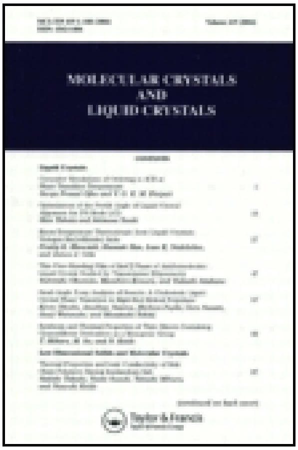

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News on Nematic-Biaxial Liquid Crystals[1]

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News on Nematic-Biaxial Liquid Crystals[1]

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Recent studies have established that not only some polymeric materials exhibit nematic biaxial phases, but that also low molecular weight compounds can do so if certain structural conditions are met.

In this paper new developments in the field of thermotropic N_b phases of low mass synthetic products are discussed regarding the relationship between structure and nematic biaxial property. Various syntheses of new structures of different geometries and some first results of investigations of such compounds are also presented.

While thus far few N_b phases have been known, their number should increase rapidly in the near future and stimulate the scientific research on this interesting topic.

Biaxial nematic phases are of great importance for the system of phase types, the theory of liquid crystals, as well as for the understanding of the molecular dynamic of mesogens, and of the discovery or development of new possibilities of application of materials in this state of matter.

Keywords: thermotropic mesogens, nematic-biaxial phases, liquid crystals

I. INTRODUCTION

Above all, *rods*, but also *discs*, are the most common geometries of central units or cores of all thermotropic low molecular weight mesogens studied so far.[2,3] In the last six years four more features of cores in this group of liquid crystals have been found which are shaped *phasmid*-like,[4] as *macro-rings*,[5] *bowls*[6] or *boards*[7-9] and form, as expected, novel types of mesophases. In this enormously growing field of interdisciplinary research among chemists and physicists studies of a type of molecular ordering, leading to the formation of biaxial nematic phases, predicted already twenty years ago,[10] are of highly current interest[11] now.

Since the discovery of this kind of mesophase in a lyotropic system ten years later,[12] biaxiality has also been detected in nematic *polymer* liquid crystals with mesogenic groups in their side chains or in the main chain.[13]

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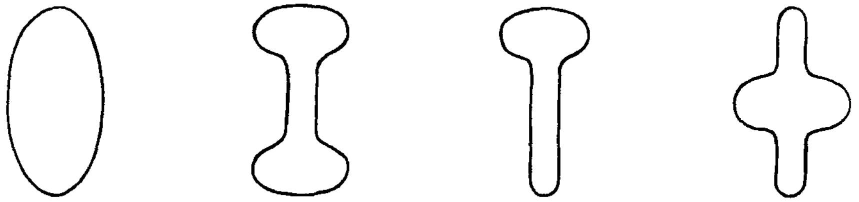


FIGURE 1 Schematic representation of realized shapes of low molecular weight biaxial nematic compounds in our view (f.l.t.r.): ellipses,[15] as well as (in two-dimensional projections) bones,[8,9] spoons,[9] and pipets.[17]

With regard to this phenomenon in *low molecular weight* thermotropic systems the suggestion, discussed at the Tenth International Liquid Crystal Conference six years ago, in a talk on the relation between molecular structure and liquid crystal properties,[14] turned out to be fruitful: the convenient way of obtaining such materials would be by bridging the gap between *rod*- and *disc*-like molecules, i.e. by preparing a mesogen that combines the features of the *rod* and the *disc* (the latter at least in part).

This concept is based on the generally held idea that molecules designed in this way should be hindered in the rotation around the long axis of their mesogenic moieties. In principle, this effect should lead to a situation in which a biaxial nematic phase structure is favoured. Such biaxial nematogens would indeed open interesting aspects for theoretical considerations and experimental investigations.

In the meantime, three research groups[7-9,15-17] in fact succeeded in synthesizing thermotropic nematic compounds of this particular type which, since we see it as a function of number and geometry of the consisting constituent units, have either an *elliptically* shaped *super-disc* core (disc-disc or a stretched disc)[15] or are formed as "two-dimensionally flat" *bones* (disc-rod-disc or twins of discs),[8,9] *spoons* (disc-rod)[9,16] or *pipets* (rod-disc-rod, a long molecule somewhat widened in the middle),[17] see Figure 1. It may not be too far-fetched to assume that other molecular architectures in this group of nematogens are also feasible.

Whereas in four of these (one: monotropic,[17] three: enantiotropic[8,9]) cases a biaxial nematic phase clearly has been observed and described convincingly,[8,9,17] in two more enantiotropic liquid crystals—a naphthalene-centered elliptical nemato-superdiscogen[15] and a "half-phasmid"[16]—this characterization is either still open[15] or has been said non-reproducible[11b,18]; the mesophase of the latter one[16] shall rather be smectic.[11b,18]

II. RESULTS AND DISCUSSION

Since our last two papers[8,9] few months ago on three novel low molecular weight liquid crystal structures—1. the dimer of 2,3,4-trihexyloxy cinnamic acid[8] (**1c**), 2. the nonyl ether[9] **7a**, and 3. the 1,12-dodecanyl twin ether[9] **9e** of pentakis[(4-pentylphenyl)ethynyl]phenol—which enantiotropically exhibit N_b phases, here, we now can report some more news.

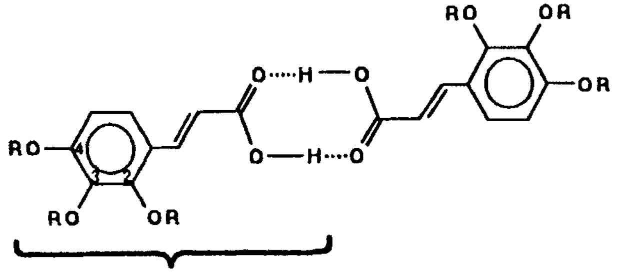
We succeeded in synthesizing 1. numerous homologues of these three systems

(**1**, **7**, and **9**), and 2. four novel molecular structures (**2**–**5**) possessing the *half-disc*-like 2,3,4-trialkoxyphenyl unit at both ends similar to the dimers of **1**, but which are different from each other in composition (now fully covalent) and length of their *rod*-like central parts. All of these new compounds appear as *bone*-shaped, see Figure 1.

We hope that these materials will stimulate future studies of N_b phases and help to improve the hitherto very poor knowledge about the relationship between the molecular structure and the exhibition of a biaxial nematic phase with either negative or positive optical character. The presentation of our results is divided into the three following chapters.

1. Hydrogen-Bridge Dimers of the 2,3,4-Trialkoxy Cinnamic Acids 1a-d, Bone-shaped N_b Mesogens of Supramolecular Architecture

The cinnamic acid derivatives **1a**–**d** form dimers based on hydrogen bonds as displayed in Figure 2—a behaviour known from other aromatic carboxylic acids too[19] and causing their mesogenity—leading to a linear tri-nuclear situation bridged by two CC-double bonds and with three alkoxy groups on either end of this assembly. These dimers shown here in *s-trans*-conformation are assumed more or less planar as a result of the conjugation between their phenyl and carboxylic groups; they represent a new structural type of *bone*-shaped mesogens, i.e. they are another kind of phasmids[4] containing the three ether functions in a *non*-symmetrical pattern relatively to the long axis of the dimers. Catalytic hydrogenation of the CC-double bond in **1** interrupts the conjugation and makes the mesogenity



1

	R	Cr		N_b		I
1a[20]	CH_3	●	173.2 (32.2)	–		●
1b	C_4H_9	●	75.6 (18.6)	{●	67.9 (0.8)}	●
1c	C_6H_{13}	●	51.2 (14.1)	●	59.6 (0.9)	●
1d	C_8H_{17}	●	54.2 (48.7)	{●	50.9 (0.5)}	●

FIGURE 2 The constitution of the planar, dimeric hydrogen-bridged structure (*s-trans*-configuration) of the 2,3,4-trialkoxy cinnamic acids **1a**–**d** with their phase transition data (d.s.c., see experimental part; heating rate 1 K/min, temperatures in °C, enthalpies in kJ/mol are put in parenthesis); **Cr** = crystalline, N_b = nematic biaxial, **I** = isotropic, values of the two monotropic transitions are given in {. . . . .}.

of **1b–d** disappear; the corresponding dihydrocinnamic acid derivatives obtained are colourless isotropic liquids.

Whereas the previously published[8] dimer of **1c** is enantiotropically nematic the two new ones, the dimers of **1b** and **d**, are monotropic only; because of the too high melting point of **1a**[20] this dimer is not thermomesomorphic anymore, see Figure 2.

The biaxial character of the nematic phase of the three dimers **1b–d** has been proven by means of conoscopic and x-ray investigations, already published[8] in some details for **1c** together with a photograph of a space filled model. The ortho- and conoscopic observations are comparable for all three dimers **1b–d**; in agreement with their dimeric structures the optical character of the N_b phases of this interestingly new type of *bone*-shaped nematogens is **positive** in all three cases **1b–d**.

Figure 3 displays the typical x-ray diffraction pattern of a magnetically aligned sample: e.g. of the dimer of **1c** at 53°C. This is also for the dimeric **1b** and **d** in their monotropic mesophases.

The maxima (a) and (c) perpendicular to each other reveal the nematic character of the mesophase, whereas the third maxima (b) at small angles and perpendicular to the magnetic field points at pecularities of the structure.[8] Both long wave periods (b) and (c) are effected by the lengthening of the molecules from **1b** to **1d**, but there is no commensurate increment corresponding to the increase of the values per methylene group (1.25 Å). Therefore, further studies are necessary before these findings can be understood conclusively.

Dimer of	(a) Å	(b) Å	(c) Å
1b	4.3	17.5	12.5
1c	4.4	19.5	14.0
1d	4.3	20.5	14.7

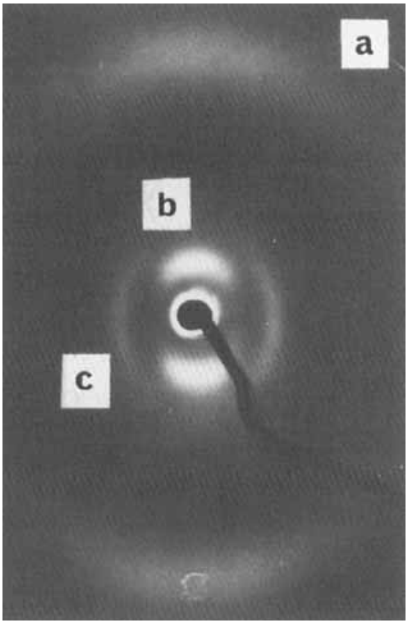


FIGURE 3 The x-ray diffraction pattern of an oriented sample of **1c** in its nematic phase at 53°C. The table shows the three reflections (a), (b), and (c) in Å of the nematogenic dimers of 2,3,4-trialkoxy cinnamic acids **1b–d**.

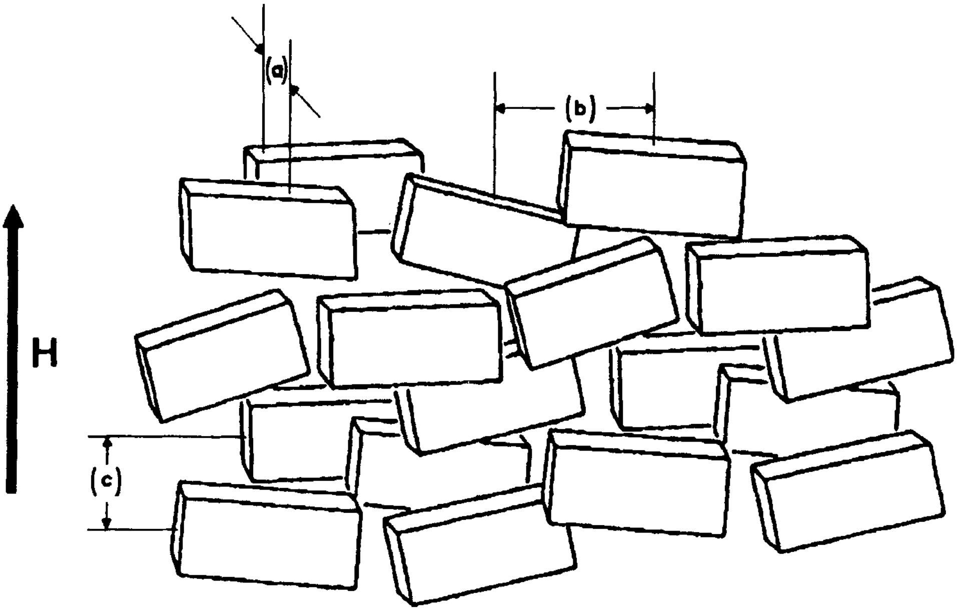


FIGURE 4 A sketch showing the biaxial arrangement of the flat board-like dimers of the 2,3,4-trialkoxy cinnamic acids **1b–c** (H = direction of the applied magnetic field), the values of (a), (b), and (c) in Å are given in the Table of Figure 3.

In our opinion, these x-ray data, however, allow the assumption of dimers of the 2,3,4-trialkoxy cinnamic acids **1b–d** which should be of flat board-like structure to explain the exhibition of the N_b phase as outlined in Figure 4.

2. Novel Straight Multi-nuclear Nematogens, The Bone-shaped Hexaethers 2–5

The formal replacement of the rod-like and partly non-covalent, mono-nuclear central part of the dimeric cinnamic acid derivatives **1** by fully covalent bridging units leads to the new bone-shaped hexaalkoxy compounds **2–5** (Figure 5) which indeed have been realized in our group very recently.

The members of the two groups of bis-imines **2** and **3** are yellow whereas those of the azo series **4** are orange in colour; **5a** and **b** are colourless. Key substances for all of these new compounds were 2,3,4-trialkoxy benzaldehydes which were accessible in two steps from pyrogallol and were condensed with hydrazine (for the data of one obtained azine see experimental part), and with the commercially available 1,4-benzenediamine, 4,4′-diaminostilbene, 4,4′-diaminoazobenzene, and *meso*-erythritol, respectively, yielding the bis-imine liquid crystals **2–4** or the two surprisingly[21] *non*-thermomesomorphic *trans*-1,3,5,7-tetraoxadecalin derivatives **5a** and **b**.

Polarizing microscopy of the three types of bis-imines **2–4** clearly proved the nematic character of their mesophases (fluid, birefringened phase with Schlieren or marbled texture) identical in all these cases. The phase transition data of all novel bone-shaped hexaethers **2–5** are collected in Table I. A comparison of the

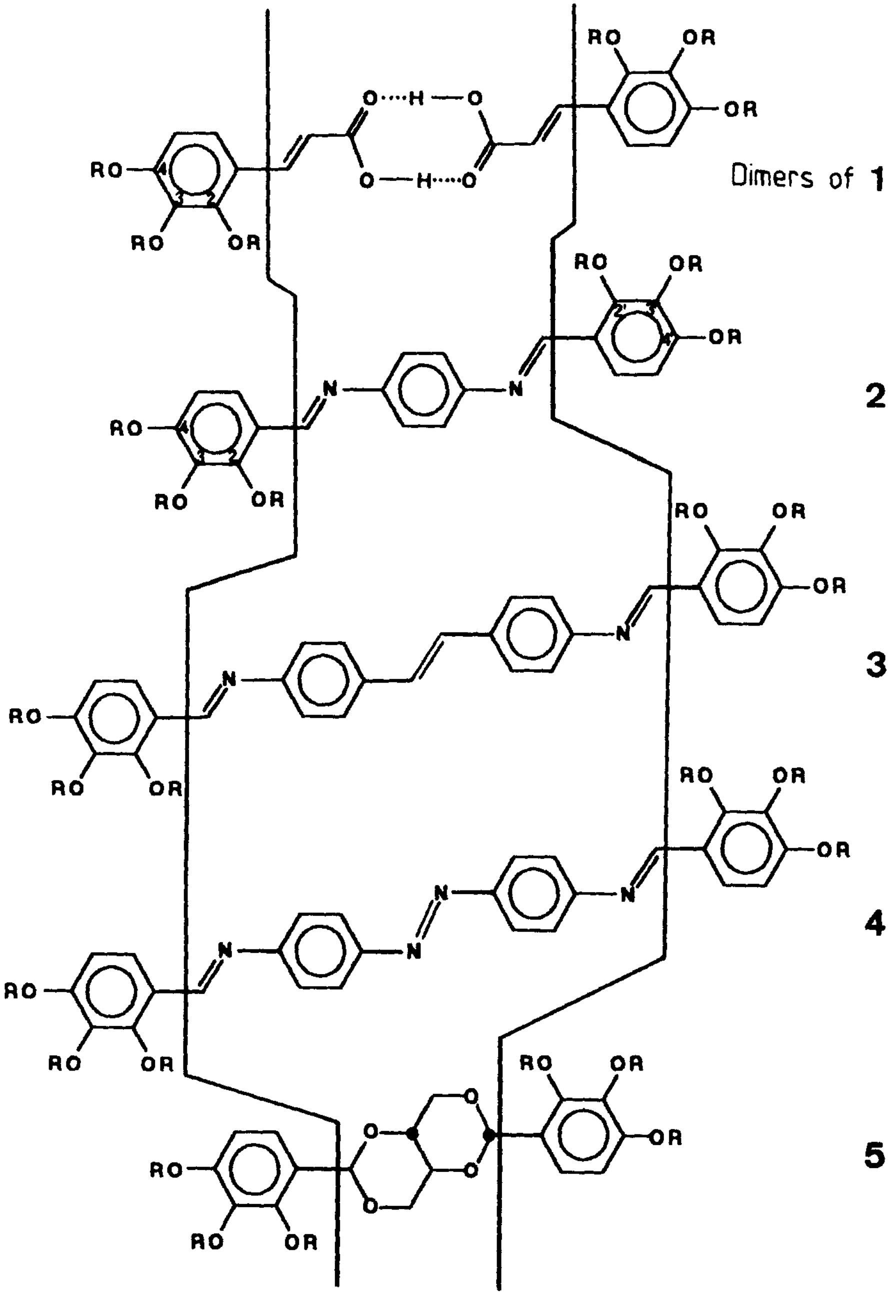


FIGURE 5 The constitution of five bone-shaped types of hexaethers—the dimers of **1**, the bis-imines **2–4**, and the 1,3,5,7-tetraoxadecalin derivatives **5**-in *trans*-configuration and -conformation synthesized and studied here; R = various alkyl, see Figure 2 and Table I. The two solid lines shall emphasize the differences of the rod-like central units in this series of compounds and make the comparison easier.

TABLE I

	R	Cr	N	I
2a	CH$_3$	● 203.7 (52.2)	{● 103.4 (—)}	●
2b	C$_4$H$_9$	● 95.8 (43.8)	{● 49.1 (—)}	●
2c	C$_6$H$_{13}$	● 62.7 (39.2)	{● 33.6 (—)}	●
3a	CH$_3$	● 232.0 (50.7)	● 292.1 (1.2)	●
3b	C$_4$H$_9$	● 145.4 (39.3)	● 154.4 (1.3)	●
4a	CH$_3$	● 225.2 (57.3)	● 268.1 (1.4)	●
4b	C$_4$H$_9$	● 150.0 (41.1)	{● 144.2 (—)}	●
4c	C$_6$H$_{13}$	● 123.8 (41.9)	{● 116.3 (—)}	●
5a	CH$_3$	● 204.1 (55.4)	–	●
5b	C$_6$H$_{13}$	● 74.3 (63.9)	–	●

The collection of phase transition data of the bis-imines **2–4** and of the 1,3,5,7-tetraoxadecalin derivatives **5** obtained by d.s.c. (see experimental part, heating rate 5 K/min, temperatures in °C, enthalpies in kJ/mol are put in parenthesis). The underlined temperature values of the five monotropic transitions (put in {. . . . .}) could be determined by hot stage polarizing microscopy only (heating rate 1 K/min); Cr = crystalline, N = nematic, I = isotropic.

transition data (Figure 2 and Table I) of the members of the four mesogen series **1–4** and of the heterocyclic *non*-mesogenic compounds of type **5** reveal interesting dependences of their mesogenity on three structural criteria: **1)** the length of the alkoxy chains at both ends of these molecules, **2)** the length of the rod-like central constituent units, and **3)** the structure of the latter ones (Figure 5).

At present we are dealing with conoscopy and x-ray diffraction investigations of the bis-imines **2–4**. Unfortunately and in contrast[8] to **1b–d**, we are faced with problems to get these new compounds aligned properly in either an electric or a magnetic field; for instance, in case of **3b**, we failed completely in our attempts. For the time being, these circumstances forced us to leave the specification of the nematic phases of compounds **2–4** open (Table I). We hope that further work on this topic will lead to a clear decision.

3. New Discotic Multiethyne Nematogens, Mesogens of Type 7 and 9 with N$_{D,b}$ Phases

In a number of papers[22,23] we described the synthesis of various novel thermotropic discogens centrosymmetric in structure through palladium catalyzed coupling reactions between brominated arenes or phenol ethers and mainly substituted phenyl acetylene.

With regard to the liquid crystalline properties of such multiethyne compounds easily accessible by that method it is important to emphasize that their ability to exhibit N$_D$ phases seems to be proportional to the diameter of their super-disc cores, i.e. the larger that core the most likely the formation of an N$_D$ phase should be.[9,23]

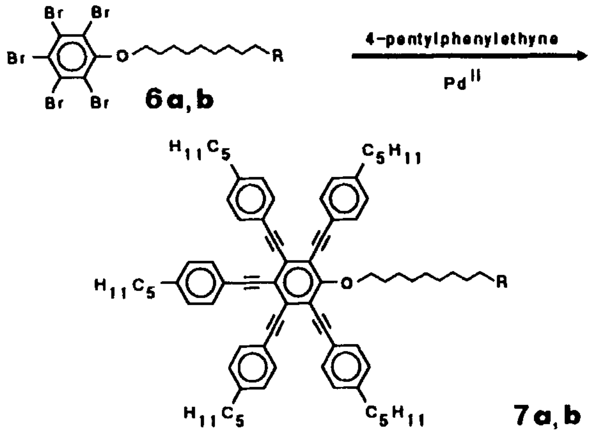
Moreover, in case of a molecular asymmetry of such a low molecular weight discotic nematogen one even should be able to observe biaxiality of the N_D phase for the first time. Its optical character should be negative which follows from the molecular geometry and from the structure of the nematic phases.

Since the properties of the two ethers **7a** and **9e** confirmed[9] our suggestion in this respect we synthesized some homologous members of these two multiethyne series for a more detailed study of this new subject. Some facts of our recent synthetic work are presented here. Conoscopic and x-ray diffraction studies are put on programme, possible results will be published later and elsewhere.

A. The Spoon-shaped Monoethers 7. In addition to the nonyl ether **7a** already published recently[9] we synthesized the undecenyl homologue **7b** (Figure 6 and experimental section) which both are yellow crystals and emit blue fluorescence in solution (e.g., in chloroform or ether). The textures of their rather fluid mesophases prove the nematic character of these two pentayne mesogens as it is already known for hexaynes: e.g. hexakis[(4-pentylphenyl)ethynyl]benzene.[23]

As first results of our conoscopic investigations of homogeneously self oriented nematic phases of these multiynes between two glass plates, using 23 μm thick spacers, which had been rubbed in a uniform direction we found that 1) the two pentayne ethers **7a** and **b** (both asymmetric) are biaxial and that 2) the mentioned radially symmetric hexayne is uniaxial.[9]

It should be added here that the conoscopic effect is unchanged in layers of a



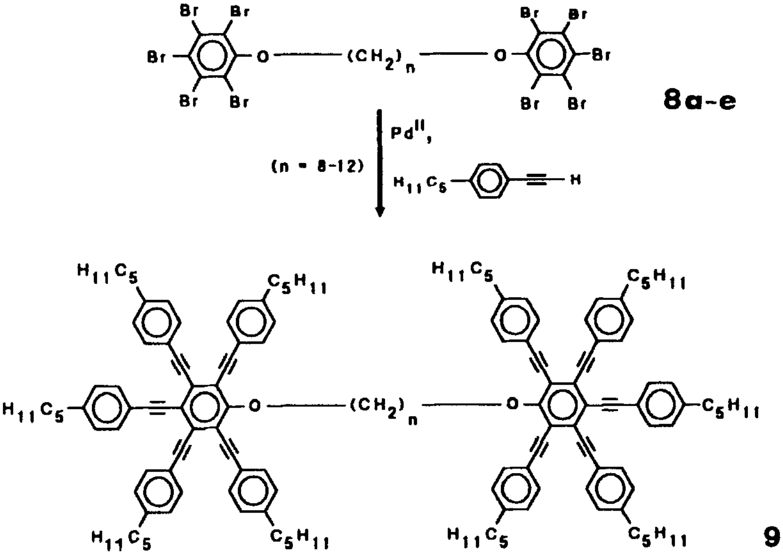
	R	Cr	$N_{D,b}$	I
$7a^9$	H	● 86.4 (42.9)	● 109.9 (0.3)	●
b	$CH{=}CH_2$	● 76.7 (36.2)	● 101.4 (0.2)	●

FIGURE 6 The constitutions of the spoon-shaped mesogens nonyl and undecenyl pentakis[(4-pentylphenyl)ethynyl]phenyl ether (**7a** and **b**), respectively, obtained in two fivefold coupling reactions[22] between the pentabromo ethers **6a** and **b** and 4-pentylphenylacetylene, and their phase transition data (d.s.c., see experimental part; heating rate 5 K/min, temperatures in °C, enthalpies in kJ/mol are put in parenthesis); **Cr** = crystalline, $N_{D,b}$ = biaxial nematic discotic, **I** = isotropic.

thickness of 85 μm. This demonstrates that the biaxiality of these multiynes is not a surface effect.

B. The Bone-shaped Twin Ethers 9. Tenfold palladium catalyzed alkynylations[22] of the five bis(pentabromo)phenyl twin ethers **8a–e** with 4-pentylphenylacetylene in one-pot reactions gave the series of yellow crystalline multiethynyl arene twin ethers **9a–d** and **e**,[9] respectively, in yields between 25 and 58%. Similar to the monoethers **7a** and **b** in chloroform or ether also **9a–e** are blue fluorescent. Their structural formulas and phase transition data are presented in Figure 7; the nematic character of the mesophase of these five compounds could clearly be established by textural observations.

Figure 8 shall emphasize an interesting odd-even effect of the clearing temper-



8a–e

9a–e

	n	Cr		$N_{D,b}$		I
9a	8	•	127.0 (61.8)	•	127.8 (--)[a]	•
b	9	•	131.0 (67.5)	(•	112.5 (--))[b]	•
c	10	•	129.1 (57.0)	•	153.5 (0.3)	•
d	11	•	118.2 (62.2)	•	140.8 (0.3)	•
e[9]	12	•	121.4 (67.9)	•	155.0 (0.4)	•

[a] The enthalpie value for this transition could not be extracted from the melting peak. [b] This monotropic transition, put in (···), could be determined by hot-stage polarizing microscopy only (heating rate of 10 K/min).

FIGURE 7 The constitutions of the bone-shaped multiethyne twin ethers, the α,ω-bis[penta(4-pentylphenylethynyl)phenoxy]alkanes **9a–e** obtained in palladium catalyzed tenfold coupling reactions[22] between the decabromo twin ethers **8a–e** and 4-pentylphenylacetylene, their phase transition temperatures (°C; determined by hot-stage polarizing microscopy with 1 K/min), and corresponding enthalpies (d.s.c., see experimental part; heating rate 5 K/min, values are given in kJ/mol and are put in parenthesis); **Cr** = crystalline, $N_{D,b}$ = biaxial nematic discotic, **I** = isotropic.

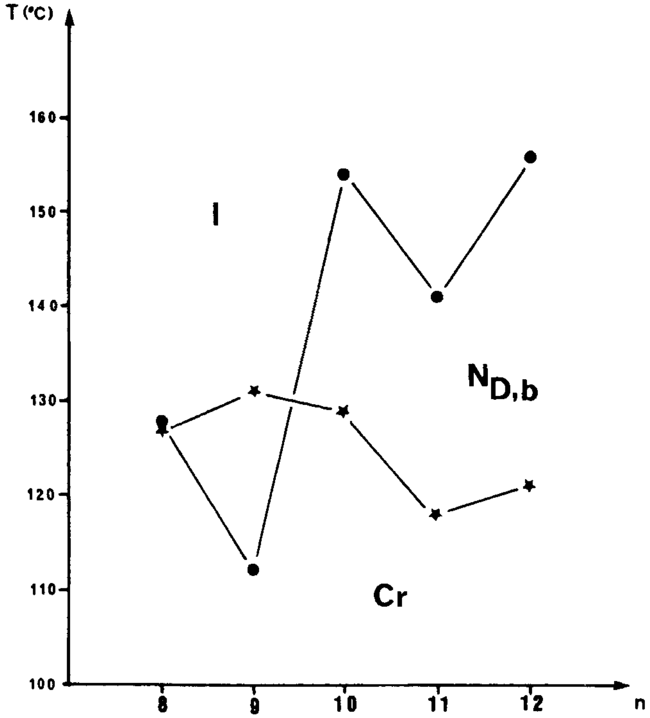


FIGURE 8 Plot of the transition temperatures of the multiethyne twin ethers, the α,ω-bis[penta(4-pentylphenylethynyl)phenoxy]alkanes **9a–e** with increasing number of methylene units in the alkyl bridge between the disc-shaped pentaethyne head units (cf. formulas in Figure 7); n = number of methylene units in the alkyl bridge, ★: melting points Cr $\rightarrow$ $N_{D,b}$ or Cr $\rightarrow$ I; ●: clearing points $N_{D,b}$ $\rightarrow$ I; Cr = crystalline, $N_{D,b}$ = biaxial nematic discotic, I = isotropic.

atures versus the length of the molecular bridge (number of carbon atoms) between the disc-shaped pentayne head units of these novel twins mesogens **9a–e**. This surprising behaviour has to be studied in more detail.

Since conoscopic studies on the asymmetric **9e** clearly showed that the nematic phase of this new low molecular weight liquid crystal is biaxial with **negative** character as expected, we now have here a group of homologues of **9e** at hand which enables us to investigate this biaxiality by applying other methods as there are e.g. x-ray diffraction, n.m.r. techniques, etc. Another aspect of interest could also be to look for the relationship between biaxiality and the intramolecular distance of the two very large, disc-shaped asymmetric pentaethyne units in this novel type of liquid crystal with a kind of disc-rod-disc-structure.

III. CONCLUDING REMARKS

The opinions put forward and our first results presented here should first of all be understood as an appeal to synthetic chemists not only to increase the number of new (homologous) compounds, but even more to design novel low molecular weight structures which 1) could exhibit thermotropic biaxial nematic phases and 2) could contribute to improve our knowledge about the relationship between structure and formation of this type of mesophase with either negative or positive optical character.

Biaxial nematic phases are of great importance for the system of phase types, the theory of liquid crystals, as well as for the understanding of the molecular dynamic of mesogens, and of the discovery or development of new possibilities of application of materials in this state of matter.

IV. EXPERIMENTAL

A. The characterization of the numerous new compounds presented in this paper are based on correct elementary analyses and on various spectroscopic data, e.g. IR, ^1H & ^{13}C n.m.r., and MS.

B. The physicochemical studies have been carried out as follows: 1) mesophase textures and phase transition temperatures: polarizing microscope Leitz Laborlux 12 Pol, hot stage Mettler FP 82; 2) conoscopy: microscope Jenapol interphako in connection with a hot stage of the type Heizkammer 400 (both instruments manufactured by Carl Zeiss, Jena, Germany), a) the alignment of the compounds **1** took place between glass plates (Teflon spacers: ~ 20 μm), coated with a transparent conductive layer in an electric field, 250 volts, frequency of 1 kHz, b) the homogeneously self-oriented nematic phases of samples of the series **7** and **9** were studied inbetween rubbed glass plates using 23 μm or 85 μm teflon spacers; 3) d.s.c.: Mettler TA 3000/DSC-30 S with TA 72 software, 4) x-ray diffraction of **1**: glass capillary of 1 mm diameter, magnetic field of 1.5 tesla, flat film camera, Ni-filtered Cu-K_α radiation monochromatized by a graphite monochromator.

C. Syntheses: 1) The unknown 2,3,4-trialkoxy benzaldehydes,[24] key compounds for the preparations of members of the series **1–5**, were obtained in two steps starting from pyrogallol via etherification and subsequent Vilsmeyer formylation after usual work-up procedure in following over-all yields: a) *2,3,4-tributyloxy benzaldehyde*, $C_{19}H_{30}O_4$ (322.4), 97%, b.p. 250°C/0.1–0.2 torr (Kugelrohr), b) *2,3,4-trihexyloxy benzaldehyde*, $C_{25}H_{42}O_4$ (406.6), 98%, b.p. 210°C/0.1 torr (Kugelrohr), c) *2,3,4-trioctyloxy benzaldehyde*, $C_{31}H_{54}O_4$ (490.8), 99%, b.p. 250°C/0.4–0.5 torr (Kugelrohr). 2) The reaction of *2,3,4-trimethoxy benzaldehyde*[24] with hydrazine gave the unknown yellow *azine*, $C_{20}H_{24}N_2O_6$ (388.4), in 84% yield which melts at 185.5°C (34.4 kJ/mol) into an isotropic liquid. 3) Condensations of these aldehydes with malonic acid yielded after usual purification a) **1a**[20] ($R = CH_3$) and the yet unknown *2,3,4-trialkoxy cinnamic acids* **1b–d**, respectively: b) **1b**, $R = C_4H_9$, $C_{21}H_{32}O_5$ (364.5), 74%; c) **1c**, $R = C_6H_{13}$, $C_{27}H_{44}O_5$ (448.6), 68%; d) **1d**, $R = C_8H_{17}$, $C_{33}H_{56}O_5$ (532.8), 69%; their melting and clearing points are compiled in Figure 2. 4) The palladium catalyzed hydrogenation of **1a–d** in dry dioxane or methanol under normal pressure furnished the corresponding *2,3,4-trialkoxy dihydrocinnamic acids* in over-all yields around 94%: a) the known one[25] with $R = CH_3$, m.p. 73–75°C (76°C),[25] and the three new ones, respectively, b)

R = C_4H_9, $C_{21}H_{34}O_5$ (366.5), m.p. by d.s.c. 7.1°C, c) R = C_6H_{13}, $C_{27}H_{46}O_5$ (450.7), m.p. below 0°C, d) R = C_8H_{17}, $C_{33}H_{58}O_5$ (534.8), m.p. by d.s.c. 15.9°C. 5) Condensation of the 2,3,4-trialkoxy benzaldehydes with the following three commercially available diamines 1,4-benzenediamine, 4,4′-stilbendiamine, and 4,4′-azobenzenediamine or with *meso*-erythritol under usual conditions and after normal work-up procedures led to the each unknown diimines **2–4**, and to the heterocyclic system **5**, respectively. **a)** The *benzene-1,4-di(2,3,4-trialkoxybenzal)imines* **2a–c**, colours yellow: α) R = CH_3, $C_{26}H_{28}N_2O_6$ (464.5), 48%, β) R = C_4H_9, $C_{44}H_{64}N_2O_6$ (717.0), 56%, γ) R = C_6H_{13}, $C_{56}H_{88}N_2O_6$ (885.3), ~ 70%; their phase transition data are given in Table I. **b)** The *trans-stilbene-4,4′-di(2,3,4-trialkoxybenzal)imines* **3a, b**, colours yellow: α) R = CH_3, $C_{34}H_{34}N_2O_6$ (566.7), ~ 23%, β) R = C_4H_9, $C_{52}H_{70}N_2O_6$ (819.1), ~ 15%. The *trans*-configuration of these stilbene derivatives is derived from the n.m.r.; their phase transition data are shown in Table I. **c)** The *trans-azobenzene-4,4′-di(2,3,4-trialkoxybenzal)imines* **4a–c**, colours orange: α) R = CH_3, $C_{32}H_{32}N_4O_6$ (568.6), ~ 54%, β) R = C_4H_9, $C_{50}H_{68}N_4O_6$ (821.1), 76%, γ) R = C_6H_{13}, $C_{62}H_{92}N_4O_6$ (989.4), 74%. Here, the *trans*-configuration of the azobenzene derivatives arises from the fact of their mesogenity; the phase transition data are presented in Table I. **d)** The *2e,6e-Bis(2,3,4-trialkoxyphenyl)-trans-1,3,5,7-tetraoxadecalins* **5a, b**, both colourless: α) R = CH_3, $C_{24}H_{30}O_{10}$ (478.5), 52%, β) R = C_6H_{13}, $C_{54}H_{90}O_{10}$ (899.3), 9%. The *trans*-configuration in these two cases results from the n.m.r., cf. related compounds published elsewhere[21]; the melting points are listed in Table I. 6)The etherification (using NaH in DMF) of commercially available pentabromophenol with the corresponding alkyl monobromide or with α,ω-dibromides gave the five new colourless intermediates (**6a** and **8e** have been described elsewhere).[9] **a)** *10-undecenyl pentabromophenyl ether* (**6b**), $C_{17}H_{21}Br_5O$ (640.9), 27%, m.p. 48°C; **b)** *1,8-bis(pentabromophenyloxy)octane* (**8a**), $C_{20}H_{16}Br_{10}O_2$ (1087.4), 40%, m.p. 170.5°C; **c)** *1,9-bis(pentabromophenyloxy)nonane* (**8b**), $C_{21}H_{18}Br_{10}O_2$ (1001.4), 56%, m.p. 154°C; **d)** *1,10-bis(pentabromophenyloxy)decane* (**8c**), $C_{22}H_{20}Br_{10}O_2$ (1115.4), 38%, m.p. 145°C; **e)** *1,11-bis(pentabromophenyloxy)undecane* (**8d**), $C_{23}H_{22}Br_{10}O_2$ (1129.5), 42%, m.p. 138°C. 7) Palladium catalyzed alkynylations[22,23] of the five bromo ethers with 4-pentylphenylacetylene gave the new yellow crystalline multialkynyl arene ethers **7b** and **9a–d**, respectively (**7e** and **9e** have been described elsewhere).[9] **a)** *10-undecenyl pentakis*[(*4-pentylphenyl)ethynyl*]*phenyl ether* (**7b**), $C_{82}H_{96}O$ (1097.7), 37%; **b)** *1,8-bis*{*pentakis*[(*4-pentylphenyl)ethynyl*]*phenyloxy*}*octane* (**9a**), $C_{150}H_{166}O_2$ (2001.0), 25%; c)*1,9-bis*{*pentakis*[(*4-pentylphenyl)ethynyl*]*phenyloxy*}*nonane* (**9b**), $C_{151}H_{168}O_2$ (2015.0), 36%; **d)** *1,10-bis*{*pentakis*[(*4-pentylphenyl)ethynyl*]*phenyloxy*}*decane* (**9c**), $C_{152}H_{170}O_2$ (2029.0), 28%; **e)** 1,1-bis{pentakis[(4-pentylphenyl)ethynyl]phenyloxy}undecane (**9d**), $C_{153}H_{172}O_2$ (2043.1) 42%.

The phase transition data of these multiynes are listed in Figure 6 and 7, respectively.

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