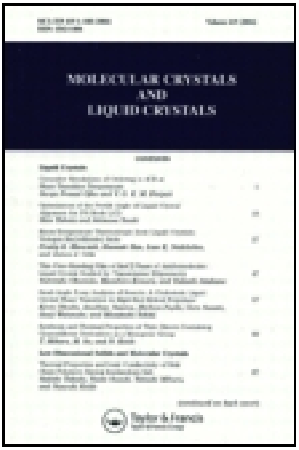

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Evidence for the Existence of More Than One Type of Nematic Phase

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Evidence for the Existence of More Than One Type of Nematic Phase

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Abstract—It is suggested that there may be three types of nematic phases: the skewed cybotactic phase, in which the molecules are arranged in groups in such a way that the centers of the molecules in each group lie in a plane making an angle α (significantly different from 90°) with the mean direction of the molecules in that group; the normal cybotactic phase, similar to the skewed one but with α close to 90°; and the classical nematic phase, in which no regular arrangement between neighboring molecules exists.

Three means of distinguishing between these phase types are discussed: the X-ray diffraction pattern, the type of the preceding smectic phase, and the microscopic textures. It is shown that the application of the last two methods to literature data yields support for the concept of different types of nematic phases.

It is well known that there are three main types of liquid crystalline phases, *viz.* smectic, nematic and cholesteric phases, and that the smectic phases can be further subdivided into several different classes (Sackmann and his coworkers have classified five different types of smectic phases so far[1]). It has generally been assumed, however, that there is only one type of nematic phase, and only one type of cholesteric phase.

That this is probably not true (at least as far as the nematic phase is concerned) follows from the recent finding[2] that the nematic phase of several of the *bis*-(4′-*n*-alkoxybenzal)-2-chloro-1,4-phenylenediamines and of 4,4′-di-*n*-heptyloxyazoxybenzene (and of most of its homologues, as can be concluded from a paper by Chistyakov and Chaikowsky[3]) is different from the " classical " nematic phase (i.e., the nematic phase as it is usually thought of);

to indicate the difference, I designated this type of phase as a cybotactic nematic phase. For the " classical " nematic phase one assumes that the only restriction on the arrangement is that the molecules (which are long and rod-like) have a more or less parallel orientation with respect to their neighbors. In the cybotactic nematic phase there is additional order: a substantial part of the molecules are regularly arranged in groups (cybotactic groups[4]); in each group the molecules are parallel to each other, and the centers of the molecules lie in a fairly well defined plane. Since the ends of the molecules will also lie in planes, parallel to the plane through the centers of the molecules, a cybotactic group is bound on two sides by parallel planes; the boundaries in the other directions may be irregular. In the compounds mentioned above the long axis of the molecules was found to make a considerable angle with the normal to the boundary planes (about 45° for a number of phenylenediamines); this kind of cybotactic group might be called a skewed cybotactic group. One would except, however, that there also would exist compounds with cybotactic groups in which the molecular axis is approximately normal to the boundary planes; these groups might then be called normal cybotactic groups. Thus there would be three different types of nematic phases: the classical one, the normal cybotactic one and the skewed cybotactic one.

It might be argued that it would not be possible to make a sharp distinction between these three types of phases, since either cybotactic type will approach the classical type as the number of molecules per cybotactic group approaches 1; also, the skewed cybotactic type will approach the normal cybotactic type as the skew angle (the angle between the molecular axis and the normal to the plane through the centers of the molecules) approaches 0°. For the purpose of this discussion we shall, therefore, define cybotactic groups as being large compared with one molecule (consisting of, say, one hundred molecules or more), and skewed cybotactic groups as having skew angles large compared with 1° (say about 30° or larger).

We shall discuss three possible ways of distinguishing between the different types of nematic phases. The first of these ways (the use of the X-ray diffraction pattern) led to the discovery of the skewed cybotactic phase,[2] and we shall show presently that application of the other two methods to literature data yields additional support for the existence of different nematic phases.

One way to distinguish the different types of nematic phases is through their X-ray diffraction pattern (recorded in a plane perpendicular to the incident beam). When there is no overall preferred orientation in the sample all three types generally give a diffraction pattern the main features of which are two diffraction rings: an inner ring, the position of which is related to the length of the molecule (similar inner rings were found by Steward and his co-workers for normal aliphatic alcohols[4] and normal fatty acids[5]), and an outer ring, the position of which is related to the average distance between neighboring molecules. When the molecules are aligned in a direction perpendicular to the incident beam (by a magnetic field or by other means), the skewed cybotactic phase has a diffraction pattern distinctly different from those of the classical and the normal cybotactic phase. The last two phase types show two maxima in the inner ring in a direction perpendicular to the direction in which the two maxima in the outer ring are found (see, e.g., Falgueirettes[6]), but the skewed cybotactic phase shows four maxima in the inner ring[2] in directions making an angle α with the direction in which the two maxima in the outer ring are found; this angle α is the complement of the skew angle. The difference between the X-ray diffraction patterns of classical and normal cybotactic nematic phases will not be so great, but should be noticeable: cybotactic groups should give a sharper inner ring than independent molecules would, and the diameter of this ring should not depend upon the degree of preferred orientation in the sample, whereas it would depend on this in the case of independent molecules.

A second way of distinguishing the different types of nematic phases is one that can be used only for compounds that also have one or more smectic phases. There are reasons to believe that for such compounds there exists a certain relationship between the type of the nematic phase and the type of the smectic phase immediately preceding this nematic phase (I am referring here to the sequence of phases found with increasing temperature in thermotropic liquid crystals). In the first place, for both homologous series mentioned earlier in this paper it was found[2,7] that the smectic phase preceding the skewed cybotactic nematic phase was a smectic phase in which the main axis of the molecule makes an angle of about 45° with the normal to the smectic plane, but in which there is no further order in the arrangement of the molecules within the smectic layer (one can call this a skewed smectic phase or a tilted smectic phase). So, the nematic phase and the preceding smectic phase are very similar in these cases. A second reason for expecting a relationship between a nematic phase and the preceding smectic phase is the following. The skewed smectic phase we just discussed, which is identical with the phase classified as smectic C by Sackmann and his co-workers,[2,8] has in several compounds been found to be followed by a smectic A phase.[8,9] In the smectic A phase the main axis of the molecule is approximately normal to the smectic plane and there is no further order in the arrangement of the molecules within the smectic layer (to distinguish this phase from the skewed smectic phase, I shall call it the normal smectic phase). Within the smectic range one thus finds that the skewed phase precedes the normal phase, and since these two phases appear to be so similar in structure to the skewed and normal cybotactic nematic phases, respectively, it would seem very unlikely that a *normal* smectic phase would subsequently be followed by a *skewed* cybotactic nematic phase. One would expect, rather, that a normal smectic phase is followed by a normal cybotactic or a classical nematic phase. Also, one would expect that a skewed cybotactic nematic phase is preceded by a skewed smectic phase, in agreement with the results mentioned above.

A third way of distinguishing the different types of nematic phases would be through microscopic studies. It is well known that several different types of textures can be observed with nematic phases, e.g. pseudoisotropic textures, marbled textures and schlieren textures. The pseudoisotropic textures (in which the optical axis lies in the direction of view, perpendicular to the supporting surfaces) are of special importance in this connection: skewed cybotactic nematic phases would be expected to show no pseudoisotropic textures at all (since this texture would require the boundary planes of all cybotactic groups to make the same special angle with the supporting surface, which is very unlikely); normal cybotactic nematic phases would be expected to show a strong tendency to form pseudoisotropic textures (since the required parallelism between the boundary planes and the supporting surface may be expected to be a preferred orientation, just as it is for smectic planes); and classical nematic phases might or might not show pseudoisotropic textures, depending upon the nature of the molecules. A similar difference in behavior as suggested here for the skewed and normal cybotactic nematic phases has in fact been observed for the corresponding skewed and normal smectic phases, smectic C and A. Although Sackmann and Demus[8] do not include the pseudoisotropic texture in their classification of the different types of smectic phases according to their textures, one can see from the list of their liquid crystalline materials[9–11] that pseudoisotropic textures were never found for smectic C phases, whereas there were several smectic A phases showing this texture. From the observation of the microscopic textures it would, therefore, be possible to draw conclusions with regard to the nature of the nematic phase, just as this is done for smectic phases.

Combining the arguments presented above for the last two methods for distinguishing between different nematic phases, we come to the classification presented schematically in Table 1. To

TABLE 1 Classification of Nematic Phases

Phase type	Pseudoisotropy	Preceding smectic phase
Skewed cybotactic	Absent	C
Normal cybotactic	Strong	Mostly A
Classical	Possible	A or C

check the value of this classification I tested it on data presented by Sackmann and his co-workers in connection with their classification of smectic phases.[9–11] In their work they identified the types of the smectic phases, and, although they do not give detailed information on the types of nematic textures encountered they mention for many nematic phases that they are " pseudoisotropic " or " mostly pseudoisotropic "; from this it may be inferred that for the other nematic phases the pseudoisotropic texture was absent or rarely found.[12] The results obtained are presented in Table 2. They are in complete agreement with

TABLE 2 Relation between Nematic Texture and the Type of the Preceding Smectic Phase‡

Nematic texture	Number of compounds with a preceding smectic phase of type A	; C
Pseudoisotropic	22	(1)§
Mostly pseudoisotropic	11	0
Not mentioned	7	4

‡ From results published by Sackmann and co-workers.[9–11]
§ This phase was not identified with certainty.

Table 1: the large majority of the nematic phases preceded by smectic A phases show a strong tendency toward pseudoisotropy (33 out of 40), and for the large majority of the nematic phases preceded by smectic C phases no pseudoisotropy was mentioned (the only exception was a nematic phase preceded by a smectic C phase of which the identity was not established with certainty).

This agreement supports the basic assumption underlying this paper, i.e. that there are different types of nematic phases.

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