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Thermotropic Liquid Crystals from Planar Chiral Compounds: Optically Active Mesogenic [2.2]Paracyclophane Derivatives[**]

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Heinz-Siegfried Kitzerow, and Henning Hopf[*]

Chiral liquid-crystalline (LC) compounds constitute a central topic of present-day research on liquid crystals. For example, not only are the well-established applications of thermochromic materials as well as twisted nematic (TN) and supertwisted nematic (STN) displays based on chirality, but so are ferro-, ferri-, and antiferroelectric, second-harmonic generation, polymer-stabilized cholesteric texture (PSCT) displays and certain photonic crystals. Thus, new chiral structures are continuously proposed that provide new insights and promising applications.[1]

The way in which chirality is introduced into the mesogenic molecule is one of the crucial factors in determining the properties of the resultant LC material. The importance of the position of the stereogenic unit relative to the liquid-crystalline core is underlined by the fact that it forms the basis for a classification system for chiral LC compounds.[2] Most chiral mesogenic compounds are classified as Type I or Type II liquid crystals. In the former case chirality is introduced through an asymmetric carbon atom located in a terminal alkyl chain, whereas in the latter it is enclosed between two liquid-crystalline core units. These LC compounds have been well-studied and widely used. In Type III liquid crystals, the chiral unit is incorporated into the rigid core itself, and is thus particularly applicable to planar and axially chiral compounds. Although properties which are important for practical application have been predicted for materials of this type (for example, shortening of helical pitch length, increase in sponataneous polarization of a chiral dopant, as well as interesting optical effects[3]), planar, chiral liquid-crystalline compounds still remain relatively unexplored.

The molecular complexity of the structural unit necessary to generate an axis or a plane of chirality often creates serious obstacles to achieving stable mesomorphic properties. Only a few examples of planar and axially chiral mesogens have so far been reported. These include: cyclohexylideneethanone[4] and allene derivatives,[5] chiral biphenyls,[6] and iron-tricarbonyl–butadiene complexes.[7] Additionally, the first 1,3-unsymmetrically disubstituted optically active LC ferrocene derivative has recently been reported.[8] However, in most of these cases the mesophases only had a narrow temperature interval and several of the compounds obtained appear to be chemically or photochemically unstable. Moreover, the difficulties of synthesis and optical resolution associated with these derivatives are probably the reason for the lack of systematic studies on the physical properties of planar and axially chiral compounds as well as of their practical application.

In our opinion, the ease of functionalization, ready optical resolution, and high configurational stability of paracyclophane (PC) derivatives[9] make these bridged aromatic compounds unique candidates for chiral LC materials.

In our first attempt to investigate the ability of the PC unit to promote mesomorphism we used several racemic derivatives.[10] As shown by these exploratory investigations, the mesogenic potential of the PC core depends on the number and position of substituents in the PC moiety: of the structures investigated, *para*-substituted PC derivatives had superior mesogenic properties with a broad interval of either nematic or smectic A (SmA) phases. Herein we describe the first family of optically active mesogenic compounds containing a PC unit. Several synthetic problems had to be solved to prepare the required chiral PC precursors.

As mentioned above, *para*-substitution of the PC moiety was shown to best induce mesomorphism,[10] but known examples of specific *para*-PC derivatives are still scarce and a

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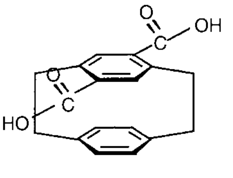
general synthetic approach to such structures is not yet available. We decided to use PC carboxylic acids, rather than the possible (and available) PC phenols or aldehydes, as the most promising starting materials to construct LC compounds. However, little is known about chiral (and optically active) PC carboxylic acids; for example, only [2.2]paracyclophane-4-carboxylic acid has been reported in an optically active form.[11]

Optical resolution of [2.2]paracyclophane-4,7-dicarboxylic acid ((±)-**1**)[10] was performed with (*S*)-phenylethylamine



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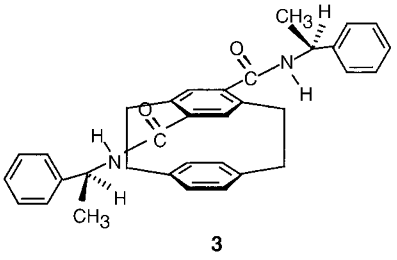

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(PEA) through formation of the diastereomeric salt (−)-**2**. The enantiomeric excess (*ee*) of (−)-**1** was determined by converting it into the corresponding amide (−)-**3** with (*S*)-PEA. As a consequence of the known stability of PC derivatives,[9] we assume that the reactions used to prepare (−)-**3** did not alter the optical purity of diacid (−)-**1**. Therefore, the determination of the diastereomeric excess (*de*) of (−)-**3** is a measure of the *ee* value of (−)-**1**, and was accomplished by ^{1}H NMR spectroscopy.[12]

Elaborate resolution techniques provided (−)-**1** with *ee*-values greater than 96% in 55% yield.[13] Additionally, an analytical sample of diacid (−)-**1** of greater than 99% *ee* was obtained and characterized. Crystallization of the salt (−)-**2** from methanol provided crystals suitable for X-ray analysis, which revealed an *R* configuration of (−)-**1** (Figure 1).[14]

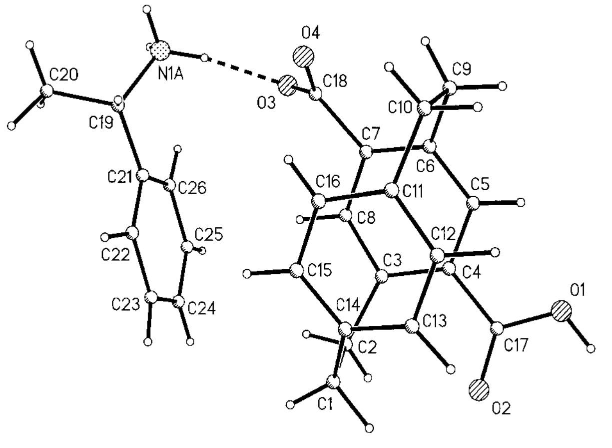

Figure 1. Structure of the diastereomeric salt derived from (*S*)-*α*-phenylethylamine and (*R*)-**1** as revealed by X-ray analysis.

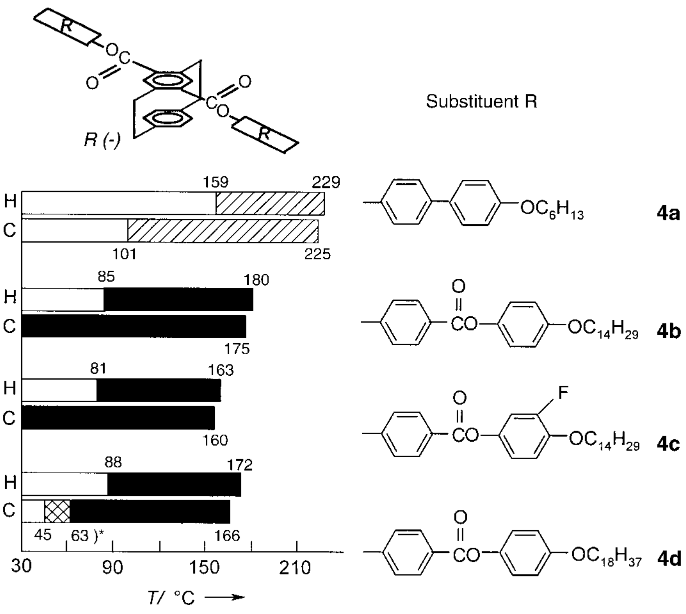

Figure 2. Phase-transition temperatures of optically active PC derivatives **4a–d**. H or C denotes a heating or cooling cycle, respectively. □: crystalline solid; ///: chiral nematic (cholesteric) phase; ■: chiral smectic A phase; × × ×: chiral smectic C phase. *: transition observed by means of PLM only.

Derivatization of diacid (*R*)-**1** to provide an elongated rigid rodlike molecular shape led to liquid-crystalline PC derivatives **4a–d** (Figure 2). Their mesomorphic behavior was studied by means of differential scanning calorimetry (DSC) and polarized optical microscopy (PLM). These studies revealed an excellent mesogenic potential of the PC core that is unusual and not predictable for molecules containing such bulky units (intraannular distances of the PC moiety is about 3.09 Å). The type of mesophase could be tuned by changing the nature of the substituents in the PC unit: a cholesteric phase was detected for **4a**, while compounds **4b–d** revealed enantiotropic SmA* phase behavior over a broad temperature interval. The formation of a monotropic smectic C* (SmC*) phase was also clearly detected by PLM for the longer-chain derivative **4d**: at the SmA*–SmC* transition, the dark homeotropic domains of the SmA* phase gives rise to a schlieren texture characteristic of the SmC* phase. The influence of lateral functionalization with fluorine atoms on the stability of the smectic phases was also investigated (**4c**). Relative to the unsubstituted analogue **4b**, introduction of the lateral fluorine atom insignificantly lowers the melting point and causes a 13 °C reduction of the mesophase interval, but this, however, still remains quite broad. Thus, when tailored properly (the SmC* phase gives rise to ferroelectric properties), structures of such a type can be considered as candidates for ferroelectric studies. The search of tilted smectic phases from PC-derived liquid crystals is currently underway.

The results presented in Figure 3 indicate values of the helical twisting power (HTP) obtained for compounds **4a–d** in a commercial nematic mixture, MLC 6260 (Merck, Darmstadt, Germany). These results reveal a sufficiently high twisting ability of the investigated compounds—the values obtained are comparable to that of commercially used chiral dopants such as 4-cyano-4′-(2-methylbutyl)-biphenylene (CB 15, 6.7 μm^{-1} at room temperature[15]). As a result of the high values of the helical twisting power, mixtures of the chiral compounds with a nematic component show selective reflection (Figure 4), which indicates that the pitch of the respective mixture is not larger than a few hundred nanometers. Of

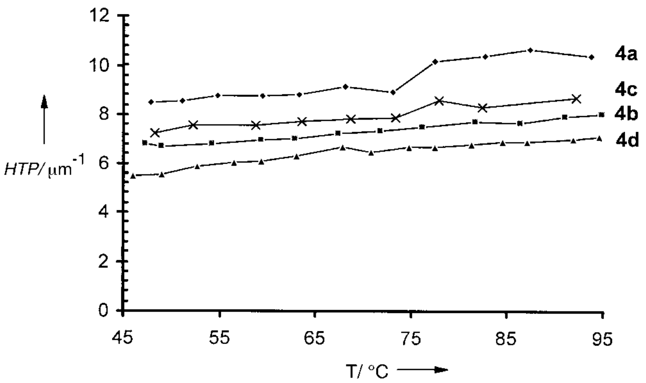

Figure 3. Helical twisting power of the investigated optically active compounds **4a–d** versus temperature. The compounds induce the formation of left-handed helices.

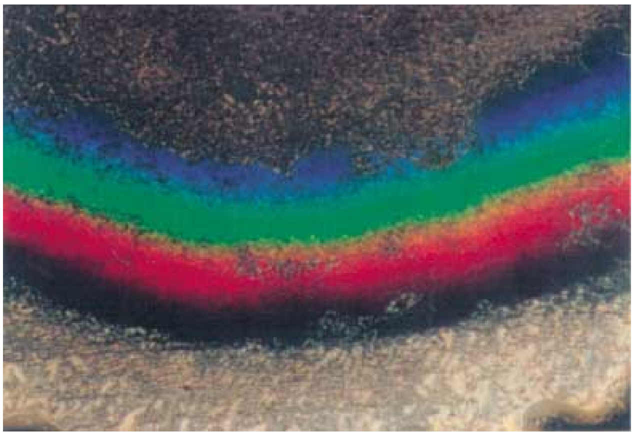

Figure 4. Selective reflection in a contact preparation between compound **4a** and the nematic mixture MLC 6260. The color of the selective reflection changes according to Bragg's law because of a gradient of the concentration, which in turn leads to a variation of the helical pitch.

course, the values of the HTP obtained are much lower than those of the highest HTP values ever observed in nematic mixtures, such as for binaphthol derivatives (up to about 100 μm^{-1})[16] or TADDOLs (300–400 μm^{-1}).[17]

In our opinion, the compounds presented (**4a–d**) demonstrate the principle of high twisting ability of planar chiral compounds. However, the structure could be further optimized: a PC unit which in this case protrudes from the overall linear molecule probably disrupts interaction between the chiral dopant and the nematic host; to overcome this problem PC derivatives bearing linear functionalizations on both decks of the PC unit are currently under investigation.

In conclusion, a family of mesogenic planar chiral compounds based on [2.2]paracyclophane have been introduced. Their availability and stable mesomorphic behavior permit the work presented here to be considered as a promising background for the study of the physical properties of this new type of liquid crystals, which up until now have remained mostly in the focus of theoretical predictions rather than practical investigations.

Experimental Section

Optical resolution of (±)-**1**:[14] Racemic **1** (0.40 g, 1.35 mmol) was suspended in acetone (15 mL) and then the resulting suspension was heated to reflux and treated with (*S*)-PEA (0.36 mL, 2.80 mmol). The salt begins to precipitate in a few min; afterwards acetone (17 mL) was added to the reaction mixture and the resulting suspension was refluxed for 5 h, before it was cooled and allowed to stand overnight at room temperature. The precipitate was filtered, dried (0.27 g), and then combined with the acetone/chloroform (5:1) mixture (12 mL); the resulting suspension was refluxed for 2 h and left to stand overnight at room temperature. Filtration and drying of the precipitate afforded 0.21 g of (−)-**2**. The salt was dissolved in the minimum amount of methanol and hydrolyzed with 2 N HCl. The precipitate was filtered off and thorougly washed with water to yield 0.11 g (55%) of (−)-**1** in >96% *ee*.

A sample of (−)-**2** was additionally crystallized from an acetone/methanol mixture (1:1). Hydrolysis of the salt as described above provided (−)-**1** of >99% *ee*. $[\alpha]_D^{20} = -269.0$ ($c = 0.25$ in methanol). Elemental analysis calcd for $C_{18}H_{16}O_4$ (296.322): C 72.96, H 5.44; found: C 72.82, H 5.41. (All spectral data are identical with those of racemic **1**.[10])

Transition temperatures were determined with a differential scanning calorimeter Rheometric Scientific DSC SP, scanning rate 10 K min^{-1}, under nitrogen. Optical studies were conducted by using an Olympus BX 50 System Microscope equipped with a Linkam-LTS-350 variable-temperature stage. HTP was measured by means of the Cano method[18] in a commercial nematic mixture (MLC 6260; Merck, Darmstadt, Germany).[14] The mass fraction of the dopant was varied up to $x = 0.1$.

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[12] Full characterization of compounds **4a–d**, experimental details of the determination of the *ee* value of (−)-**1** and detailed description of the HTP measurements are given in the Supporting Information.

[13] The data on both enantiomers and optimized resolution conditions will be reported separately.

[14] Crystal structure detrmination of $[C_8H_{12}N]^+[C_{18}H_{15}O_4]^-$: $C_{26}H_{27}NO_4$ ($M_r = 417.49$), 0.5 × 0.3 × 0.2 mm, monoclinic, space group *C*2 (no. 5), at 163 K, $a = 20.503(9)$, $b = 7.028(3)$, $c = 14.943(5)$ Å, $\beta = 97.04(3)°$, $V = 2137.0(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.298$ g cm^{-3}, $\mu = 0.087$ mm^{-1}, $F(000) = 888$. Single-crystal X-ray diffraction experiments were carried out with a Syntex P2$_1$ instrument, using graphite monochromated

$Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\theta/2\theta$ scans, $2\theta < 56°$) at 163 K. A total of 3466 refelctions were measured, 2908 ($R_{int} = 0.0364$) independent reflections were used in further calculations and refinement. The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic (for non-hydrogen atoms) and isotropic (for H atoms) approximation. The refinement converged to $R1 = 0.0632$ (from 1914 unique reflections with $I > 2\sigma(I)$) and $wR2 = 0.1591$ (from all 2795 unique reflections), the number of the refined parameters is 388, GOF = 1.022. All calculations were performed on an IBM PC/AT using the SHELXTL software (G. M. Sheldrick, SHELXTL-97, Version 5.10, Bruker AXS Inc., Madison, WI, 53719, USA). CCDC-182770 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Color-Tunable Transparent Mesoporous Silica Films: Immobilization of One-Dimensional Columnar Charge-Transfer Assemblies in Aligned Silicate Nanochannels**

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Katsuhiko Ariga, and Takuzo Aida*

Charge-transfer (CT) complexes in solution and in the crystalline state have attracted much attention in the fields of organic chemistry, photochemistry, solid-state physics, and so forth.[1] For a variety of applications utilizing CT complexes, long-range structural ordering of donor/acceptor assemblies would be important. From this point of view, disclike molecules that form columnar phases are potential candidates for the formation of infinite, one-dimensional CT assemblies, which may be useful for optoelectronic applications including photoconductive materials, solar cells, and thin-film transistors.[2] Triphenylene derivatives are representative of those molecules whose columnar phase is known to be stabilized upon complexation with suitable acceptors.[3] Immobilization of such columnar CT assemblies in optically transparent solid supports would be of great interest for materials science and device fabrication. Mesoporous silicates are particularly interesting[4] because they can provide highly ordered, unidirectional channels that are optimal for the long-range structural ordering of CT assemblies. Here we report the fabrication of novel mesostructured silica films by using triphenylene-based CT complexes as templates for sol–gel synthesis. The films were highly transparent and color-tunable from blue to red depending on the nature of the intercalating electron acceptor, and showed red-shifted CT absorption bands in the aligned silica nanochannels.

Amphiphilic triphenylene derivatives **1** and **2** were found to form CT complexes with electron acceptor molecules such as 2,4,7-trinitro-9-fluorenone (TNF), 2,3,6,7,10,11-hexacyanohexaazatriphenylene (HAT), 7,7,8,8-tetracyanoquinodimethane (TCNQ), chloranil (CA), and 1,2,4,5-tetracyanobenzene (TCNB, Figure 1). A typical procedure for the fabrication of mesostructured silica films is as follows: **1** (35.8 mg, 16.8 μmol) was added to a solution of TNF (5.28 mg, 16.8 μmol) in benzene, and the mixture was evaporated to leave a brown residue, which was then dissolved in a mixture of EtOH (1.18 g), 12 N hydrochloric acid (6.18 mg), and water (81 mg). Tetrabutoxysilane (TBOS; 324 mg, 1.01 mmol) was

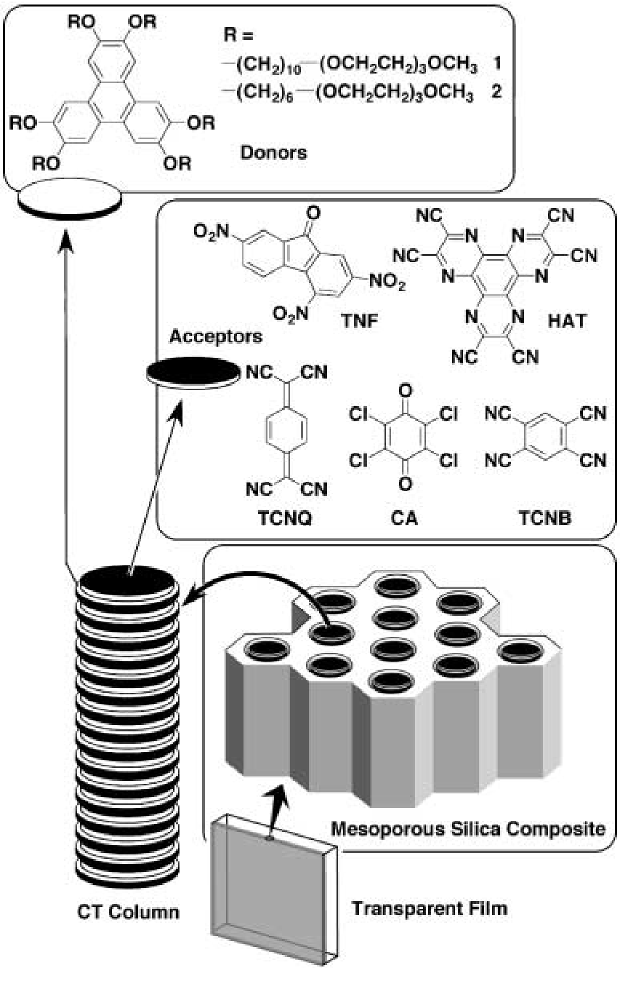

Figure 1. Formulas of donors **1**, **2**, and acceptor species, and a schematic representation of a mesoporous silica film containing one-dimensional columnar charge-transfer (CT) assemblies immobilized in a hexagonal array of nanoscopic channels.

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