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New inductions of columnar mesophases in nematic discotic multiyne mesogens [1]

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In examples of two large naphthalene- and triphenylene-centred hexaynes exhibiting only the nematic discotic (N_D) type of mesophase, a new kind of phase induction was observed. These disc-shaped nematogens were doped with numerous dipolar carbocyclic compounds leading to the induction of two types of columnar mesophase (i.e. D_{ro} and D_{ho}). The phase behaviour of these binary systems, depending on the structure of the dopant applied, was studied by polarizing microscopy.

1. Introduction

In thermotropic liquid crystalline systems, the type of mesophase is determined by the molecular shape of the constituent molecules and by specific interactions between them leading to mesophases with supramolecular architectures, for example by multimerization of promesogenic molecules via hydrogen bonding [2].

In general, the self-aggregation of molecules to higher ordered mesophases is strongly influenced by specific intermolecular interactions arising out of for example hydrogen bridge formation, charge transfer, dipole–dipole or steric situations/geometric conditions promoting the formation of a two dimensional lattice in layered or columnar liquid crystalline phases.

By varying these intermolecular forces through doping, changes in the mesomorphic behaviour of a system are possible. In most of these organized systems only a destabilization is observed, but with suitable dopants a change of self-aggregation can occur resulting in a stabilization or induction of mesophases.

It is known from several cases that by mixing different compounds with calamitic structures, variation and induction of mesophases can take place [2]. Even in mixtures of two non-mesogenic calamitic compounds (‘potential mesogens’), charge transfer induced liquid crystalline phases have been reported [2].

Up to now, in discotic systems, inductions and variations of mesophases are known only through charge transfer interactions [3–6]. Binary systems composed of electron rich disc-shaped compounds (including polymers) and strong electron acceptors, such as for example 2,4,7-trinitrofluorenone (TNF), exhibit mostly columnar hexagonal ordered mesophases (D_{ho}) [4]—even if the pure components are non-liquid crystalline.

Very recently, two research groups independently reported two different examples of charge transfer induced thermotropic nematic columnar phases (N_c) observed in

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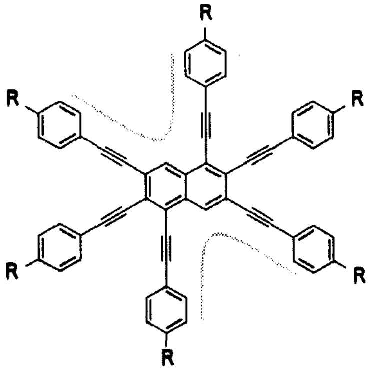
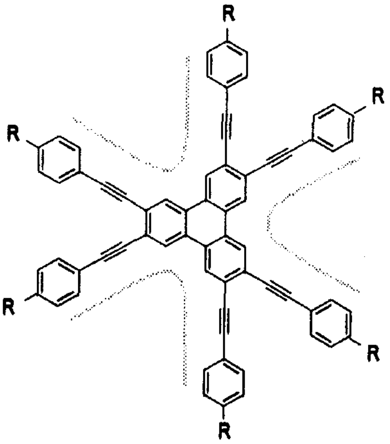


1a: R = C_8H_{17}
b: R = C_9H_{19}



2 : R = C_7H_{15}

Figure 1. Structures of the naphthalene- and triphenylene-centred hexakis(4-alkylphenylethynyl)arenes **1a**, **b**, and **2** exhibiting induced columnar phases. The drawn parabolic curves in **1** and **2** mark the 'bay' regions discussed in this paper.

mixtures of (i) non-mesogenic alkyl pentakis(phenylethynyl)phenyl ethers and TNF [5] as well as in (ii) columnar discotic hexakis(pentyloxy)triphenylene (D_{ho}) and a TNF derivative with long alkyl chains [6].

Such induced mesophases formed by charge transfer interactions between electron acceptors and disc-shaped donors are composed of ordered columns due to enhanced forces between the two types of molecules perpendicular to their disc planes [4–6].

In this paper we report a novel type of induction and variation of columnar mesophases observed in two series of highly unsaturated alkyl substituted hexakis(phenylethynyl)arenes. With numerous carbocyclic, mostly aromatic compounds as dopants, inductions of columnar phases are found for derivatives of

Table 1. Phase transition temperatures† (°C) for the disc-shaped mesogens **1a** and **b** [7] and **2** [8]; C: crystalline, N_D: nematic discotic, D: columnar discotic (ro: rectangular ordered, ho: hexagonal ordered), and I: isotropic phase.

Hexayne	C		N_D		D_{ro}		D_{ho}		I
1a	●	60·3	●	112·6	●	136·6	●	~200	●
1b	●	68·2‡	●	109·9	—		—		●
2	●	121·3	●	174·8	—		—		●

† Determined by polarization microscopy.

‡ The melting point of the highest melting modification of **1b** after annealing. However, its melting temperature drops to 47°C after rapid crystallization from the melt.

hexakis(phenylethynyl)naphthalene (for example, **1a** and **b**) [7] as well as for hexakis(4-heptylphenylethynyl)triphenylene (**2**) [8]. These disc-shaped, highly unsaturated, liquid crystalline hydrocarbons of type **1** and **2** contain apparently easily polarizable 'super-disc-cores' with diameters of about 21·7 and 24 Å, respectively, and exhibit the nematic discotic kind of mesophase (N_D). Both the naphthalene centred compound **1b** and the triphenylene derivative **2** are mono-mesomorphic, whereas the naphthalene derivatives with shorter alkyl chains, as for example **1a**, exhibit a complex multi-mesomorphism with the inverse phase sequence $C \rightarrow N_D \rightarrow D_{ro} \rightarrow D_{ho} \rightarrow I$ [7, 9]. The phase transition data of these three mesogens selected for this investigation are summarized in table 1.

2. Results and discussion

In the course of attempts to purify naphthalene centred hexaynes of type **1** by crystallization, we observed differences in the mesomorphic behaviour of the isolated materials depending on the solvents used. Thus, both **1a** and **1b** no longer showed the N_D phase if crystallized from acetone/1,2-dichlorobenzene, instead each now exhibited two types of columnar phase.

Further investigations of contact samples of these two hexaynes with numerous dipolar aromatic compounds established a complex mesophase induction. For instance, doping the nonyl mesogen **1b** with chloro- or bromo-benzene causes the induction of one columnar phase with a typical D_{ro} texture (see figure 2 (*a*)) known from pure samples of lower homologous members of this family of liquid crystals, for example of **1a**. However, with various other dopants, as for example with 1,2-disubstituted benzene derivatives, a second columnar phase displaying a D_{ho} texture (see figure 2 (*b*)) is observed. The results of these studies are summarized in table 2. Because of the evaporation/sublimation of the dopants and the decomposition of the mesogens at high temperatures, bromobenzene and 4,5-dibromo-*o*-xylene were chosen for further examinations of defined mixtures.

The basic features of the phase diagram for the binary system hexayne **1b** with bromobenzene are sketched in figure 3, and a very similar behaviour is developed in contact samples of **1b** with chlorobenzene. With increasing content of bromobenzene, a decrease in the clearing temperature of the N_D phase occurs. In mixtures of **1b** with bromobenzene between 35 and approximately 78 mol% of the dopant, an additional, highly viscous mesophase appears. The maximal clearing temperature of 116°C is found at a concentration of about 42 mol% bromobenzene in this mixture. In all mixtures, biphasic regions are observed between the D_r and the N_D or the isotropic

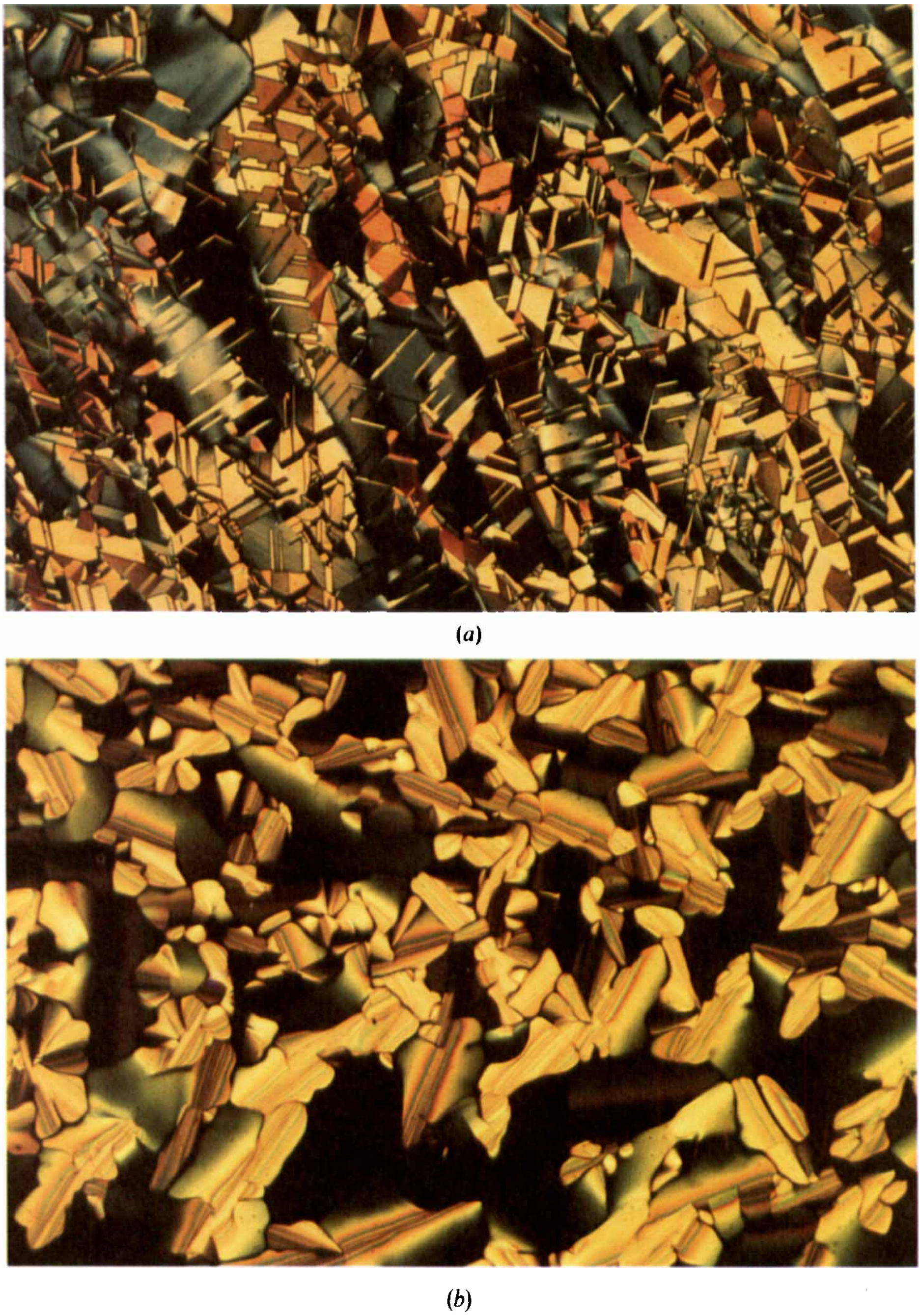


Figure 2. Textures of the induced columnar mesophases of hexakis(4-nonylphenylethynyl)naphthalene (**1b**) in mixtures with dopants, magnification × 32 in a 24 × 36 mm microscope camera, photoautomat Wild MPS 51, crossed polarizers: (*a*) D_{ro} phase in a contact sample of **1b** doped with bromobenzene at 83°C on cooling from the isotropic phase; (*b*) mosaic texture of the D_{ho} phase of a mixture of **1b** with 46 mol% of 4,5-dibromo-*o*-xylene at 109°C on cooling from the isotropic phase.

Table 2. Phase behaviour of mixtures (contact method) of hexakis(4-nonylphenylethynyl)naphthalene (**1b**) with different doping agents: $T_{\mathrm{DI,max}}$ = maximum transition temperature: mesophase→isotropic liquid (I), T_t = triple point temperature D_{ho}–D_{ro}–I; for explanations of D_{ho} and D_{ro} see table 1.

Dopant	μ/D [10]	$T_{\mathrm{DI,max}}$/°C	T_t/°C
1,2-Dicyanobenzene	—	>244†	137
1,2-Dinitrobenzene	6·00	>235†	137
Phthalic anhydride	5·21	>208†	132
2-Chlorobenzonitrile	4·73	202	137
2-Bromonitrobenzene	3·98	201	138
2-Chloronitrobenzene	3·96	200	138
1,3-Dicyanobenzene	—	192	135
1,3-Dinitrobenzene	3·78	187	134
Nitrobenzene	4·24	185	138
2-Chloro-α,α,α-trifluorotoluene	—	>180†	139
Benzonitrile	4·10	180	138
Phthalide	—	177	134
1-Nitronaphthalene	3·88	169	134
1,8-Dichloronaphthalene	2·82	166	131
1,2-Dichlorobenzene	2·25	161	137
1,2-Dibromobenzene	2·12	159	137
2-Chlorobromobenzene	2·26	159	134
4,5-Dibromo-*o*-xylene	2·86	148	126
Bromobenzene	1·53	116‡	—
Chlorobenzene	1·59	115‡	—

† Because of strong decomposition of the mixture and/or evaporation of the dopant, only the lower limit for the clearing temperature can be given.

‡ Transition temperature D_{ro}→I.

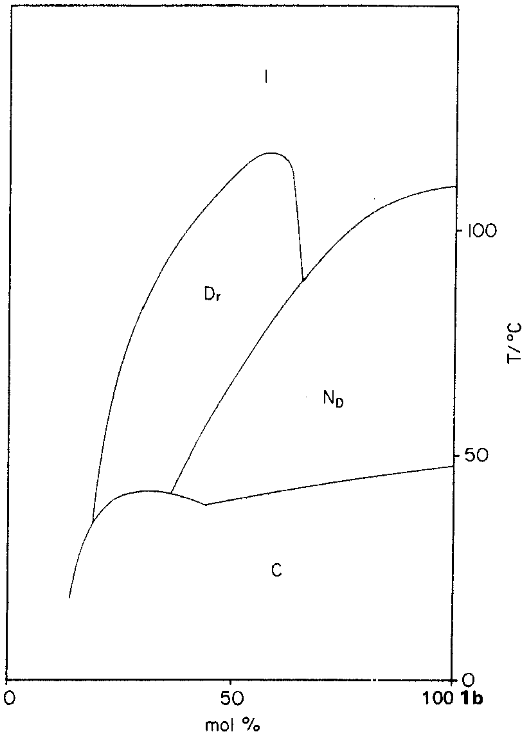


Figure 3. Preliminary schematic phase diagram of hexakis(4-nonylphenylethynyl)naphthalene (**1b**) doped with bromobenzene.

phase, respectively, at least in part due to inhomogeneities of the samples because of the volatility of the dopant and the multi-morphism in the solid state. Therefore, figure 3 simply sketches roughly the ranges of temperature and concentration in which the D_{ro} phase is found.

The texture of this induced columnar phase shown in figure 2 is identical to that of the D_{ro} phase of undoped **1a** [7], and the biaxiality of this phase is also confirmed by preliminary ^2H NMR measurements on mixtures of **1b** with perdeuteriated bromobenzene [11]. Miscibility studies on defined mixtures of the nonyl substituted naphthalene derivative **1b** and bromobenzene with the hexayne **1a** by the contact method are difficult because of the high vapour pressure of the dopant, but seem to confirm the identity of the induced D_r phase with the D_{ro} phase of undoped **1a**. X-ray measurements [12] also seem to indicate a structure for this induced D_r phase similar to that observed for undoped homologues of **1b** with shorter alkyl chains [7, 9].

A more complex phase behaviour is found for mixtures of **1b** with 4,5-dibromo-*o*-xylene. The schematic phase diagram for the naphthalene derivative **1b** with this type of dopant, also based on numerous mixtures, is depicted in figure 4.

Doping the hexayne **1b** with more than 15 mol% 4,5-dibromo-*o*-xylene causes a mesophase induction. With less than 15 mol% of this *o*-xylene derivative, the clearing

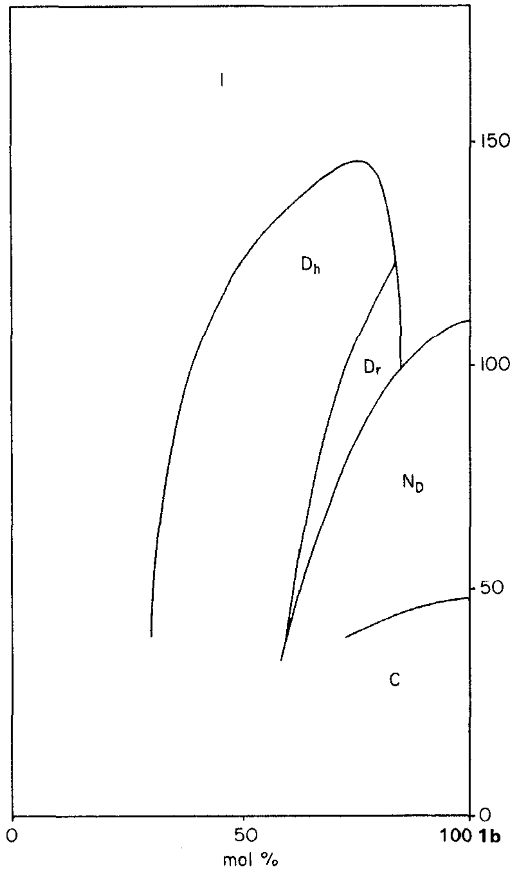


Figure 4. Preliminary schematic phase diagram of hexakis(4-nonylphenylethynyl)naphthalene (**1b**) doped with 4,5-dibromo-*o*-xylene.

temperature of the N_D phase simply decreases. Contents up to about 40 mol% of the dopant lead to a phase sequence $C \rightarrow N_D \rightarrow D_{ro} \rightarrow D_{ho} \rightarrow I$ as was observed for lower undoped homologues of this family of naphthalene centred mesogens, as for example for the octyl derivative **1a** [7]. Towards higher concentrations, up to about 70 mol% of 4,5-dibromo-*o*-xylene, the D_{ho} phase is seen; the maximal clearing temperature of 148°C is found for a mixture containing 22 mol% 4,5-dibromo-*o*-xylene.

In all mixtures, biphasic regions are present between the various phases, only in part due to inhomogeneities of the samples. Figure 4 sketches roughly the ranges of temperature and concentration in which the induced columnar phase exist. The textures of these induced columnar D_{ro} and D_{ho} phases (see figure 2) are identical with those known for undoped **1a** [7]. The indentity is apparently confirmed by miscibility studies by the contact method between such mixtures of **1b** with 4,5-dibromo-*o*-xylene and undoped **1a**. First X-ray results [12] are also in agreement with a hexagonal lattice (($a_{hex} = 29{\cdot}4$ Å) of columns similar to the D_{ho} phase of undoped lower homologues of **1b** with shorter alkyl chains [7, 9].

Apart from differences in the temperature for the $D_{ho} \rightarrow I$ transition, analogous phase behaviour is observed in contact samples of **1b** with the other dopants listed in table 2. Interestingly, despite great differences in the stability of the D_{ho} phase and consequently in $T_{DI,max}$, the triple point temperatures (D_{ho}–D_{ro}–I) found are very much the same for all mixtures of **1b** with the various dopants of table 2 applied in this study.

We found on the other hand that numerous substances not causing any phase induction in mixtures with the nonyl hexayne **1b** do change the mesomorphic behaviour of the homologous octyl substituted mesogen **1a**. For instance, in contact samples with iodobenzene and 2-chloronaphthalene, a direct $C \rightarrow D_{ro}$ transition and the disappearance of the nematic discotic phase in the contact zone (also found with the compounds of table 2) is observed, while benzamide, 1,3-dibromobenzene, 1,3-dichlorobenzene, 1,2,3,4-tetrachlorobenzene and α,α′-dibromo-*o*-xylene simply decrease the transition temperatures to the D_{ro} and D_{ho} phases. A slight decrease in the $N_D \rightarrow D_{ro}$ transition is also found with *o*-xylene, toluene and 1,2-dimethoxybenzene.

There seems to be a qualitative relationship between the dipole moment of the dopants and the temperature $T_{DI,max}$ and therefore the stability of the induced columnar phases. Thus,

(i) we found no phase induction or variation on adding dopants without an appreciable permanent dipole moment (for symmetry reasons), as for example 1,3,5-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,4,5-tetracyanobenzene, and also 1,4-disubstituted benzene derivatives;

(ii) with decreasing efficiency, iodobenzene (1·58 D), 2-chloronaphthalene (1·72 D), 1,3-dichlorobenzene (1·48 D), 1,3-dibromobenzene (1·55 D), α,α′-dibromo-*o*-xylene, 1,2,3,4-tetrachlorobenzene (1·90 D), and benzamide (3·6 D) as dopants simply stabilize the two columnar phases of the octyl mesogen **1a**, but have no effect on the phase behaviour of the nonyl derivative **1b**;

(iii) all dopants listed in table 2 induce columnar phases in mixtures with the nematic discotic nonyl hexayne **1b**. Moreover, bromo- and chloro-benzene simply induce one D phase (D_{ro}) and the other listed compounds cause the occurrence of two (D_{ro} and D_{ho}). The maximal clearing temperatures of the latter phases depend on steric effects and the dipole moments of the dopants. The highest clearing temperatures are found for mixtures of **1b** with 1,2-substituted benzene derivatives carrying strong electron withdrawing functions.

Also, the triphenylene centred nemato-discogen **2** [8] (see figure 1 and table 1) develops an induced columnar phase by doping with the compounds of table 2; for instance, the maximal clearing temperature $T_{\mathrm{DI,max}}$ of such a binary system containing 1,2-dichlorobenzene is around 260°C. Most surprisingly, even with chlorocyclohexane (2·3 D), a columnar phase up to temperatures higher than 250°C is induced.

Strong decomposition of these mixtures prevented exact determinations of their clearing temperatures (all above 250°C) and also the formation of typical textures in contact samples. A texture typical for hexagonal columnar phases (D_h) is observed by using the following method: on the hot stage at 100°C, a few milligrams of **2** placed between a glass plate and a cover slip were dissolved in chlorocyclohexane and annealed until an isotropic solution was obtained. On cooling such a sample, a fan texture with homeotropic regions of hexagonal symmetry was formed in areas with high contents of **2**. Preliminary X-ray studies [12] on a mixture of **2** with 4,5-dibromo-*o*-xylene (75 mol%) also prove the hexagonal arrangement ($a_{\mathrm{hex}} = 32{\cdot}0$ Å) of the columns.

Finally, we want to point out that the mesomorphic behaviour of some other nemato-discogens such as (hexakis(4-alkylphenylethynyl)benzenes [4(*a*), 8, 13] and alkyl pentakis(4-alkylphenylethynyl)phenyl ethers [14]) is not affected by doping them with the compounds of table 2. In these latter cases, strong electron acceptors such as 2,4,7-trinitrofluorenone (TNF) only give a D_{ho} inducing effect as found by us with similar charge transfer complexes of the mesogens **1** and **2** with TNF.

We feel that this kind of mesophase induction with TNF, by formation of ordered columns with suitable types of acceptor molecule intercalated in the columns, is obviously completely different from that reported here for mesogens of type **1** and **2**, respectively, after having been doped with, for instance, 4,5-dibromo-*o*-xylene, which cannot be considered as a typical electron acceptor; no indication for charge transfer interactions (for example a change in colour) could be observed.

3. Conclusions

From comparisons of the textures, as well as from miscibility studies by the contact method, we assume that the two induced columnar phases of the nonyl mesogen **1b** obtained by doping with 4,5-dibromo-*o*-xylene are identical with the D_{ro} and D_{ho} phases found in the case of the undoped octyl mesogen **1a**.

In contrast to the pentayne ethers and the benzene centred hexaynes, the mesogens of type **1** and **2** possess two or three relatively wide 'structural bays', respectively, in their 'super-disc-cores', as pointed out in figure 1; these in our opinion seem to be essential for this new type of mesophase induction.

The inverse phase sequence $C \rightarrow N_D \rightarrow D_{\mathrm{ro}} \rightarrow D_{\mathrm{ho}} \rightarrow I$ published [7] for the undoped octyl substituted naphthalene derivative **1a**, and also found here by induction in the case of the (in its pure state) mono-mesomorphic nematic discotic compound **1b**, obviously indicates a preferred formation of columns for such types of molecules. A slight variation of the intermolecular forces caused by doping these systems leads to changes in the self-aggregation of these mesogens of types **1** and **2**.

The dopants are carbocyclic compounds with a permanent dipole moment; for the naphthalene centred hexayne **1b** aromatic rings are essential, while for the triphenylene derivative **2**, even saturated carbocycles such as chlorocyclohexane are effective in the induction of a D_{ho} phase. A possible explanation of this novel type of phase induction is provided by dipole/induced dipole interactions between the dopant and the apparently easily polarizable hexakis(phenylethynyl)-naphthalene and -triphenylene 'super-disc-cores', as suggested by the dipole moment dependency of the stability of the induced columnar phases (cf. table 2). The dopant molecules, therefore, seem not to be intercalated between the 'super-disc-cores', but may improve the space filling in the core regions by filling up dead volume, possibly caused by the molecular 'bays' of **1** and **2**.

Further investigations by X-ray diffraction and spectroscopic methods, such as ^{2}H NMR, are expected to confirm the phase characterizations discussed and could provide information about the mechanism of this novel type of phase induction in disc-shaped systems.

4. Experimental

The synthesis and liquid crystalline behaviour of the radial hexaynes **1** and **2** are reported in detail elsewhere [7, 8]. The dopant 4,5-dibromo-*o*-xylene was synthesized by bromination of *o*-xylene [15]; the other dopants are commercially available and were used without further purification.

The contact samples were prepared as follows: the compound with the higher melting point was melted between a glass plate and a cover slip. Thereafter, the lower melting substance was put close to one side of the cover slip and heated to give the isotropic liquid or nematic discotic phase. Due to capillary forces, both compounds then came into contact with each other.

The preparation of mixtures of the nonyl substituted naphthalene derivative **1b** with bromobenzene and 4,5-dibromo-*o*-xylene, respectively, was carried out by melting each of the binary systems in sealed DSC pans (Mettler), annealing them in their isotropic phase for 15 min (Mettler hot stage), and subsequent rapidly cooling them in liquid nitrogen.

The thermal behaviour of all mixtures, as well as of the contact samples, was studied by polarizing microscopy using a Leitz Laborlux 12 Pol equipped with a Mettler FP 2 hot stage. The heating rates were 2–5 K min^{-1} or 10 K min^{-1} in the case of temperatures above 200°C or with volatile dopants. However, some problems did arise from decomposition of the mixtures and/or from the volatility of the dopants preventing successful DSC measurements.

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References

[1] Part 72 on liquid crystalline compounds; part 71: SABASCHUS, B., SINGER, D., HEPPKE, G., and PRAEFCKE, K., 1992, *Liq. Crystals*, **12,** 863.

[2] For examples see the papers cited in [5 (*a*)].

[3] DAVIDSON, P., LEVELUT, A.-M., STRZELECKA, H., and GIONIS, V., 1983, *J. Phys. Lett.*, **44,** L-823.

[4] For low molecular weight disc-shaped systems see (*a*) Bengs, H., Ebert, M., Karthaus, O., Kohne, B., Praefcke, K., Ringsdorf, H., Wendorff, J. H., and Wüstefeld, R., 1990, *Adv. Mater.*, **2,** 141. (*b*) Kranig, W., Boeffel, C., Spiess, H. W., Karthaus, O., Ringsdorf, H., and Wüstefeld, R., 1990, *Liq. Crystals*, **8,** 375. (*c*) Praefcke, K., Singer, D., and Gündogan, B., 1992, *Molec. Crystals liq. Crystals*, **223,** 181. For polymeric discotic phases see (*d*) Ringsdorf, H., Wüstefeld, R., Zerta, E., Ebert, M., and Wendorff, J. H., 1989, *Angew. Chem.*, **101,** 934, or 1989, *Angew. Chem. Int. Ed. Engl.*, **28,** 914. (*e*) Ringsdorf, H., Wüstefeld, R., Ebert, M., and Wendorff, J. H., 1989, *A.C.S. Polym. Prep.*, **30,** 479.

[5] (*a*) Praefclke, K., Singer, D., Kohne, B., Ebert, M., Liebmann, A., and Wendorff, J. H., 1991, *Liq. Crystals*, **10,** 147. (*b*) Praefcke, K., Singer, D., Langner, M., Kohne, B., Ebert, M., Liebmann, A., and Wendorff, J. H., 1992, *Molec. Crystals liq. Crystals*, **215,** 121.

[6] Bengs, H., Karthaus, O., Ringsdorf, H., Baehr, C., Ebert, M., and Wendorff, J. H., 1991, *Liq. Crystals*, **10,** 161.

[7] Praefcke, K., Kohne, B., Gutbier, K., Johnen, N., and Singer, D., 1989, *Liq. Crystals*, **5,** 233.

[8] Praefcke, K., Kohne, B., and Singer, D., 1990, *Angew. Chem.*, **102,** 200, or 1990, *Angew. Chem. Int. Ed. Engl.*, **29,** 177.

[9] Levelut, A. M., private communication (May and July 1988) on X-ray results identifying the columnar mesophases of the hexakis(4-hexylphenylethynyl)naphthalene (**1a**) as D_r ($a = 43{\cdot}3$ Å, $b = 26{\cdot}7$ Å) and D_h ($a = 26{\cdot}4$ Å) with an intracolumnar distance of 3·6 Å and a correlation length of about 10–15 molecules for each of these phases; see also [7].

[10] Landolt, H., and Börnstein, R., 1951, *Zahlenwerte und Funktionen aus Naturwissenschaften und Technik*, 6th edn, vol. I/3 (Springer-Verlag), Berlin-Göttingen-Heidelberg.

[11] Luz, Z., private communication (October 1991) on ^{2}H NMR investigations.

[12] Möller, M., and Wendorff, J. H., private communication (May 1991), on X-ray results.

[13] Kohne, B., and Praefcke, K., 1987, *Chimia*, **41,** 196.

[14] Praefcke, K., Kohne, B., Singer, D., Demus, D., Pelzl, G., and Diele, D., 1990, *Liq. Crystals*, **7,** 589. Praefcke, K., Kohne, B., Gündogan, B., Singer, D., Demus, D., Pelzl, G., Diele, D., and Bakowsky, U., 1991, *Molec. Crystals liq. Crystals*, **198,** 393.

[15] Piechocki, C., and Simon, J., 1985, *Nouv. J. Chim.*, **9,** 159.