of vibration. In some cases *two* parallel dark lines very close together instead of one dark strip are seen when the “spine” is in extinction. The extinction on either side of this central strip is usually slightly oblique and not quite complete.

Owing to the low birefringence of diisobutylsilanediol the polarisation colours shown by both the crystalline phase and the mesophase when prepared as a thin film between a slide and cover-slip are usually not higher than first-order grey and white. The photomicrographs referred to so far lose little, therefore, by being in monochrome and give a very good impression of what is actually seen under the microscope: the bâtonnets, for example, look just like the sections of bright steel tubing, or parts of mediæval armour that the photographs suggest.

A careful optical examination of the bâtonnets has shown that their apparently rounded cross-sectional shape is, to a large extent at least, an illusion. The following observations show that the gradual fall in polarisation colour from white down the middle to grey or black at the edges is mainly or wholly due to a change in orientation of the internal structures rather than to a decrease in thickness. In convergent light between crossed Nicols, the dark borders show centred or nearly centred negative uniaxial interference figures, and as the spine of the bâtonnet is approached the inclination of the optic axis (or acute bisectrix; see below) of the structure steadily increases and so, therefore, does the birefringence of the medium for normally incident light. In some bâtonnets the optic axis becomes inclined towards the spine, with reference to the direction of vision; in others, away from it. The two cases are, of course, the same structure, the one being merely the other in an inverted position.

The spine of the bâtonnet appears to mark a discontinuity in the structure, since when

the analyser is removed the spine can be resolved as a faint dark or bright line (depending on the position of focus of the microscope tube). Thus in Fig. 7, which shows the same subject as Fig. 6 but with the analyser removed, the spines of the bâtonnets *A* and *B* can be clearly traced, and those of others also. Fig. 7 also shows that the boundary line between two bâtonnets meeting at an angle is in equally sharp focus throughout its length (*e.g.*, the boundary *C*), showing that it does not vary appreciably in height as it would do if the bâtonnets were rounded in section. There is some variation in relief along the line, but this is to be expected since the relative orientations of the structures, and therefore the difference between their refractive indices, are not the same at all points. (A high-aperture, 4-mm. objective was used for these observations, with a depth of focus much less than the distance between the slide and cover-slip, so that very small changes of level in the bâtonnets could have been detected.)

Between the bâtonnets are domains which between crossed Nicols remain in extinction in all positions of rotation of the microscope stage, *e.g.*, domain *D* in Figs. 6 and 7. These domains give centred, negative, uniaxial, interference figures, and thus correspond to the homeotropic structure in ordinary smectic phases, except for the optical sign.

Two other features of the bâtonnets may be mentioned: (i) It has often been observed that interference figures obtained near the spine are slightly biaxial, suggesting that here there is some distortion of the structure which prevails elsewhere. (ii) The bâtonnets frequently show what appears to be a notched ornamentation at or near the edges: this is seen on some of the bâtonnets in Fig. 6. The structural significance of this feature is not clear.

When the cover-slip on a bâtonnet preparation is moved laterally, the whole structure moves bodily with it, so that there appear to be no linkages with the slide. This may be due to the cover-slip's being at a slightly lower temperature than the slide so that the bâtonnets form in the first instance on the cover slip and then subsequently remain isolated from the slide by a thin layer of the liquid decomposition product.

To sum up, the bâtonnet structure consists of domains probably showing little or no variation in thickness, separated by boundary surfaces or thin junction zones of some kind (possibly analogous to the zones of focal conics, which according to Friedel, *loc. cit.*, connect differently oriented homeotropic regions in an ordinary smectic phase). In some of these domains the optic axis is perpendicular to the glass surfaces throughout. In others (the so-called bâtonnets) the optic axis is progressively inclined towards a straight central surface or junction zone (the "spine").

The striated band structure and the bâtonnet structure are not, as their appearance might suggest, distinct mesophases each with its own temperature range of stability, since if we start with the striated band structure and raise the temperature until the bands are partially melted, and then lower it, bâtonnets grow into the liquid as continuations of the striæ. Again, we have made preparations under a temperature gradient, containing both striated bands and bâtonnets, and no phase boundary between the two structures could be seen. The two structures appear to be able to intermingle freely without change. Moreover, portions of bâtonnet structures are often seen which are indistinguishable from the striæ in the band structure, as for example domain *E* in Fig. 6. Thus it may be supposed that a striated band consists essentially of a succession of small bâtonnets linked side by side.

Experiments on Large Single Crystals.—When the mesophase is prepared between a slide and cover-slip either as striated bands or as bâtonnets and is then allowed to cool, crystallisation occurs from a number of centres as spherulites as already mentioned. These spherulites rapidly invade and replace the mesomorphic structure, and the orientation of the latter appears to have no effect on that of the crystals. A different result is obtained if a large single crystal (obtained from solution) is slowly heated and cooled between a slide and a cover-slip. In this case, the crystal (Fig. 8) becomes a striated band (Fig. 9), and on cooling, crystallisation of this band takes place as an interface reaction to give a single crystal with the original orientation. There is some change of shape as compared with the original crystal because of sublimation on to the cover-slip during the process and possibly because the fluid mesophase suffers some deformation as a result of the pressure of the cover-slip. A noteworthy phenomenon accompanying these changes is that the polarisation colour of the mesophase as a whole is distinctly lower than that of the original crystal, and that on recrystallisation of the mesophase the original colour is regained. Thus, in one example studied, the original and the final crystal showed a strong first-order orange, and the mesophase a pale yellow, corresponding to a fractional fall in relative retardation of about one-quarter.

DISCUSSION

If optically negative silicon-hydroxyl chains packed side by side to form layers exist in the crystalline state, as is suggested by the X-ray evidence, there appear to be two main alternative possibilities regarding the structure of the mesophase, one involving a parallel association of chains, and the other a system of parallel layers, and these will be discussed separately.

(1) The first possibility (which at first sight is the more attractive since it involves the smaller *internal* disturbance of the structure) is that the mesophase consists essentially of a parallel or near-parallel association of silicon-hydroxyl chains with a random lateral arrangement, so that the layer structure of the crystal is not preserved. The chain direction which is the acute bisectrix (α) in the crystal thus becomes the optic axis of the uniaxial mesophase, and since for both phases this is the vibration direction corresponding to the smallest refractive index, no pronounced change in the optical properties of the medium is involved in passing from one phase to the other. Silicon-hydroxyl chains, which in the crystal are held together primarily by van der Waals forces (if Kakudo and Watase's smallest oxygen-oxygen distances between neighbouring chains in diethylsilanediol, *viz.*, 3.64 Å, are applicable in the present case), simply become loosened from one another, but preserve their parallel or a near-parallel arrangement. Difficulties are, however, involved in this simple picture, and it is not adequate to explain all the properties of the mesophase, as the following considerations show. In the first place it would imply that the cross-sectional structure of the bâtonnets is as depicted in Fig. 11 (a), where the lines drawn between the upper and the lower surface represent the mean directions of the chains. This in turn would mean that the chains, which in the crystal are endless and lie parallel to the glass supporting surfaces, break up into finite lengths and orientate themselves obliquely or normally to those surfaces when the temperature reaches the mesomorphic region. This at once raises the question as to whether the presence of the glass surfaces, or one such surface, is essential for the development of the mesomorphic structures which we have described. One possibility that suggests itself is that the endless chains break as a result of the input of thermal energy, and then the end Si-OH groups attach themselves firmly to the glass by interaction with its Si-O linkages. The following experiments show, however, that the glass does not play an essential rôle. (a) When an uncovered crystal is laid across a small hole etched in a cover-slip and is heated, it becomes a striated band bridging the hole. In other words, this characteristic structure is formed where the substance is not in contact with any solid surface at all. (b) Crystals heated on a film of rhombic sulphur supported on a slide develop the striated band structure apparently just as readily as on glass.

One phenomenon has been observed in which the presence of a glass surface does appear to have an effect on at least the coarser details of the mesomorphic structure. In the experiment just described of heating a crystal laid across a hole, it is frequently seen that the parts of the crystal in contact with the glass adopt a convoluted shape, which we will call the "scalloped" structure, when the mesophase forms. In some cases the part of the crystal which was over the hole withdraws to the side of the hole, and the whole crystal then develops the scalloped structure. A rather poor example of this is shown in Fig. 10. The hole in the glass can just be discerned below the middle part of the mesophase.

The mere requirement that the silicon-hydroxyl chains remain parallel would give us a phase with typical nematic properties; it is evident that we are dealing with something which is structurally more restricted than that, and if parallel chains are present there must also be some additional restraint on the system. The formation of bâtonnets from the liquid phase instead of the spherical anisotropic drops which appear in the case of nematic substances may be cited as probably the strongest argument against classifying diisobutylsilanediol as nematic.

(2) The second possibility is that the system of parallel layers in the solid crystal is preserved in the mesophase and is the cause of the optically negative character of the

latter. The optic axis must now be normal to the layers, whereas in the crystal this direction was γ , the approximate direction of the *isobutyl* chains. Furthermore, the layers must become singly refracting for this direction of propagation, since the mesophase is uniaxial. Thus in passing from the crystalline phase to the mesophase, the vibration direction corresponding to the greatest refractive index becomes that corresponding to the smallest refractive index. To account for this and for the change to uniaxial character it would seem necessary to suppose that quite considerable changes in the bonding within the layers, and in the inclination of the *isobutyl* chains to the layer planes, occur, but since the birefringence of the crystalline phase is small (0.013) the structural changes necessary on passing to the mesophase need not be prohibitively large. The fact that just such a difference in optic orientation exists between crystalline diisobutyl- and diethyl-silanediol, as mentioned earlier, emphasises this point if, as we have been assuming, their structures are indeed similar. What is not so easy to understand is how layers consisting of silicon-hydroxyl chains, linked laterally by van der Waals forces, can become isotropic for normally incident light when the temperature is raised. The change would appear to require the breakdown of the hydrogen bonding of the chains to give place to

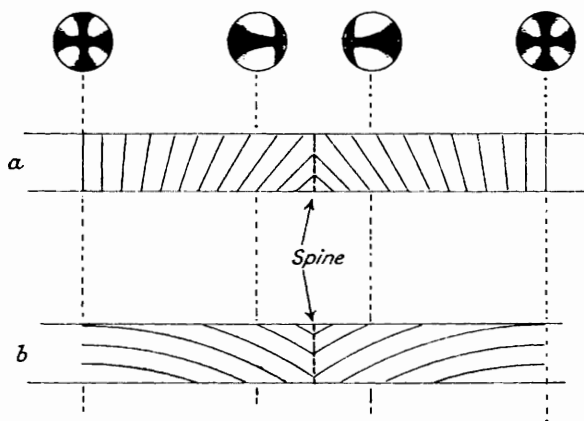


FIG. 11. Possible cross-sectional structures of a bâtonnet with typical interference figures shown by different parts.

The vertical and sloping lines in (a) represent the mean directions of silicon-hydroxyl chains. The curved lines in (b) represent layers.

a statistically non-directional interaction (within the planes of the layers) between the hydroxyl groups, sufficiently strong to hold each layer together.

If the mesophase possesses such a layer structure, there will be much less disturbance of the crystal structure when transformation of this to the mesophase takes place than that which, as we have seen, must be supposed to occur if the structure of the mesophase is based on possibility (1). Regions of the crystalline phase in which the layers are already parallel to the glass surfaces can easily form homeotropic domains giving centred uniaxial figures in the mesophase and birefringence will be favoured wherever the layers are tilted with respect to the glass surfaces, though the cause and exact nature of the relationship between the crystal and mesophase orientations must for the present remain obscure, particularly as the glass surfaces appear to play little or no part in determining the latter. The cross-sectional structure of a bâtonnet might be as depicted in Fig. 11 (b).

The fall in polarization colour observed when a single crystal passes into the mesophase agrees with expectation for both the chain and layer pictures. In both cases the changes in optical properties and orientation are such that the directions of propagation corresponding to low or zero double refraction tend to be normal to the plane of the slide.

Proof of the presence of layers in the mesophase would go some way towards accounting for its pseudo-smectic properties, and it is hoped that future work will yield more information about this, and other details of its structure. It may then prove possible to identify it with one of the 18 geometrically possible states intermediate between true liquids and true crystals which have been conceived on theoretical grounds by Hermann (*Z. Krist.*, 1931, 79, 186).

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