# 174. TADDOLs with Unprecedented Helical Twisting Power in Liquid Crystals

Preliminary Communication

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A large number of TADDOL (*α,α,α′,α′-t*etra*a*ryl-1,3-*d*ioxolan-4,5-*d*imethan*ol*) derivatives has been tested as chiral dopants for inducing conversion of nematic to cholesteric phases. With the *Merck* liquid-crystal materials **ZLI-1695** and **K15**, it was demonstrated that some TADDOLs have unprecedentedly high helical twisting powers (HTP). Thus, the TADDOL with four 9-phenanthryl α-substituents has a HTP in the achiral mesophase 4-(4-pentylphenyl)benzonitrile of 405 $\mu m^{-1}$ between 24 and 34°. The temperature-dependent HTP measurements have been performed by analyzing *Grandjean* textures microscopically (*Cano* method). The structure-dependent HTP of various types of TADDOL dopants is discussed. There are similarities between size and sign of HTP on the one hand, and between degree and relative topicity of enantioselectivity in reactions, on the other hand, as caused by TADDOLs and by 1,1′-binaphthols.

The conversion of achiral into chiral mesophases is of great importance for technical applications (displays, production of certain polymers, printing, paints) [1]. One procedure for this conversion involves addition of a chiral dopant to a nematic phase. Similar to the situation in catalysis, one of the goals is to induce a 'maximum helicity' in a cholesteric phase with as little dopant as possible[2]). A measure for the efficiency of a dopant is the so-called helical twisting power (HTP, see *Eqn.*)[3]), as determined by the *Cano* method [3] with solutions of the dopant in the host mesophase. In spite of the great practical importance of chiral mesophases, it has been impossible, so far, to derive a relationship between the molecular structure of the chiral dopant and the 'chiral induction' (*cf.* pitch and sense of cholesteric helix)[4]). In view of the fact that each chiral conformer *i* has a contribution to the HTP of the guest-host system (*Eqn.*), it is desirable to study dopants with a fixed and known conformation, and with a structure which is subject to combinatorial optimization. The TADDOLs (*α,α,α′,α′-t*etra*a*ryl-1,3-*d*ioxolan-4,5-*d*imethan*ols*) **A** (*Fig. 1*) introduced (15 years ago [6]) and thoroughly investigated as ligands for enantioselective organometallic syntheses by one of our groups [6][7]

[1]) Part of the projected Ph.D. thesis of *B. W.*, Universität Kaiserslautern.

[2]) Actually, an optimum has to be found between the accuracy of the dosis amount, the handling on a technical scale, and changes of the host's phase properties.

[3]) For an early review article with leading references, see [2].

[4]) Attempts to derive a theoretical model and to systematize the effects, see [4b][5].

$$\mathrm{HTP} = \left[\frac{dp^{-1}}{dx}\right]_{x=0} \cong \frac{p^{-1}}{x} = \sum_i x_i(\mathrm{HTP})_i$$

| | |
|---|---|
| HTP [µm⁻¹] | helical twisting power for small concentrations |
| $p$ [µm] | pitch of induced helix, + for (*P*)-, – for (*M*)-helix |
| $x$ | mole fraction of the dopant |
| $\sum_i$ | sum over all chiral conformers of the dopant |
| $x_i$ | mole fraction of conformer *i* |

appeared to be candidates as chiral dopants: *i*) They contain aryl groups, a structural element typical of chiral dopants [4]; *ii*) most of them are of point symmetry group $C_2$, derived from tartaric acid, and thus available in both enantiomeric forms; *iii*) numerous X-ray crystal structures (**B** in *Fig. 1*) of pure TADDOLs and of their inclusion compounds show that one of the OH groups is generally incorporated in an *intra*molecular H-bonded ring, while the other one is engaged in *inter*molecular H-bonding[5]), thus reducing conformational freedom; *iv*) they have been found to bind enantioselectively to compounds containing H-bond-acceptor N- and O-atoms, both in the solid state [7][10], and in solution [11], *i.e.*, by interactions which might be important for a dopant to engage with a host; *v*) their structure can be widely modified in four distinct sections of the molecule (*Fig. 1*, **A**, (*a*)–(*d*)); *vi*) they are chemically stable, and, in most cases, their solubility in polar organic solvents is sufficiently high; *vii*) most of them show no light absorption in the visible spectral region.

Motivated by a promisingly high HTP of *ca.* 100 $\mu m^{-1}$, observed with the original TADDOL **1** (≡ **A**, Aryl = Ph) and a commercial liquid-crystal material in 1995, we embarked in a systematic investigation, preliminary results of which are described herein[1]).

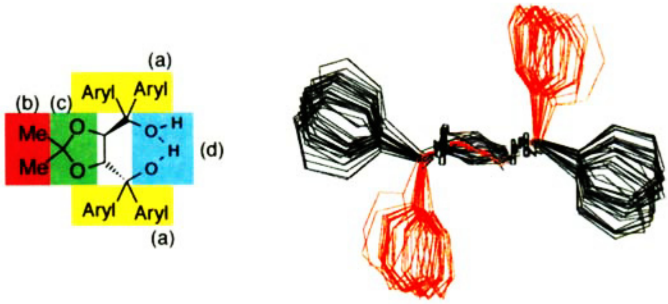
All together, we have included *ca.* 50 different TADDOLs, as well as derivatives and analogs thereof, in our study. Results reported in this communication were obtained with the compounds **1**–**19**[6]), of which **1**–**9** and **14**–**19** are $C_2$-symmetrical. In **2**–**7**, only the aryl substituents are varied (*cf. Fig. 1*, **A**, (*a*)), as compared to the original TADDOL **1**; in **8**–**12**, the substitution pattern at both, the exo- and endocyclic positions of the dioxolane ring are varied (*cf. Fig. 1*, **A**, (*a*) and (*b*)), in **13**–**16** the OH groups are derivatized (*cf. Fig. 1*, **A** (*d*)), and compounds **17**–**19** are actually no TADDOLs but aliphatic or seven-ring analogs (variation of (*c*) in *Fig. 1*, **A**).

We chose as guest systems the phases **ZLI-1695** and **K15** (in its nematic phase) with alkyl-substituted bi(cyclohexyl)-carbonitrile and biphenyl-carbonitrile structures[7]) and

[5]) In July 1994, there were *ca.* 60 TADDOLs with *ca.* 20 X-ray structures described [8]; in August 1996, these numbers for TADDOLs and analogs were *ca.* 120 and 35, respectively [9].

[6]) Most of these products have been described previously [6][8][11a][16]. The new compounds, **4**, **5**, **7**, **11**, **13**, **15**, and **16**, have been prepared by standard procedures [6c] and will be described in a forthcoming full paper [17].

[7]) **ZLI-1695** was obtained from *E. Merck* (Darmstadt), **K15** from *E. Merck* (Great Britain).




**A** **B**

Fig. 1. *Molecular formula* (A) *and structural superposition* **B** *of TADDOLs.* In **A**, the parts of the structure which can be modified are framed: (*a*) Aryl groups, introduced in the reaction of tartrate esters with ArylMgX [6–8]; (*b*) substituents in the 2-position of the dioxolane ring, derived from aldehydes or ketones [6–8]; (*c*) dioxolane ring can be replaced by carbocycle (also by bicyclic or other heterocyclic systems) [12]; (*d*) OH groups can be etherified, esterified (OR, $OSiR_3$, $OPR_2$, $OSO_nR$ *etc.*), or substituted by other heteroatoms (halogen, N, S) [13]. In **B**, 29 X-ray crystal structures of TADDOLs are superimposed [6c][7b][8][12][14], the limit at the time[5]) being only computer capacity and MacMoMo program [15] limitations.

determined the HTP by adding the dopants **1**–**19** (*Scheme*) and measuring the distances between disclination lines of the texture with a microscope (*Cano* method, *Fig. 2*) at temperatures between 17.5 and 65° for the aliphatic and between 24 and 34° for the aromatic mesophase (*Fig. 3*)[8])[9]). Although an extensive discussion and interpretation must be reserved for a full paper [17], we should like to make the following points:

*i*) The naphthyl, phenanthryl, and fluorenylidene TADDOLs, **4**, **5**, and **9**, respectively, show by far the highest HTP effects of any compound known to date[10]); such large HTPs allow for applications with a very low concentration of dopant, so that the properties of the guest system (often optimized for special applications) can be conserved.

*ii*) In the series α,α,α′,α′-tetraphenyl, -biphenyl, -naphthyl and -phenanthryl, the HTP in **ZLI-1695** increases (see **1**, **6**, **3**, and **5**); also, reduction or removal of the H-bond-donating ability of the TADDOLs leads to diminished HTP (**1** → **13**, **14**, **15**, and **3** → **16**); thus, the size of the HTP of TADDOL derivatives can be readily adjusted for special requirements.

*iii*) In almost all cases, the HTP decreases with increasing temperature; there are, however, notable exceptions: in **ZLI-1695**, both the naphthyl and the phenanthryl derivative **4** and **5** give rise to an increasing HTP almost over the entire temperature range measured (this is also true for **4** in **K15**); in the **K15** phase the phenanthryl-TADDOL **5** shows essentially no temperature dependence of the HTP (*Fig. 3*); thus, compounds in

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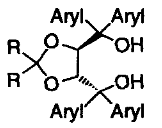
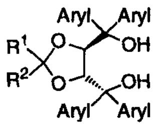
[8]) The disclination lines form a double spiral $r^2 = k\varphi$ with $k$ being proportional to the pitch [3b]. $r$ is the distance between the origin and the point of the spiral with an azimuth $\varphi$. For details, see [3c].

[9]) **ZLI-1695** exists as a nematic phase between 13 and 72.5°, **K15** between 23 and 35°.

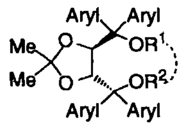
[10]) For previous record values, see [4c].



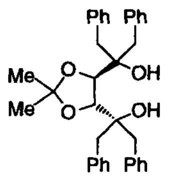
**1–9**



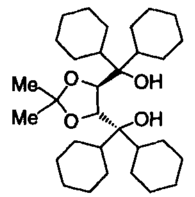
**10–12**



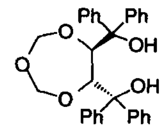
**13–16**



**17**

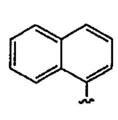


**18**

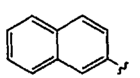


**19**

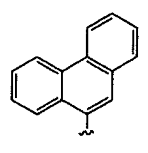
| Comp. | R | Aryl | Comp. | $R^1$ | $R^2$ | Aryl |
|---|---|---|---|---|---|---|
| **1** | Me | Ph | **10** | Me | Me | Ph |
| **2** | Me | 1-$C_{10}H_7$ | **11** | Me | 1-$C_{10}H_7$ | Ph |
| **3** | Me | 2-$C_{10}H_7$ | **12** | H | 1-$C_{10}H_7$ | Ph |
| **4** | Me | 6-HO-2-$C_{10}H_6$ | | | | |
| **5** | Me | 9-$C_{14}H_9$ | **13** | H | Me | Ph |
| **6** | Me | 4-Ph-$C_6H_4$ | **14** | Me | Me | Ph |
| **7** | Me | 9,9-$C_{13}H_8$- | **15** | | $-SiMe_2-$ | Ph |
| **8** | Ph | Ph | **16** | | $-SiMe_2-$ | 2-$C_{10}H_7$ |
| **9** | 9,9-$C_{13}H_8$- | Ph | | | | |



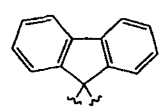
1-$C_{10}H_7$



2-$C_{10}H_7$



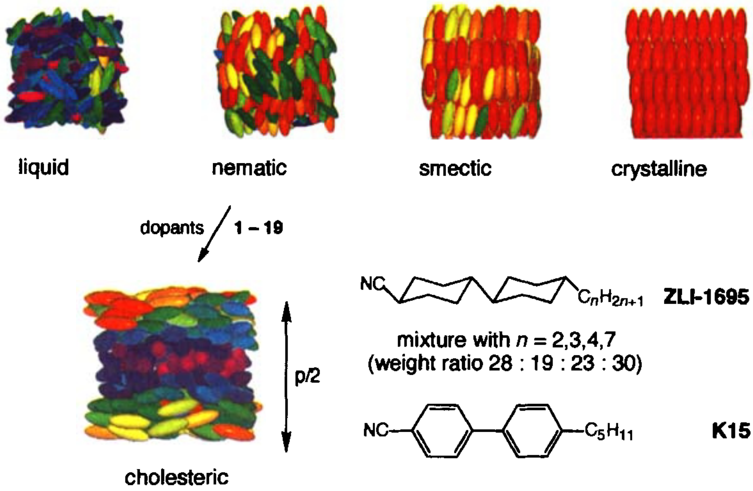
9-$C_{14}H_9$



9,9-$C_{13}H_8$

this series with almost temperature-independent, high HTP from 17 to 65° are likely to be found; also, the positive or negative gradients of HTP temperature dependence, especially in **ZLI-1695**, with different TADDOL-type dopants will allow for compensation of temperature effects.

Scheme. *Induction of Cholesteric Phases by Addition of TADDOL Dopants to a Nematic Phase.* Schematic presentation of various characteristic phases and liquid crystals **ZLI-1695** and **K15** used in this investigation. The phases are represented by snapshots of Monte Carlo simulations (printed by courtesy of *R. Memmer* [18]).



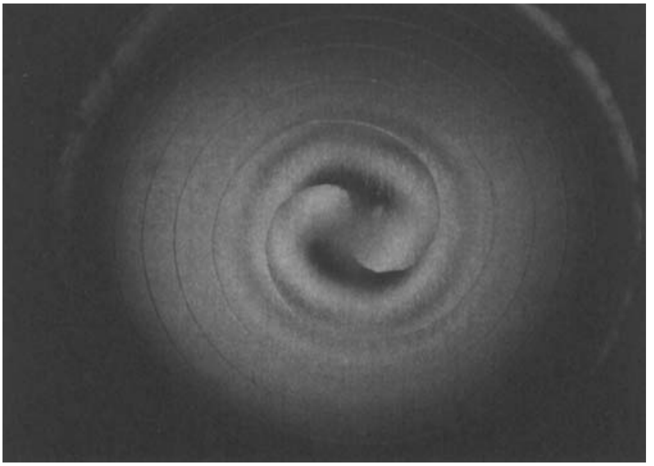



Fig. 2. *Disclination lines with right-handed helix of* **2** *in* **K15** *at 28°.* The pitch is 12 µm. For details about the measuring technique and the apparatus used, see *Footnote 8.*

*iv)* The (*R*,*R*)-TADDOLs induce right-handed or (*P*)-helices. An (*M*)-helix is induced in **ZLI-1695** only by the fluorenylidene derivative **7** and by the 'non-TADDOLs' **17** (*Fig. 3,a*) and **19** (*Fig. 3,b*)[11]).

*v)* There is an intriguing resemblance between poor or unusual performance of certain diols in this series as ligands in enantioselective catalysis and as dopants for inducing

[11]) Like these two, the compounds **A** in which the Aryl groups are replaced by H or alkyl (**A**, Aryl = H or Me in *Fig. 1*) all have a small HTP value and induce an (*M*)-helix!

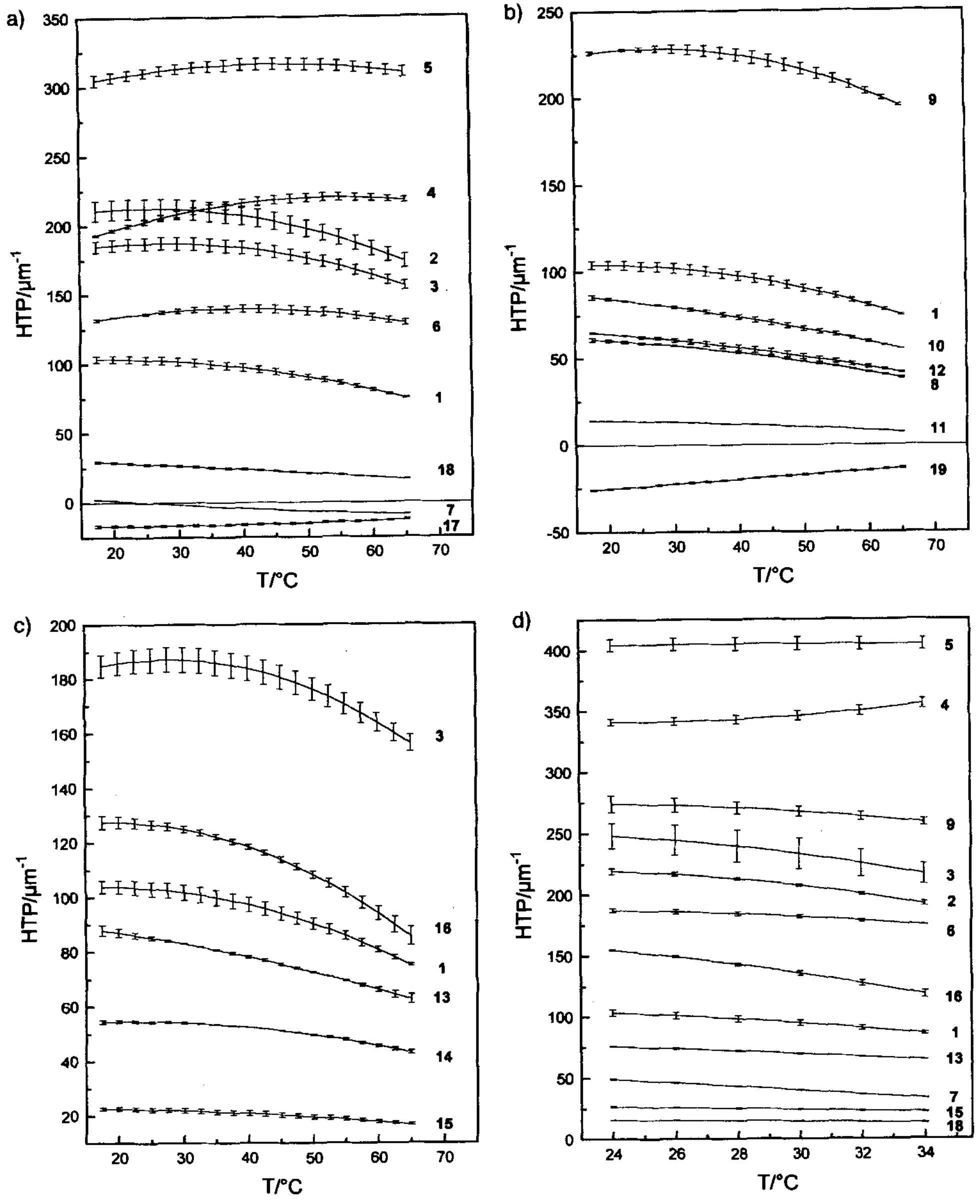



Fig. 3. *Temperature dependence HTP values in* **ZLI-1695** *(a–c) and in* **K15** *(d) induced by the TADDOL dopants* **1–19**. *a*) Various types of TADDOLs with variation of the aryl groups (molecular section (*a*) in *Fig. 1*, **A**); *b*) α,α,α′,α′-Tetraphenyl-TADDOLs with different substituents at the acetal center (*cf.* molecular section (*b*) in *Fig. 1*, **A**); *c*) 2,2-dimethyl-TADDOL derivatives with free (**1** and **3**) and etherified (**13** and **14**), or silylated (**15** and **16**) dimethanol groups (*cf.* **A** (*d*)); *d*) selected TADDOLs as dopants in the aromatic nematic phase. TADDOL **4** used in these experiments was an inclusion compound with acetone (molar ratio 1:1); this was accounted for in the calculation of the HTP; the concentration of **4** during the measurement was $1.5 \cdot 10^{-3}$ mol/l.

helicity in a nematic phase. Thus, all diols without or with aliphatic instead of aromatic substituents on the dimethanol moieties (*cf.* **17**, **18**, and those alluded to in *Footnote 11*) show small HTP and give titanates which cause poor enantioselectivity in *Lewis*-acid-mediated reactions [8][12][19]; also, a reversal of the stereochemical course of certain reactions has been observed when going from the original TADDOL **1** to other TADDOLs [8]; the bisfluorenylidene **7**, for instance, has a smaller HTP than **1** and gives rise to a change of sign in **ZLI-1695** (*Fig. 3,a* and *d*); on the other hand, replacement of **1** by **7** as ligand in a chiral *Lewis* acid led to enantiomeric products in one of the reactions catalyzed by the corresponding *Lewis* acid[12]).

*vi*) There is another striking similarity between helical twisting power and enantioselective reactivity: we have noticed that the use of (*R*,*R*)-TADDOLates and of (*P*)-1,1′-binaphtholates (BINOLates) as ligands in organometallic reactions generally gives rise to the preferred formation of products of the same absolute configuration [8][9][13]); it turns out that (*R*,*R*)-TADDOLs (this paper) and (*P*)-BINOLs [22] generally also induce the same sense of helicity in both **ZLI-1695** and **K15** (positive sign of HTP)!

*vii*) From the observations described under the three previous items, and from additional spectroscopic measurements[1])[14]), it appears that the TADDOL dopants are most suitable for the analysis of the relationship between structure and HTP size and sign[15]).

The practical applications of the TADDOL's HTP is being explored by a commercial institution [24]. Further experiments, such as the synthesis and the measurement of specifically and fully deuterated TADDOLs, are under way in our laboratories, with the goal of elucidating the mechanism of the induction described, and, hopefully, with the result of a deeper understanding of common supramolecular interactions which govern both catalytic generation of chiral mesophases and catalytic enantioselective synthesis. Question: can HTP measurements serve to optimize ligand efficiency for enantioselective catalysis? It could well be that the direction of the TADDOL's orientation axis with respect to the binding partner (for instance in a *Lewis* acid/*Lewis* base interaction) has an influence on catalytic activity and/or absolute configuration of the product!

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[12]) In the Ti-TADDOLate catalyzed enantioselective addition of $BuTi(OCHMe_2)_3$ to PhCHO, the use of (*R*,*R*)-spirofluorene derivative **7** gives rise to the formation of mainly (*R*)-product, that of (*R*,*R*)-TADDOL **1** of almost exclusively (*S*)-product [20].

[13]) An interpretation on the basis of structural similarity between the two types of ligands was also presented [8][9]. (*P*)-BINOL in the revised *CIP* system [21] corresponds to (*S*)-BINOL in the old *CIP* convention.

[14]) Most TADDOLs have structured polarized UV and CD spectra, especially in the region of the exciton transitions; they can be specifically and fully deuterated so that the order parameters and the principal axes of the order tensor may be determined by $^2$H-NMR spectroscopy.

[15]) See the intriguing cases (**7**, **17**, and **19**) in which there is a reversal of HTP sign, even though all dopant molecules, **1**–**19**, are homochirally similar (for a definition of this term, see [23]).

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