Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

New switchable columnar liquid crystals

Günter Scherowsky[a]; Xin Hua Chen[a]
[a] Institut für Organische Chemie, TC2, Technische Universität Berlin, Berlin, Germany

To cite this Article Scherowsky, Günter and Chen, Xin Hua(1994) 'New switchable columnar liquid crystals', Liquid Crystals, 17: 6, 803 — 810
To link to this Article: DOI: 10.1080/02678299408035473
URL: http://dx.doi.org/10.1080/02678299408035473

LIQUID CRYSTALS, 1994, VOL. 17, NO. 6, 803–810

New switchable columnar liquid crystals†

by GÜNTER SCHEROWSKY* and XIN HUA CHEN
Institut für Organische Chemie, TC2, Technische Universität Berlin,
Straße des 17 Juni 124, Berlin 10623, Germany

(*Received 5 January 1994; accepted 29 March 1994*)

Penta- and hexa-substituted phenanthrenes and penta-substituted benzo[c]-phenanthrenes have been synthesized; these exhibit columnar phases and are electrically switchable when bearing chiral side chains. The liquid crystalline and electro-optical properties are described. A strong tri-state switching behaviour is observed with the phenanthrene derivatives. A helical phase structure, responsible for this switching behaviour, is proposed and the possible mechanism of the columnar phase switching process is discussed.

1. Introduction

Liquid crystals consisting of disc-shaped molecules were discovered by Chandrasekhar [1] 16 years ago. Up to now, about 1000 compounds which show discotic mesophases are known. Great attention has recently been attracted by new discotic compounds with potential optical, electrical and magnetic applications.

Like classical liquid crystals, discotic phases are classified into different types according to their phase structures—N_D, D_h, D_r, D_t, etc. Among these discotic phases, the tilted columnar phase D_t has been presumed to be ferroelectric [2]. However, due to steric hindrance between columns, the columnar phase was considered to be ferroelectrically unswitchable [3]. Recently Bock and Helfrich [4], observed for the first time ferroelectric switching in a tilted columnar phase of a polysubstituted dibenzopyrene bearing chiral side chains.

To investigate the switching properties of columnar phases and their relation to molecular structure and type of mesophase, we started to synthesize new electrically switchable discotic compounds. Discotic mesogens generally possess flat disc-shaped cores with four to eight long, side chain substituents. Because of this structural characteristic, polysubstituted phenanthrenes are of interest to us, because they not only have a flat, banana-shaped core, but they also possess fewer aromatic rings than most of the known discotic mesogens and might, therefore, exhibit lower viscosity than the dibenzopyrenes. Here we report 1,2,3,6,8-penta-substituted and 1,2,3,6,7,8-hexa-substituted phenanthrenes. As a further modification of the banana-shaped core we have also synthesized half-moon shaped benzo[c]phenanthrenes, which possess five side chains at positions 2, 3, 4, 7 and 9 (see figure 1).

2. Synthesis

To synthesize penta- and hexa-substituted phenanthrenes (see scheme 1), 2,3,4-trimethoxybenzyl alcohol, **1**, was brominated and the product reacted with triphenylphosphine to yield the phosphonium salt, **3**. Wittig reaction with

---

*Author for correspondence.
†Presented at the IV FLC conference, Tokyo 1993.

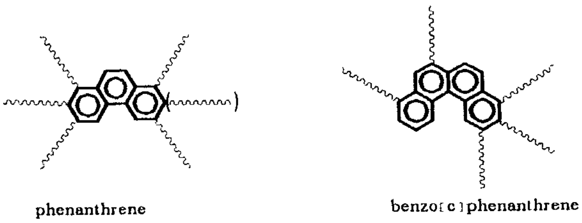
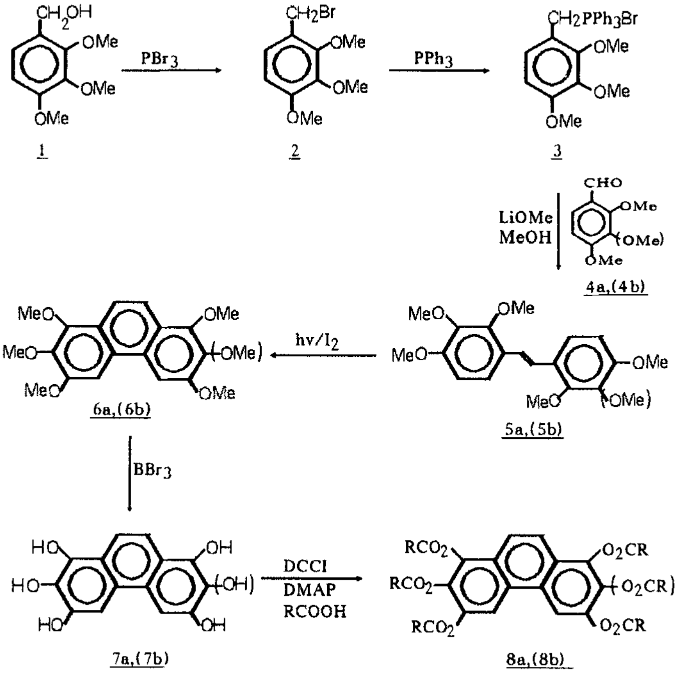


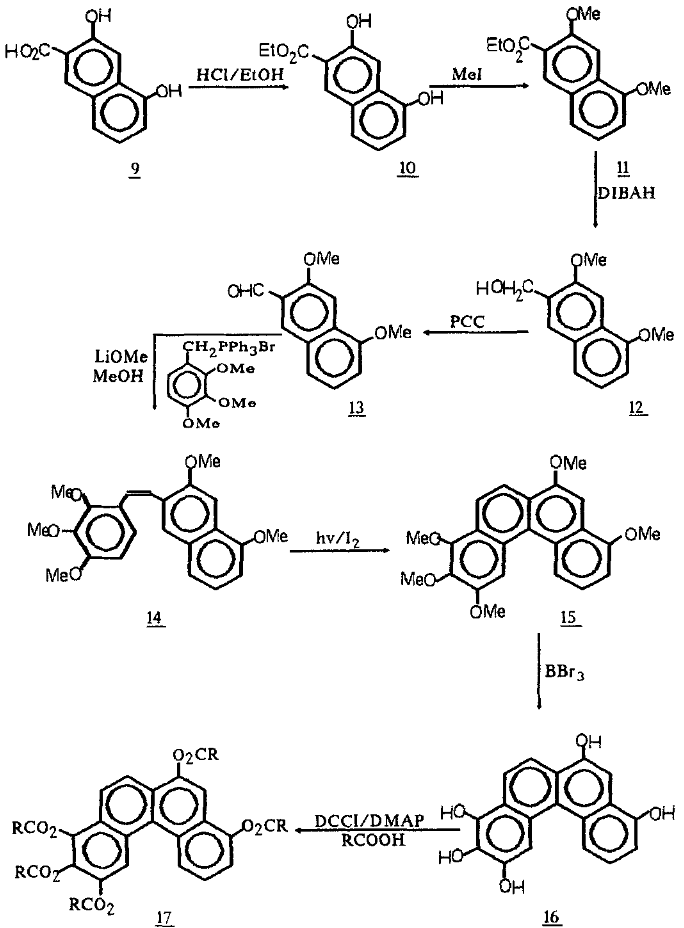
Figure 1. General structures of phenanthrene and benzo[c]phenanthrene derivatives.



Scheme 1. Synthesis of phenanthrene derivatives.

2,4-dimethoxy- or 2,3,4-trimethoxy-benzaldehyde, **4a**,(**4b**), gave the penta- or hexa-substituted stilbene, **5a**,(**5b**). Photocyclization of the polysubstituted stilbene was carried out on benzene or cyclohexane solutions using irradiation with a UV lamp, to yield **6a**,(**6b**). Demethylation of **6a**,(**6b**) was performed with BBr_3 in dichloromethane solution. The Steglich method was used for the final esterification of the polyhydroxyphenanthrenes.

As starting material for the synthesis of penta-substituted benzo[c]phenanthrenes (see scheme 2), the commercially available 3,5-dihydroxynaphthalene-2-carboxylic acid, **9**, was selected. By esterification and methylation, **9** was converted into ethyl 3,5-dimethoxynaphthalene-2-carboxylate, **11**, which was reduced with DIBAH to yield **12**. PCC oxidation of **12** afforded 3,5-dimethoxynaphthalene-2-carboxaldehyde



Scheme 2. Synthesis of benzo[c]phenanthrene derivatives.

13. The subsequent reaction steps are analogous to those for the synthesis of the phenanthrene derivatives.

3. Results and discussion

3.1. *Mesomorphic properties*

From the table, we can see that 2,3,4,6,7,8-hexa-substituted phenanthrenes, when associated with normal alkyl chains, exhibit only monotropic columnar phases. They crystallize very rapidly from the mesophases. The monotropic columnar phase disappears when the chain length $n = 10$. Variation of the chain length n from 6–10 has a weak influence on the mesophase range. Insertion of oxygen into the side chain, increasing the polarity of the side chain, stabilizes the columnar phase. In the case of compound **VII**, the methyl group at the chiral centre is too near to the mesogenic core to maintain the column stacking of the molecules, due to strong steric hindrance. Nevertheless, the 1:1 mixture of compounds **VII** and **II** forms a stable columnar phase. When the methyl branching point is moved away two more atoms from the core, as shown with compound **X**, a broad stable enantiotropic

Phase transitions (°C).

	1,2,3,6,8-penta-substituted phenanthrenes	1,2,3,6,7,8-hexa-substituted phenanthrenes	2,3,4,7,9-penta-substituted benzophenanthrenes
n-$C_nH_{2n+1}CO_2$–			
$n=6$		$C\xrightarrow[90\,D\,96]{117{\cdot}5}I$ **(I)**	
7		$C\xrightarrow[63\,D\,79]{107{\cdot}3}I$ **(II)**	
8		$C\xrightarrow[83\,D\,89]{110}I$ **(III)**	
10		C 112 I **(IV)**	C 66 I **(V)**
$C_7H_{15}O\overset{*}{C}HCO_2$– $|$ [*S*] CH_3	$D^{\dagger}\xrightarrow{51}I$ **(VI)**	C 75·4–77·1 I **(VII)**	m.p. < −20 **(VIII)**
$C_6H_{13}\overset{*}{C}HCH_3$ $|$ [*R*] OCH_2CO_2–	$D^{\dagger}\xrightarrow{75}I$ **(IX)**	$C\xrightarrow[-15{\cdot}8]{-12{\cdot}5}D\xrightarrow[138]{145}I$ **(X)**	

† No crystallization can be observed down to − 100°C.

columnar phase is observed. Compound **VI**, despite its methyl branching near to the core, unexpectedly exhibits a relatively broad enantiotropic columnar phase. A plausible interpretation is that the penta-substituted phenanthrene molecule favours a cross-like packing within a column, so decreasing the disturbance by the methyl group.

The poly-substituted benzo[c]phenanthrene derivatives, which possess a larger, flat mesogenic core, do not however exhibit any discotic mesophase. Seemingly, the 2,3,4,7,9-substitution pattern is not favourable for the columnar stacking. We have made mixtures with 1,3,5,7,9,10-hexa-(2-methyl-3-oxadecanoyloxy)anthracene, **X**, which exhibits columnar phases from room temperature to 145°C, and found that no remarkable destruction of the columnar phase was observed when the concentration of the penta-substituted benzo[c]phenanthrene, **VIII**, is below 10 per cent.

3.2. *Textures and phase structures*

The phenanthrene derivatives carrying normal alkyl chains exhibit a branched dendritic texture as shown in figure 2. This texture has also been observed by other researchers [5, 6] and confirmed to be characteristic of a tilted rectangular columnar phase. From the texture observation alone, we cannot however exclude another kind of columnar phase, and verification of this phase structure by X-ray investigation is under way.

When the phenanthrene ring system is carrying chiral 2-methyl-3-oxadecanoyloxy or 4-methyl-3-oxadecanoyloxy substituents, a pseudo-focal-conic texture similar to that of a hexagonal phase is observed, as shown in figure 3. The difference from the branched dendritic texture discussed above may be caused by the polarity and chirality of the side chains. Mixtures of compounds **VII** and **II** show a similar pseudo-focal-conic texture. A similar texture was also observed by Malthete *et al.* [7], for a columnar phase of a chiral hexa-substituted triphenylene and verified by X-ray as a D_r phase. Therefore, this pseudo-focal-conic texture may represent another rectangular phase with different symmetry from the branched dendritic texture.

Furthermore, from our investigation of the switching properties of the chiral poly-substituted phenanthrene derivatives, to be discussed in the following section, we conclude that a helical structure could exist in the chiral columnar phase and be responsible for the observed tri-state switching behaviour caused by deformation or unwinding of the helix by an electrical field. Although this evidence for a helical structure in the columnar phase is limited, we would like to discuss it. In view of the molecular orientation in a helix of disc-like molecules, several possible structures could exist as shown in figure 4. In a columnar phase, the molecular discs can be orthogonal or tilted with respect to the columnar axis (see figure 4(*a*), (*b*)). These two cases can also occur in a helical arrangement, which can be formed either from the whole column or within the column, as seen in figure 4(*c*), (*d*), (*e*). Detailed investigations of the phase structure by X-ray and the corresponding theoretical calculations of the lattice energy are in progress.

4. Electro-optical switching behaviour

The switching experiments on our newly synthesized compounds were performed using an analogous method to that employed for classical liquid crystals. Cells with polyimide surface layers were utilized.

All the phenanthrene derivatives carrying non-racemic, chiral substituents are electrically switchable. The 1:1 mixture of **VII** and **II** shows a strong electro-optical effect. The switching angle for this mixture is +/−5° under $+/-5\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ and rises to +/−20° under $+/20\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ at 70°C. The increase is linear with the electric field and exhibits only a weak dependence on temperature. At 30°C the switching can be observed with an electric field of above $2\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ with a response time of about one second. The other chiral penta- and hexa-substituted phenanthrenes (**VI**, **IX** and **X**) exhibit a similar switching behaviour. Characteristic for this electroclinic-like switching is the fact that, starting from the zero field state, one can obtain two different states when applying a positive or negative field, as shown in figure 5. Those states relax back to the zero field state when the field is off. As discussed above, this behaviour could be caused by zero field helical structure. Alternatively, an antiferroelectric ordering of the tilted columns could be the reason.

The chiral, non-racemic poly-substituted benzo[c]phenanthrenes possess no columnar phases, but they can be used as dopants in non-chiral columnar hosts to give a switchable columnar phase. A 10 wt% mixture of (*S*)-2,3,4,7,9-penta-(2-methyl-3-oxadecanoyloxy)benzo[c]phenanthrene, **VIII**, in 1,3,5,7,9,10-hexa-(2-methyl-3-oxadecanoyloxy) anthracene **X** is electrically switchable.

5. Mechanism of the switching process

The mechanism of the switching process in columnar phases is still an open question. As we know, in a columnar phase, the molecular plane can be perpendicular or tilted with respect to the axis of the column and the switching can only take

Figure 2. The branched dendrite texture of compound **II** at 78°C.

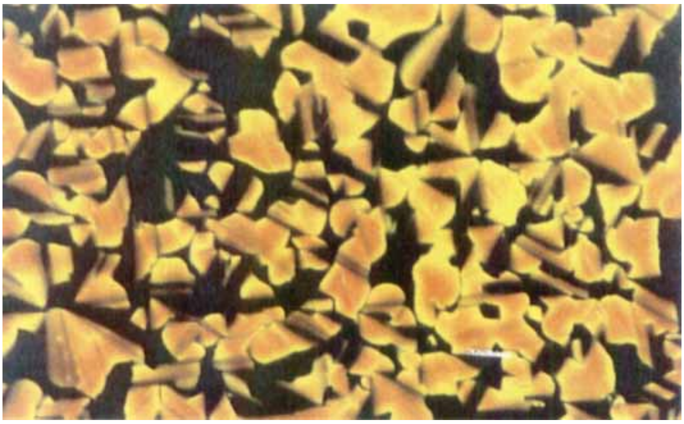


Figure 3. The pseudo-focal-conic texture of compound **VI** at room temperature.

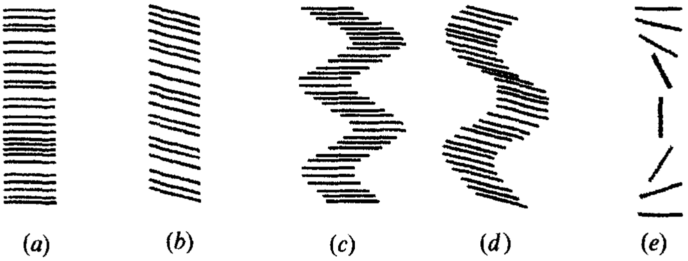


Figure 4. The molecular orientation in a column and possible helical structures. (*a*), (*b*) columns in which molecular discs lie orthogonal and tilted with respect to the columnar axis; (*c*), (*d*) possible helical structures of the columns formed from columns (*a*) and (*b*), respectively, through introduction of chiralty; (*e*) possible helical orientation of molecules within one column.

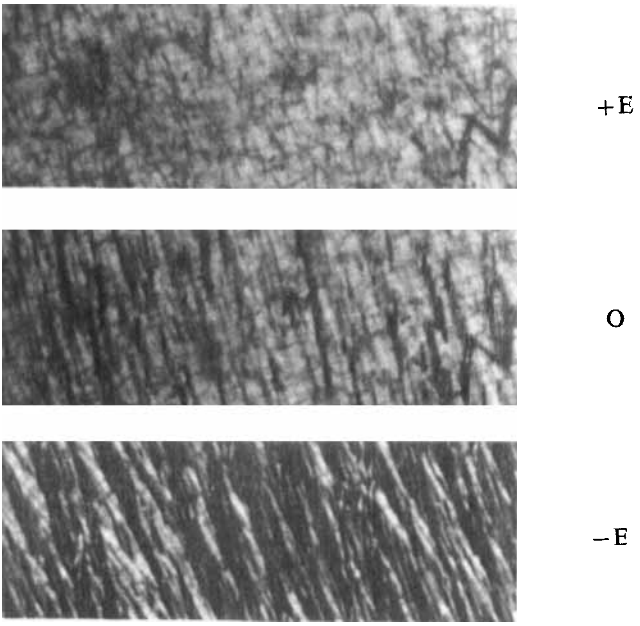


Figure 5. Three switching states of compound **VI** at room temperature. Sample oriented through shearing in a 4 μm cell. $E = +/-15\,\mathrm{V}\,\mu\mathrm{m}^{-1}$.

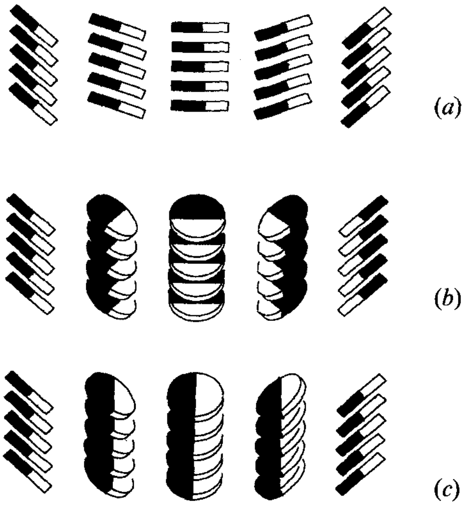


Figure 6. Three possible switching processes in columnar systems. The black and white representation of the discs is chosen for an easier understanding of the different motions along a single column: (*a*) switching through an untilted state; (*b*) director precession and column rotation; (*c*) only director precession.

place when at least one tilted state is included in the switching process. For ferroelectric switching, two tilted states are required. Concerning the pathway from one tilted state to another Bock and Helfrich [4] have suggested two models as shown in figure 6 (*a*), (*b*). In the case of (*a*), the switching process is through an untilted state and the chains rotate to change the direction of the dipole. In the case of (*b*), the whole column rotates around the axis of the column and the side chains remain unchanged. In addition to these two cases, we propose a third possibility as seen in figure 6 (*c*). The difference between (*b*) and (*c*) is that in the case of (*b*) the director precesses around the columnar axis and the columns rotate too, whereas in the case of (*c*), only the director precesses and the substitution positions of the side chains only move up and down parallel to the columnar axis. The direction of the dipole is reversed through rotation of the side chains. In all three models, the motions from one state to another are caused by the interaction of the electric field with the lateral dipoles in the chiral side chains and an energy barrier at the transition state has to be overcome, which is strongly dependent on the molecular and phase structure. One of these pathways could be preferred, or the switching mechanism in the columnar system may involve all three.

6. Conclusion

The newly synthesized discotic compounds exhibit strong electro-optical switching properties. Relations between molecular structure and phase behaviour, and some observations on phase structure and switching behaviour are discussed. A helical structure in the chiral columnar phase is proposed, and a possible mechanism for the switching process in the columnar system is also discussed.

We wish to thank Mr H. Bock and Professor W. Helfrich for helpful discussions. This work was supported by the Deutsche Forschungsgemeinschaft through SFB 335.

References

[1] Chandrasekhar, S., Sadashiva, B. K., and Suresh, K. A., 1977, *Pramana*, **9**, 471.

[2] Prost, J., 1981, *Comptes Rendus Du Colloque Pierre Curie: Symmetries and Broken Symmetries*, edited by N. Boccara (Inst. Dev. Sci., Educ. Technol., Paris).

[3] Levelut, A. M., Oswald, P., Ghanem, A., and Malthete, J., 1984, *J. Phys., Paris*, **44**, 745.

[4] Bock, H., and Helfrich, W., 1992, *Liq. Crystals*, **12**, 697.

[5] Frank, F. C., and Chandrasekhar, S., 1980, *J. Phys,. Paris*, **41**, 1285.

[6] Destrade, C., Bernaud, M. C., Gasparoux, H., Levelut, A. M., and Nguyen Huu Tinh, 1979, *Proceedings of the International Liquid Crystal Conference*, Bangalore, edited by S. Chandrasekar, p. 29.

[7] Malthete, J., Jacques, J., Nguyen Huu Tinh, and Destrade, C., 1982, *Nature, Lond.*, **298**, 46.