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Thermotropic Biaxial Nematics:[1] Highly Desirable Materials, Still Elusive ?

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On the basis and with the inclusion of results described in a previous paper [2], submitted for publication almost two years ago, we add some comments on very recent developments regarding both the design and synthesis of thermotropic nematogens of low-molecular weight, supposed biaxial in character, as well as puzzles, still unsolved, with methods of their unambiguous identification. In general, this update may demonstrate the complexity and problematic nature inherent in this topical subject of research indicated by a struggle over a very relevant, but very difficult matter.

I Introduction

The existence of a biaxial nematic (N_b) phase has been a subject of growing interest since 1980 [3], about ten years after its prediction [4]. However, whereas the *micellar* type of biaxial nematic phase [3] has in the course of time been quite well established experimentally, including recent studies on changes of the micellar form in a polydisperse system of solution [5-7], the occurrence and observation of related *thermotropic* N_b phases of a certain number of single, low-mass chemical compounds are still open to question for physicists and synthetic chemists [8-18].

This assessment of the situation and the commitment to new tasks encouraged several research groups to an increasing degree, mainly in Europe, also to focus their efforts on the design, synthesis, and identification - the latter measure: a non-trivial task - of low-mass molecules supposed to exhibit biaxial nematic behaviour. Hitherto, a real breakthrough on that fascinating, but very difficult topic of research, possibly also significant for technological applications [19] of such materials, has not yet been achieved. One is tempted to compare this struggle with the search for a needle in a haystack. Further comments on this deficient situation are known in a greater number [20]. Nevertheless, an indisputable example of a thermotropic biaxial nematic phase is surely expected to be found in the nearer future.

II Reflections on the design of thermotropic biaxial nematics

In contrast to a lyotropic state in which an *aggregate* of molecules is the principal feature, the structural element of thermotropic mesogens is a *molecule*, as in standard molecular systems. This fundamental difference with all its consequences for the construction of these two mesomorphic states does, surely in the latter case, cause major synthetic difficulties. Indeed they, actually, still seem to be invincible, e.g. regarding *pure* thermotropic systems with biaxial nematic properties consistently accepted by the scientific community. Without doubt, it appears necessary that their molecular shape should deviate from the classical calamitic type possessing approximate cylindrical symmetry.











At first glance, it seems to be clear that the issue of phase biaxiality is well based on molecular biaxiality but not necessarily on shape biaxiality only [15], and yet most work has been done designing such thermomesogens according to geometrical principles, i.e., making them somewhat shorter and broader [13 (the overview)]. For instance, it was suggested quite early and more firmly [21] that N_b behaviour may most likely be developed by compounds containing structural features both of a rod- and a disc-like moiety, as depicted by sketches of a few models some years later [22]. The molecular biaxiality needs to allow for quite pronounced lateral organisation, and a shape criterion [13, 23] of 5:3:1 was suggested within the constraints that the molecules ought not to be exposed too much. Molecular biaxiality can be promoted by complementary and/or specific *intermolecular* interactions in the direction perpendicular to the main nematic director,





or at least leading to a certain degree of order in that direction [15]. In the meantime, as can be learned from the literature [13], various organic molecules have been prepared and investigated by several research groups hoping these materials, designed in the manner referred to above, would exhibit the N_b phase as a result of hindrance in rotation about their long axis. As many of such activities have shown, however, it turned out that severe problems have arisen from the fact that also broader molecules of pure materials, nevertheless, strive to reduce the effect of their board-like molecular shape to a minimum. For instance, very fast conformational changes are one reason that a local N_b situation, if at all formed only in very narrow temperature ranges, is not lasting over a wide area during a sufficiently long time. The fact that the *calamitic* molecules in a usual nematic phase rotate around their short and long axes on a time scale of millions per second or even about one million times faster around the latter one demonstrates the inherent problems faced here with *thermotropic* nematogens, attributed to show biaxial behaviour, regarding their design and realization by geometrical criteria [21, 22] and chemical synthesis, respectively.

In an extensive overview [13] it was tried to summarize activities (known so far and documented until the end of 1997) on the design of low-molar-mass thermomesogens in the search for biaxial nematic liquid crystals discussing a huge number of such *pure* chemical compounds very different in their basic molecular structures and broader as usually known for classical calamitics. But so far, among all of these many substances synthesized and tested through conoscopy and birefringence measurements, it seems not one is fully accepted yet as a biaxial nematic, cf. the overview in [13].

Furthermore, another feasibility of the creation or promotion of the biaxial character of the nematic phase, focused on here, is conceivable and may lie in the *flanks* of the molecules due to intermolecularly *side-to-side* interacting forces of attraction and repulsion. This situation results, desirably, in a certain reduction of their mobility, i.e. again, especially the hindrance of rotation about their long axis, assumed the chief requirement for the occurrence of biaxiality, see above. In this connection it is important to learn from computer simulation studies [24] that thermotropic biaxial nematics *indeed* can *exist*, a great stimulant for further work on the design and preparation of promising new substances as well as on the development and expert use of indisputable analytical methods in this important section of synthetic organic and physical chemistry.

However, such *lateral effects* resulting in intermolecular attractions should be rather balanced in strength, since otherwise - in these specific cases - undesired physical (e.g. smectic [25] or even crystalline) properties are to be feared. From a synthetic viewpoint, the inability to control this balance is the problem here.

For instance, situations of molecular face-to-face interactions [25] or strong hydrogen bonding, the latter always straight (!) in geometry, would give rise to other, a *more rigid* kind of supramolecular structures, consequently, different in behaviour compared to their thermomesomorphic precursors. On the other hand, since the introduction [26] of the *first laterally long-(flexible-)chain* (illustrated by : ) substituted (mainly) standard nematics (illustrated by: ) in the early eighties followed by a greater number of various analogues up to our days [27-29], it is known that this kind of chemical alteration of their respective double-into a triple-ended ( \rightarrow  ) structure [30] usually keeps the mesogenic feature of the initial double-ended one. Anyway, biaxial nematic phenomena have never been observed in connection with this or any other type of laterally monografted nematogens [26-29,31]. The same is true [31] with nematogens having *two long-chain* substituents mostly in opposite lateral arenyl positions [28,32-35]. Surprisingly, the fact of preservation of the type of mesophase has, to our knowledge, not received general attention in view of using the triple-ended [30] nematic mesogens ( ) for further synthetic purposes directed toward biaxial nematics. Of course, this could only work with a suitable chemical function x present at the tip(s) of the implanted *long-chain* spacer(s) as depicted in the following example:    . The single instance, up to now, of such a synthetic approach has been described already over fifteen years ago [36] and refers to a C=C-double bond in the terminal position x. Several examples of starting mesogens, each monotropical nematic, yielded the respective high-molecular-mass products after polymerisation, each now exhibiting an enantiotropic nematic phase. The assignment [36] of these mesophases as biaxial nematic, among them the first example of a chiral nematic one, appears also not to have been universally accepted as such [12]; for instance, to our knowledge, none of these interesting cases of a nematic phase has not yet been examined with ^2H -NMR. Although these particular liquid crystalline products are (side-chain) polymers, anyhow, this building principle of *lateral attachment* deserves further synthetic work, see below.

Beside these polymers [36,37] in which x forms the polymeric chain constituting the molecular backbone, a few years later [27], a second (identical) calamitic nematic unit () has been put on instead, furnishing now twin molecules [27a] or ligated twins [27b] which, in most cases, are also thermomesomorphic, mainly smectic [38-42], but not (biaxial) nematic [31] in character. Their formal H- or "catamaran"-like molecular shape may be illustrated by the following sketch:    .

Other structural variations in this particular group of *twin* materials began in Germany [43-45] and England [46] in the early nineties, after the first example of a novel type of unsymmetric disc-rod ethers shown in Fig. 1 was published [43,47]. Their ne-

matogenic properties are clearly determined by the dominating, alkyl substituted, flat “superdisc” segment pentakis[(4-alkylphenyl)ethynyl]phenyl depicted here in Fig. 1.

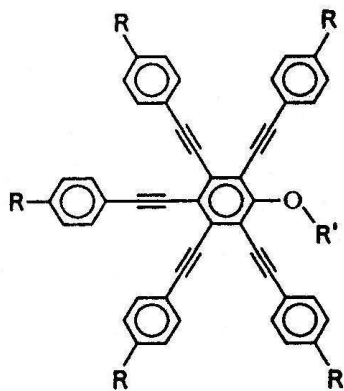


Figure 1. The basic molecular structure of “superdisc”-rod ethers, R or R', e.g., pentyl or long alkyl, respectively [43].

Based on precursors of this big discotic shape, disc-disc [43] and also some disc-rod [45,46] twin compounds, the latter provided with different groups calamitic in structure, as such thermomesomorphic (smectic), and covalently, always *terminally*, linked to the “open” end of R' have been prepared and studied carefully. Unfortunately, the disc-rod dimers prepared so far turned out to be either non-liquid crystalline [45] or are at best monotropic nematic-(discotic) [45,46]. On the other hand, such disc-disc dimers, actually, exhibit the thermotropic nematic-(discotic) phase enantiotropically as expected, but its biaxiality stated by the authors [43] is disputed since then [e.g.: 9,12,15,18,24].

As research developed other disc-rod dimers having the rod-like moiety for the first time *laterally* attached to the (long) spacer at that “superdisc” segment, represented in Fig. 1 and used [44] here too, could now indeed be synthesized and also purified [48]. This very viscous material possesses a monotropic nematic phase of a substantial molecular biaxiality as has been characterized by ^2H -NMR spectroscopy. Their results indicate that the side-on way of linking the rod-like part with the alkoxy-“superdisc”, see Fig. 1, introduced here successfully for the design of a single molecular entity could indeed be a promising approach [44] towards low-molar-mass thermotropic biaxial nematics [48].

Moreover, these British researchers found still a second new approach to the realisation of the biaxial nematic phase [49]. This case is based on specific side-to-side molecular interactions in 1:1 mixtures of partly

fluorinated Palladium(II) complexes, see Fig. 2, due to the fact that like parts of a molecule prefer to associate leading here to micro-segregation at the molecular level; ^2H -NMR and x-ray studies prove their findings [49].

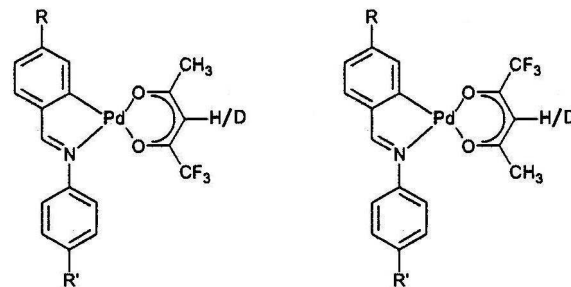


Figure 2. The molecular structures of the two isomeric Pd(II) complexes, R=R'=hexyloxy or R=hexyloxy and R'=hexyl, both are monotropically nematic [49].

In the face of instructive comments published recently [18] on bent-core or banana-shaped molecules and the exhibition of the biaxial nematic phase a third activity in this field, the author has just learned about, can be mentioned here [50]. Subject are polar liquid crystal materials derived from 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole by esterification with 4-substituted benzoic acid carrying either a heptyl or a dodecyloxy group, having a $\sim 134^\circ$ bend angle of a rigid, boomerang-type core [cf. 22] with a dipole moment of ~ 4 D. Reported are results of X-ray diffraction and electro-optical measurements on their mesophases: a nematic and two smectic ones. It is concluded that the three systems the authors investigated show a biaxial nematic phase below the isotropic liquid [50].

Probably another kind of *lateral effect* (see further above) or interaction with intra- and intermolecular consequences must be involved in the phase behaviour of very interesting novel, oligomeric, at least 75-membered gigantoheterocycles [51] based on each three units of 1-(4'-hydroxybiphenyl-4-yl)-2-(4-hydroxyphenyl)butane and flexible spacers. This type of cyclic multimeric liquid crystals has *no chain ends* and yet exhibits each an enantiotropic nematic phase on heating [51,52]. This mesophase formation is explained as a consequence of molecular alignment following a “self-parallelisation” of the “ultralarge” rings [52]. Obviously, the reason for this intramolecular process is due to electronic *trans-annular* (here, naturally, also *intermolecular*) effects of attraction and repulsion - in other words: to *through-space-interactions*. This yields a somewhat higher *rigidity* of such rings, but still remaining flexible enough, combined with their *widening* due to the parallel arrangement, i.e. *intramolecular* doubling of thickness versus simple linear molecules. It may be conceivable that this combination of circumstances subsequently obstructs the rotation about the

long axis of these and, imaginably, similar giant cyclic as well as heterocyclic materials (cf. above) to an optimal degree allowing biaxiality of their nematic phase to occur strong enough and becoming detectable by various methods. However, to our knowledge, no examination with ^2H -NMR has yet been carried out. Hopefully, this stimulating type of nematic material will induce more synthetic work on this important subject for which, first of all, the methods of preparation, isolation, and purification of such and other “ultralarge” cyclic products must furnish substantially higher chemical yields lying, at present [51,52], below five per cent only. Apart from their mesogenic relevance such gigantocycles may also be of interest in the field of nanochemistry.

In summary, it seems apparent that the design of nematogens with sufficient biaxiality to exhibit an N_b phase remains an especially challenging task. Synthetic chemists have still much to do here; this topic is certainly not by any means exhausted. Therefore, one can hope that thermotropic N_b phases will soon become indisputably real so that physicists and other people, eventually, can start studying such material in detail and looking for technological applications.

III Remarks on the identification of thermotropic N_b phases

The high degree of disappointment, but nevertheless – since recently [48-50] – also with some increasing hope of success regarding attempts to prepare examples of this important kind of nematics stressed in the previous chapter is, from the viewpoint of a synthetic organic chemist, still burdened by the uncertainty [12,13,15,18] stemming from most of the methods employed so far in the identification of the mesophase and interpretation of the results observed. Several important concerns outlined in detail recently [12,13,15,18] must be taken into account when a *thermotropic* N_b phase is subject to investigation.

The advantage of the ^2H -NMR spectroscopy is [e.g., 8,11,18] that *bulk* samples, either deuteriated as such – but, unfortunately, very seldom the case – or doped (less sensitive) with suitable deuteriated solvents, can be studied so that surface effects are negligible in contrast to optical methods, such as conoscopy studies of nematic materials, where *surface* or (cell) *wall effects* [53] may, misleadingly, *induce* a weak phase biaxiality. Leading cases in which this technique has been used are such investigations elegantly carried out by G.R. Luckhurst [8,11,18] or the determination [54] of the magnitude of the phase biaxiality for a *lyotropic* system [3].

IV Conclusion and Outlook

This short insight into the still prevailing situation of a very delicate matter of liquid crystal research shows some of the problems which must be brought under control in order to realize true thermotropic N_b materials. Their syntheses were, are, and will always be *tricky balancing acts*.

However, on the basis of so-called *lateral effects* between the molecules in a nematic phase discussed in chapter 2 and their circumspect utilization, an optimistic view or even a promising perspective seems to be possible for the realization of, hopefully, unquestionable thermotropic N_b phases. Presumably, twin, bis-twin, or gigantocyclic molecules could be the best candidates for a successful N_b -hunting.

In addition, mixtures between their homologues would also be of interest; these may even be more useful than pure materials since the compounds then can stabilize each other better, similar to the state of lyotropic systems.

Acknowledgement

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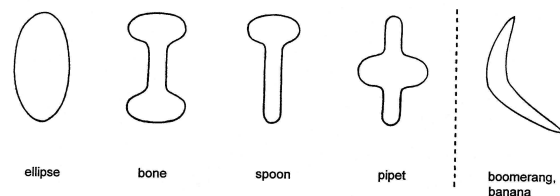
In particular, the author is very much indebted to his numerous former co-workers as well as to his perfect technician and committed expert in computer application and waste management, Mr. A. Eckert, for their engaged and very successful collaboration in our various branches of research work. With great pleasure he also thanks his colleagues, the Professors S. Chandrasekhar, Centre for Liquid Crystal Research, Bangalore, India, D.W. Bruce, University of Exeter, U.K., G.R. Luckhurst, University of Southampton, U.K., Satyendra Kumar, Kent State University, Ohio, U.S.A., C. Tschierske, Martin-Luther-Universität, Halle-Wittenberg, Germany, Mrs. Lia Q. do Amaral and A.M. Figueiredo Neto, both University of São Paulo, Brazil, and L.R. Evangelista, see above, Brazil, for fruitful scientific discussions and preprints of papers on the hot topic of thermotropic biaxial nematics by D.W. Bruce, G.R. Luckhurst (both U.K.) and Satyendra Kumar (U.S.A.) during the last months of 2001.

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Unfortunately, the *boomerang*- or *banana*-like model (right-hand side) for *bent* molecules, since the nineties a great stimulus in liquid crystal research, has not been dared by us to be included in this cartoon already nearly one decade earlier simply due to the regrettable circumstance that the first *cis*-tetraoxadecalin derivatives (*bent*, "roof-like" in structure, and chiral, synthesized by us, see below), having either two hexyl, two pentyloxy or two heptyloxy chains, do

- not exhibit any thermomesophase. Their linear *trans*-tetraoxadecalin analogues with pairs of equal substituents from methoxy to hexyloxy, however, do display nematic, smectic A or both of these phases on heating, see B. Kohne, K. Praefcke, R. Shabana Omar, and F. Frolow, *Z. Naturforsch.*, **41b**, 736 (1986).
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