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The Synthesis and Mesomorphic Properties of Liquid Crystals Containing Three-membered Ring Systems

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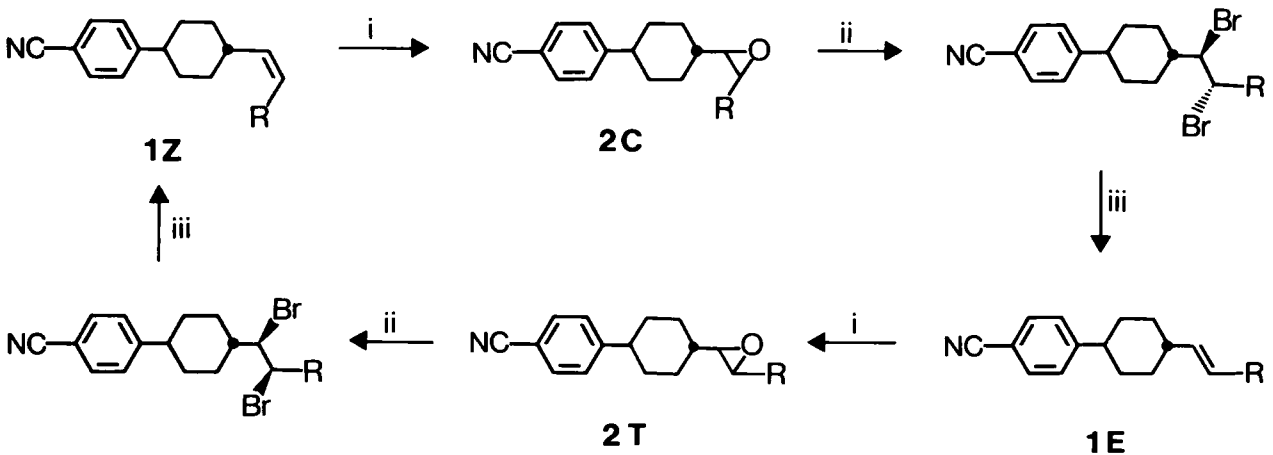
Various mesogenic benzonitriles containing *trans*-epoxy- or *trans*-cyclopropane rings at different positions have been synthesized. The influence of these three-membered ring elements on the mesomorphic properties is discussed and the observed nematic thermal stabilities (*cf.* Table 1) are compared with those of the corresponding *trans*-ethenyl- and dimethylene-linked analogs.

Keywords: liquid crystals, nematic phases, cyclopropane rings, epoxides

INTRODUCTION

In the course of the synthesis of alkenylsubstituted cyanophenylcyclohexanes[1] and cyanophenylethylcyclohexanes[2] the need arose to control the configuration of the olefinic units inserted into the apolar side chains of these compounds. By application of Sonnet's olefin inversion procedure,[3] as delineated in Scheme 1 for 1-alkenylsubstituted cyanophenylcyclohexanes, it was found, that by this method a *cis*-olefin, e.g. *1Z*, is converted stereospecifically to the corresponding *trans*-olefin, e.g. *1E*. The reverse transformation, i.e. conversion of *1E* to *1Z*, proceeds less stereoselectively. However, during the investigation of this latter route it was noticed, that the initially formed *trans*-epoxides, e.g. *2T*, were mesogenic exhibiting nematic mesophases only. This surprising result led us to prepare a number of bicyclic benzonitriles with *trans*-epoxy or *trans*-cyclopropane rings incorporated at various positions, with the aim of estimating the



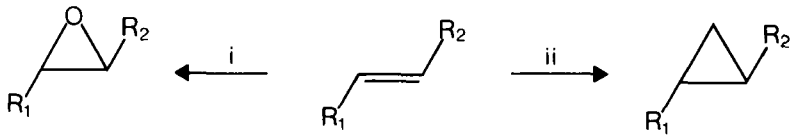
SCHEME I
i: MCPBA/K_2CO_3 ii: $(C_6H_5)_3P{\cdot}Br_2$ iii: Zn/AcOH

a) For the numbering system used cf. Table I, footnote a.

general usefulness of such three-membered ring systems as new structural elements in LC-materials. In this paper the synthesis and mesomorphic properties of some of these compounds are discussed.

PREPARATION OF MATERIALS

As depicted below both *trans*-epoxides and *trans*-cyclopropanes may be generated stereospecifically from an *E*-configurated olefin as a common precursor.



i: MCPBA/K_2CO_3 ii: CH_2I_2/Zn–Cu

Accordingly, all of the new *trans*-epoxides listed in Table I were obtained in high yield by treatment of the corresponding known E^- olefins[1,2,7] with *m*-chloroperbenzoic acid (MCPBA) in the presence of potassium carbonate as base.

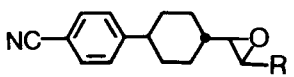
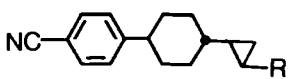
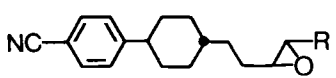
On the other hand, the introduction of a *trans*-cyclopropane unit proved to be considerably more difficult. Thus reaction of olefin *1E3* with methylene iodide in the presence of a zinc-copper couple[4] gave the desired *trans*-cyclopropane *3T3* in low yield only. Due to the disappointing mesomorphic properties of this compound (cf. Table I) no effort was made to either optimize the conditions of this cyclopropanation reaction or to prepare additional representatives of this series.

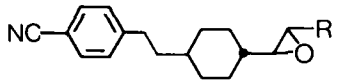
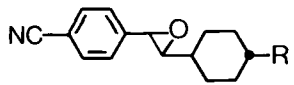
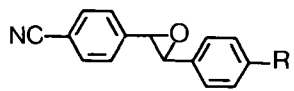
RESULTS AND DISCUSSION

As witnessed by the vast number of existing LC-materials[5] 1,4-disubstituted 6-membered ring systems have in the past clearly proven to be the most successful structural elements which preserve an optimal linearity and consequently provide potential mesogens with the necessary rod-like shapes. Small deviations from this linearity caused by the incorporation of e.g. 1,3-disubstituted 5-membered or 1,4-disubstituted 7-membered ring systems normally lead to less favourable transition temperatures or ultimately to the total loss of the mesomorphic properties.[6] In the light of these findings it is not sur-

TABLE I

Transition temperatures and enthalpies of bicyclic benzonitriles contianing *trans*-epoxy or *trans*-cyclopropane rings

Code[a]	Compound	R	T^{b}_{C-N} (°C)	T^{c}_{N-I} (°C)	ΔT^{d} (°C)	ΔH (kcal/mol)
2T1		CH_3	68.7	69.1	0.4	4.95
2T2		C_2H_5	45.9	60.4	14.5	4.21
2T3		C_3H_7	21.5	58.0	36.5	
3T3		C_3H_7	30.0	(−27.0)	−57.0	5.07
4T1		CH_3	71.2	72.0	0.8	5.75

5T1		CH_3	54.0	55.2	1.2	4.32
5T2		C_2H_5	49.4	50.5	1.1	4.94
5T3		C_3H_7	19.5	50.0	30.5	
5T4		C_4H_9	41.1[c]	45.2	4.1	6.73
5T5		C_5H_{11}	30.2	50.5	20.3	6.27
6T5		C_5H_{11}	9.8	49.0	39.2	
7T7		C_7H_{15}	80.2	(40.6)	−39.6	

[a]The capitals E, Z, T and C refer to the configuration of either the isolated C,C-double bonds (E = *trans*, Z = *cis*) or of the epoxide and cyclopropane units (T = *trans*, C = *cis*). The numbers following these letters denote the total number of carbon atoms of the alkyl group R, whereas those preceding are simply structure numbers.

[b]Crystal-nematic transition (m.p.)

[c]Nematic-isotropic transition (clearing point). Monotropic transition transition temperatures are denoted by ( ) brackets around the recorded temperatures.

[d]$\Delta T = T_{N-I} - T_{C-N}$ = meso-range; a negative sign indicates monotropy.

[e]Second modification melts at 38.8°C.

prising, that a similar incorporation of 1,2-disubstituted 3-membered ring systems was regarded as being even less attractive, and had not been previously investigated. In the following discussion we attempt to evaluate the suitability of epoxy- and cyclopropane ring systems for the design of new LC-materials.

Epoxides

As mentioned above, we discovered rather accidentally, that insertion of *trans*-epoxy rings at various positions of bicyclic benzonitriles lead to new mesogens exhibiting nematic mesophases only. At present we do not have a reasonable explanation for this unexpected result. Inspection of the corresponding Dreiding models reveals that the epoxy units project out of the planes of these molecules and therefore appear to disturb the optimal rod-like shape. Furthermore we would not expect the presence of epoxy rings to promote an anti-parallel correlation, which would enhance the molecular pairing of these compounds.

The mesomorphic properties of the new LC-materials containing epoxy ring systems are summarized in Table I.

By comparing these data with each other or with those of the corresponding *trans*-ethenyl and dimethylene linked analogs a number of conclusions may be drawn, some of which are presented below.

Thus in Figure 1 the transition temperatures of a homologous series of *trans*-1,2-epoxyalkylsubstituted cyanophenylethylcyclohexanes are compared with those of the corresponding alkylsubstituted counterparts. The following tendencies may be noticed:

(i) All members of the new epoxides show enantiotropic nematic behaviour.

(ii) Their T_{N-I}-values are similar (n = 3,4,5) or even higher (n = 1,2) than those of the corresponding alkyl analogs and they alternate very weakly.

(iii) The homologues with n = 3 and n = 5 exhibit low melting points thereby providing these compounds with attractive meso-ranges. In contrast to the T_{N-I}-values, the melting points (T_{C-N}) alternate strongly.

Similar trends may be observed for the members of the corresponding series of cyanophenylcyclohexanes, three of which (*2T1*, *2T2*, *2T3*) have been prepared. Again the homologue containing five carbon atoms in its side chain (*2T3*) is distinguished by a remarkable meso-range.

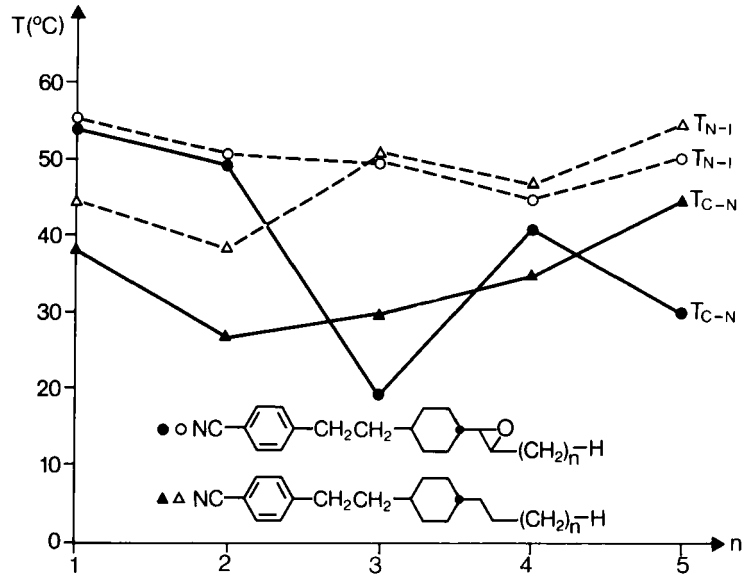
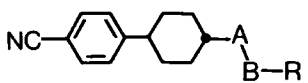
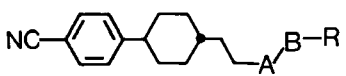


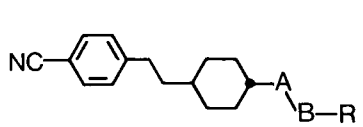
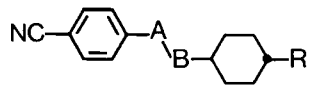
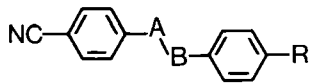
FIGURE 1 Comparison of the transition temperatures of *trans*-1,2-epoxyalkylsubstituted cyanophenylethylcyclohexanes with those of the corresponding alkylsubstituted analogs.

By varying the position of the epoxide moiety and/or the central core ring system further new LC-materials were obtained. The transition temperatures of some of these variants are listed in Table II together with those of the corresponding *trans*-ethenyl and dimethylene bridged analogs. With the exception of epoxide *7T7* all these compounds contain five carbon atoms in their terminal groups and thus allow for a direct comparison. The following comments appear to be valuable in this context: Shifting an epoxide unit from the 1,2- to the 3,4-position within a side chain of defined molecular length (cf. *2T3* with *4T1*) causes a rise in both T_{C-N} and T_{N-I}. This behaviour clearly parallels that of the corresponding *trans*-olefins (cf. *10E3* with *9E1*). In *6T5* and *7T7* the epoxide moieties represent part of the central core system and are flanked by one or two phenyl rings, respectively. Although sterically even more demanding, these compounds still show mesomorphic properties. If compared with the corresponding styrene derivatives *12E5 and 14T5*, respectively, the pronounced decrease of the T_{N-I}-values by *ca.* 60°C is not unexpected (loss of conjugation). With regard to the ethanes *13* and *15*, however, the observed T_{N-I}-values compare suprisingly well. Thus, whereas the clearing points of *6T5* and *13* are similar, the T_{N-I}-value of *7T7*

TABLE II

Comparison of the transition temperatures of bicyclic benzonitriles containing *trans*-epoxy and *trans*-cyclopropane rings with those of the corresponding *trans*-ethenyl and dimethylene linked analogs.[a]

Code	Compound	A-B	R	T_{C-N} (°C)	T_{N-I} (°C)	°T (°C)	Ref.
3T3			C_3H_7	30.0	(−27.0)	−57.0	
2T3			C_3H_7	21.5	58.0	36.5	
1E3		CH=CH	C_3H_7	15.6	58.5	42.9	1
8		CH_2—CH_2	C_3H_7	30.0	55.0	25.0	8
4T1			CH_3	71.2	72.0	0.8	
9E		CH=CH	CH_3	59.8	73.7	13.9	1
8		CH_2—CH_2	CH_3	30.0	55.0	25.0	8

5T3		CH—CH	C_3H_7	19.5	50.0	30.5	
10E3		CH=CH	C_3H_7	25.1	47.5	22.4	2
11		CH_2—CH_2	C_3H_7	30.9	52.5	21.6	8
6T5		CH—CH	C_5H_{11}	9.8	49.0	39.2	
12E5		CH=CH	C_5H_{11}	53.5	107.2	53.7	7
13		CH_2—CH_2	C_5H_{11}	30.9	52.5	21.6	8
7T7		CH—CH	C_7H_{15}	80.2	(40.6)	−39.6	
14T5		CH=CH	C_5H_{11}	55.5	101.0	45.5	7
15		CH_2—CH_2	C_5H_{11}	62.0	[−24.0]	−86.0	7

[a]For the abbreviations used and additional remarks see Table I, footnotes a–d.

is raised by 65°C if compared with *15*. An explanation for this latter result is still lacking.

Cyclopropane 3T3

On the basis of the promising results obtained with epoxides a logical extension appeared to be the investigation of the corresponding carbocyclic analogs, i.e. cyclopropanes. From the point of view of size one might anticipate that these should not differ markedly from the epoxides and therefore would possibly exhibit similar mesomorphic properties.

As mentioned earlier, the only representative which we have prepared is the *trans*-cyclopropane *3T3*, the *trans*-configuration of which was confirmed by a 400 MHz H^1-NMR spectrum. Contrary to all expectations this compound exhibited a monotropic clearing point of only −27°C (cf. Table I). Accordingly, replacement of an oxygen atom in epoxide *2T3* by a methylene group has induced a decrease of the clearing point by as much as 85°C! We do not know what is responsible for this dramatic effect, and this example nicely illustrates the dangers inherent in speculation about the relationships between molecular structure and T_{N-I}-values.

CONCLUSIONS

Starting from *E*-olefins[1,2,7] both *trans*-epoxides and *trans*-cyclopropanes have been prepared stereospecifically in a single step. The mesomorphic properties of the resulting LC-materials incorporating three-membered ring systems diverge strongly. Thus, whereas the cyclopropane *3T3* has a disappointingly low monotropic T_{N-I}-value, the new epoxides in general exhibit enantiotropic nematic behaviour and are in some cases also distinguished by surprisingly large temperature ranges for the mesophases. The influence of inserted epoxy units on the transition temperatures depends on the position of these new structural elements and essentially parallels that observed earlier for the corresponding *trans*-olefin series.[1,2]

Acknowledgments

We wish to thank Mr. G. Daub and Mr. J. Reichardt for their competent collaboration during the preparation of the new materials and Mr. F. Wild and B. Halm for carrying out the differential thermal analyses.

EXPERIMENTAL

General

All reactions were carried out under argon. Solvents were passed through alumina (activity I) or distilled before use. Usual workup refers to successive washing of the organic phases with sat.aq. $NaHCO_3^-$ solution and/or H_2O and sat.aq. NaCl-solution followed by drying ($MgSO_4$ or K_2CO_3) and removal of the solvents at reduced pressure. Thin layer chromatography (TLC) was performed using Merck 0.25 mm (60 F 254) silica gel plates. Preparative flash chromatography was carried out according to Still[9] at a pressure of 0.5 bar using silica gel (Merck, 230–400 mesh). The transition temperatures and enthalpies of the new compounds, listed in Table I, were determined on a Mettler DTA TA 2000 and are corrected. Gas chromatography (VPC) was carried out on a Perkin-Elmer Sigma 3B + 10B using a glass column (2.2 m ID, 2.0 m, stationary phase Gaschrom Q 120/140 mesh coated with 2% *trans*-4-(*p*-propylphenyl)-cyclohexyl-4'-(*trans*-4-pentylcyclohexyl-4-biphenylcarboxylate at 6.5 bar N_2 and temperatures of 170–230° (isotherm). All IR, ^{1}H-NMR and mass spectra of the new compounds are in agreement with their assigned structures.

Preparation of epoxide 5T3

To a mixture of *m*-chloroperbenzoic acid (85%, 767 mg, 4.0 mmol) and powdered potassium carbonate (1.52 g, 11.0 mmol) in dry methylene chloride (30 ml) at 0°C, a solution of *trans*-olefin *10E3*[2] (1.125 g, 4.0 mmol) in dry methylene chloride (10 ml) was added over 15 min. The ice bath was removed and after 75 and 105 min, additional portions of *m*-chloroperbenzoic acid (85%, 383 mg each, 2.0 mmol) were added. Stirring was continued for another hour before the heterogeneous reaction mixture was poured into sodium thiosulfate solution (10%, 30 ml). Extraction with methylene chloride (3 × 50 ml), followed by washing the organic layers with sat. sodium carbonate solution and the usual work up, furnished a liquid crystalline oil (1.2 g). Flash chromatography of this material on silica gel (methylene chloride) and bulb-to-bulb distillation (230°C/0.04 mm) gave epoxide *5T3* (1.04 g, 88%) as a colourless nematogenic oil. TLC (methylene chloride): R_f (*10E3*) 0.61, R_f (*5T3*) 0.35.

Preparation of cyclopropane 3T3

To a slurry of zinc-copper couple, prepared from zinc dust (1.41 g, 21.5 mmol) and cupric acetate monohydrate (79.4 mg, 0.40 mmol)

according to Ref. 4, a solution of methylene iodide (0.2 ml, 2.5 mmol) in dry ether (5 ml) was added. After stirring for 5 min the suspension was heated to reflux, before a solution of *trans*-olefin *1E3* (1.09 g, 4.30 mmol) and methylene iodide (1.53 ml, 19.0 mmol) in dry ether (5 ml) was added dropwise over 30 min. After stirring for 21 h under reflux the reaction mixture was poured into water (50 ml). Extraction with ether (3 × 50 ml) followed by the usual work up produced a brown oil (1.61 g), which upon flash chromatography on 80 g of silica gel (petroleum ether/ethyl acetate 97 : 3) gave a yellow oil (869 mg). According to VPC-analysis, this material contained olefin *1E3* (ca. 70%) and cyclopropane *3T3* (ca. 28%). Due to its inseparability by chromatography this mixture was redissolved in methylene chloride (20 ml) and treated at −10°C with a solution of bromine in methylene chloride (ca. 0.1 M) until a slight yellow colour persisted. After stirring for an additional 10 min the reaction mixture was poured into sodium thiosulfate solution (10%, 50 ml). Extraction with methylene chloride (3 × 50 ml) followed by the usual work up afforded a brown solid (1.0 g), which upon flash chromatography on 140 g of silica gel (petroleum ether/ethyl acetate 97 : 3) furnished cyclopropane *3T3* (162 mg, 14%) and the *erythro*-dibromide derived from olefin *1E3* (764 mg, 43%). Recrystallization of the former from methanol (5 ml, RT → −78°C) gave pure cyclopropane *3T3* (102 mg, purity according to VPC: 99.7%): R_f (*3T3*) 0.21. The specific *trans*-configuration of the cyclopropane moiety in this compound follows from a 400 MHz NMR-spectrum.

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