

Novel liquid crystalline cuneane-caged derivatives. Structure property relationship study

Gyula Bényei^{1,2}, István Jalsovszky¹, Aniko Vajda³, Antal Jáklí^{3,4}, Dietrich Demus⁵, Shankar Rao⁶, Krishna Prasad⁶, Katalin Fodor-Csorba³

¹Department of Organic Chemistry, Eötvös Loránd University,
H-1117 Budapest, Pázmány Péter sétány 1/A., Hungary,

²Gedeon Richter Ltd. H-1475, Budapest, 10. P.O. Box 27, Hungary,

³Research Institute for Solid State Physics and Optics,
Hungarian Academy of Sciences, H-1525 Budapest, P.O.Box 49, Hungary,

⁴Liquid Crystal Institute, Kent State University, Kent, OH44242, USA,

⁵International Scientific Consulting Office, Veilchenweg 22, 06118 Halle, Germany,

⁶Centre for Liquid Crystal Research, Jalahalli, Bangalore 560 013, India

Abstract

The synthesis and phase behavior of the first cuneane derivatives with liquid crystalline properties are reported. This new class of liquid crystalline materials is the homologous series of bis[4-(n-alkoxyphenyl)]cuneane-2,6-dicarboxylates. They were synthesized by two different methods: either by isomerization of the formerly prepared bis[4-(n-alkoxyphenyl)]cubane-1,4-dicarboxylates or by direct esterification of the cuneane-2,6-dicarboxylic acid. Enantiotropic nematic phases were observable for the first four homologues, whereas the higher homologues exhibited enantiotropic smectic A phase. The bis[4-(n-octylphenyl)]cuneane-2,6-dicarboxylate exhibited the SmA phase at lower temperature, than its octyloxy analogue. The mesophases were investigated and established by polarization optical microscopy, differential scanning calorimetry and X-ray diffraction methods. Quantum chemical calculations suggest an elongated structure of these new liquid crystalline compounds.

Introduction

During the more than one hundred years of liquid crystal research over hundred thousands of liquid crystals have been synthesized [1,2]. They are mainly aromatic moieties, but numerous cyclohexane [3], bicyclohexane [4], bicyclo-[2,2,2]-octane [5], bridged-ring [6], carborane [7] mesomorphic compounds have also been prepared. It is well known that not only the morphological aspects, but the delocalization plays an important role in the mesophase formation. A new subfield of today's liquid crystal research has developed for the investigation of banana-shaped or bent-core molecules having different architecture comparing with the conventional calamitic compounds [8-10]. Until now only little work has been devoted to the compounds having cubane moiety in their molecular architecture [11,12]. Few cubane-1,4-dicarboxylic acid derivatives are reported formerly [13,14] with enantiotropic or monotropic nematic phase. Recently we published numerous achiral and chiral cubane-1,4-dicarboxylate derivatives with liquid crystalline properties [15]. No references were found in the literature, where cuneane-2,6-dicarboxylates were used as central unit of the liquid crystal molecules.

The cuneane skeleton (pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane) first was reported in 1968.[16] The name "cuneane" is derived from the Latin "cuneus", meaning a wedge [16]. Comparing the cubane skeleton with the cuneane-cage, it was shown, that cuneane should be 30-40 kcal/mol less

strained than cubane itself. [17] The first rearrangement reaction of the mono-substituted cubanes and 1,4-disubstituted cubane dicarboxylates was reported in 1970 [18], where silver (I) or palladium (I) salts were used as effective catalyst.

In this paper the mono and dimethyl cubane-1,4-dicarboxylates were quantitatively isomerized into the cuneane system. Theoretically there is the possibility of the formation of ten isomers in the rearrangement reaction of the disubstituted cuneane skeleton, , but only two of them were actually found. Especially the dimethyl cubane-1,4-dicarboxylate was transformed into dimethyl cuneane-2,6-dicarboxylate and dimethylcuneane-1,3-dicarboxylate in 20:1 ratio[18].

Our aim was to investigate whether our formerly synthesized bis[4-(n-alkoxyphenyl)]cubane-1,4-dicarboxylates could be isomerized into cuneane derivatives. We were also interested in knowing if this method leads to the degradation of the molecule, and whether the new compounds – if the reaction takes place - have mesomorphic properties at all?

Materials and methods

Dimethyl cubane-1,4-dicarboxylate (2) was prepared according the method described earlier [9]. The synthesis of the bis[4-(n-alkoxyphenyl)]cubane-1,4-dicarboxylates was described earlier [10]. 4-n-alkoxyphenols as methoxy-, ethoxy- propoxy-, butoxy-, hexyloxy- and heptyloxyphenols were purchased from Sigma-Aldrich Co., pentyloxy- and octyloxy- analogues were obtained from Avocado Research Chemicals (ABCR GmbH).

The chemical structure of the new compounds was characterized by ^1H NMR, ^{13}C NMR spectroscopy. The spectra were taken with a 250MHz Bruker equipment at 20°C in CDCl_3 solution. The assignment of the NMR signals were made according to Figure 1.

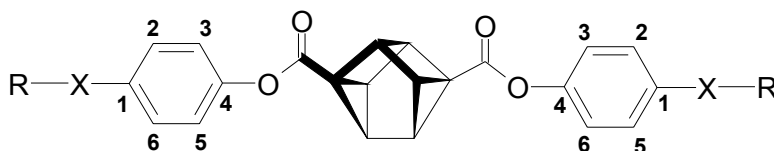


Figure 1. Assignment of the NMR signals

Gas chromatographic analyses were carried out on a Chrompack Cp 9001 system equipped with a 25m CP Sil 13CB column, using a H_2 gas flow (5ml/min) and flame ionization detector. High performance liquid chromatographic analysis was performed using a Merck Hitachi LaChrom HPLC system with L-7450 dioda array detector, L-7100 pump, L-7200 autosampler, L-7614 degasser. LiChrospher 100 RP-8 column (150×4 mm ID, 5 μm particle size) was eluted by water-acetonitril mixture using the elution program: initial 95% water and 5% acetonitril, followed by a linear gradient elution at 100% acetonitril until 20minutes, finally an isocratic elution for more than 15minutes. The flow rate was 1,0ml/min. Chromatographic data were collected by HSM software, the chromatogram type was fixed WL at 215nm.

The thermal behavior of the compounds was studied by polarizing optical microscopy (POM) with an Amplival POL U equipment on a Boetius hot stage and differential scanning calorimetry (DSC) using a Perkin Elmer Pyris Diamond DSC. The thermal transition temperatures were taken as the maxima of the transition peaks. Calibration of the instrument was performed using an indium standard. The heating and cooling rate was 5°C/min.

The X-ray diffraction experiments were done using $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) from a fine focus sealed-tube generator in conjunction with double mirror focusing optics. The mirror optics provides a nearly parallel beam over a long working distance. The detector was an image plate

detector (MAC Science, Japan, model DIP 1030) with an effective resolution of 100 μm x 100 μm .

Synthesis

Dimethyl cuneane-2,6-dicarboxylate (3)

Silver perchlorate (6.2g, 30mmol) was freshly dried over phosphorus pentoxide in vacuo at 120°C for 10 hours and added under argon to a stirred solution of methyl-cubane-1,4-dicarboxylate (2) (10g, 45.5mmol) in anhydrous, thiophene free 200mL benzene while the solution turned into red. The reaction proceeded under argon at 60°C in a stirred sealed bottle for five days with exclusion of light. Finally the solution was quenched with water and extracted with ethyl acetate. The combined organic extracts were washed with water, until the silver halogenide test become negative, and then dried over Na₂SO₄. Removal of solvent left a white solid. The crude product contained 94% of 3, 4% of dimethyl cuneane-1,3-dicarboxylate and 2% of starting material according to GC analysis. After crystallization from n-hexane/1,2-dichloroethane (10:1) 6.1g (61%) dimethyl cuneane-2,6-dicarboxylate was obtained. According to GC analysis, it was 99.9% pure.

Cuneane-2,6-dicarboxylic acid (4)

Solution of sodium hydroxide (2.0g 50mmol) in 40ml methanol and 2ml water was added to a stirred solution of 3 (3.52g, 16mmol) in 100ml methanol for about 5 minutes. After 1 hour the reaction mixture was heated to reflux for 5 hours, and then stirred overnight at room temperature. The solvent was removed, and the white solid obtained this way was dissolved in 14ml water. The solution was acidified drop-wise with 4.4mL cc. hydrochloric acid at 0°C. The white precipitate formed was collected, washed three times with 4mL ice-cold water, and dried in vacuum. 3.01g (98.0%)

Method A

Bis[4-(n-alkyloxyphenyl)]cuneane-2,6-dicarboxylates (5a-i)

The 4-(n-alkyloxy)phenol (3.80mmol) was added to a suspension of cuneane-2,6-dicarboxylic acid (360mg, 1.88mmol) in dichloromethane. The reaction mixture was cooled to 0°C and the solution of 4-(N,N-dimethylamino)pyridine (90mg, 0.7mmol, 1/5equiv) in 10mL dichloromethane, and thereafter the solution of N,N-dicyclohexylcarbodiimid (860mg 4.17mmol, 1.1 equiv.) in 10mL dichloromethane were added. The stirring was continued for 1 hour at 0°C, and then overnight at room temperature. The reaction mixture was filtered on celite 545, and then the solvent was removed. The solid residue was dissolved in 5mL dichloromethane, and cleaned by flash chromatography on Kieselgel 60 (0.063-0.02mm) eluted with dichloro-ethane/etanol 10:1 mixture. The appropriate fractions were collected, evaporated in vacuo. The product was purified by crystallization from n-hexane/ethanol 5:1. The yield was between 60-85%.

Bis[4-(methoxyphenyl)cuneane-2,6-dicarboxylates (5a): 4-(methoxy)phenol 473mg, (3.80mmol) other reagents as given above. **5a:** 494mg, (65%), C₂₄H₂₀O₆=404.42
¹H-NMR (δ , 20°C, CDCl₃, 250MHz), 6.97 (m, 4H, Ph^{2,6}), 6.86 (m, 4H, Ph^{3,5}), 3.78 (s, 6H, OCH₃), 3.36 (m, 2H, cuneane), 3.30 (m, 4H, cuneane). ¹³C- NMR (δ , 20°C, CDCl₃, 250MHz), 169.3 (2C, COO), 157.6 (2C, Ph⁴), 144.3 (2C, Ph¹), 122.7 (4C, Ph^{2,6}), 114.8 (4C, Ph^{3,5}), 56.0 (2C, OCH₃), 45.0 (2C, cuneane), 44.2 (2C, cuneane), 41.7 (2C, cuneane), 39.1 (2C, cuneane).

Bis[4-(ethoxyphenyl)]cuneane-2,6-dicarboxylates (5b): 4-(ethoxy)phenol 525mg, (3.80mmol), other reagents as given above. **5b:** 634mg, (78%), $C_{26}H_{24}O_6=432.48$

1H -NMR (δ , 20°C, $CDCl_3$, 250MHz), 6.95 (m, 4H, $Ph^{2,6}$), 6.85 (m, 4H, $Ph^{3,5}$), 4.00 (q, 4H, OCH_2), 3.36 (m, 2H, cuneane), 3.30 (m, 4H, cuneane), 1.40 (t, 6H, CH_3). ^{13}C - NMR (δ , 20°C, $CDCl_3$, 250MHz), 169.3 (2C, COO), 157.0 (2C, Ph^4), 144.2 (2C, Ph^1), 122.6 (4C, $Ph^{2,6}$), 115.4 (4C, $Ph^{3,5}$), 64.2 (2C, OCH_2), 44.9 (2C, cuneane), 44.2 (2C, cuneane), 41.7 (2C, cuneane), 39.1 (2C, cuneane), 15.2 (2C, CH_3).

Bis[4-(n-propyloxyphenyl)]cuneane-2,6-dicarboxylates (5c): 4-(n-propoxy)phenol (578mg, 3.80mmol), other reagents as given above. **5c:** 615mg, (71%), $C_{28}H_{28}O_6=460.53$

1H -NMR (δ , 20°C, $CDCl_3$, 250MHz), 6.95 (m, 4H, $Ph^{2,6}$), 6.85 (m, 4H, $Ph^{3,5}$), 3.88 (t, 4H, OCH_2), 3.36 (m, 2H, cuneane), 3.29 (m, 4H, cuneane), 1.79 (m, 4H, OCH_2CH_2), 1.02 (t, 6H, CH_3). ^{13}C - NMR (δ , 20°C, $CDCl_3$, 250MHz), 169.3 (2C, COO), 157.2 (2C, Ph^4), 144.1 (2C, Ph^1), 122.6 (4C, $Ph^{2,6}$), 115.4 (4C, $Ph^{3,5}$), 70.3 (2C, OCH_2), 44.9 (2C, cuneane), 44.2 (2C, cuneane), 41.7 (2C, cuneane), 23.0 (2C, OCH_2CH_2), 10.9 (2C, CH_3).

Bis[4-(n-butyloxyphenyl)]cuneane-2,6-dicarboxylates (5d): 4-(n-butyloxy)phenol (632mg, 3.80mmol), other reagents as given above. **5d:** 643mg, (70%), $C_{30}H_{32}O_6=488.59$

1H -NMR (δ , 20°C, $CDCl_3$, 250MHz), 6.95 (m, 4H, $Ph^{2,6}$), 6.85 (m, 4H, $Ph^{3,5}$), 3.93 (t, 4H, OCH_2), 3.36 (m, 2H, cuneane), 3.30 (m, 4H, cuneane), 1.75 (m, 4H, OCH_2CH_2), 1.48 (m, 4H, $OCH_2CH_2-CH_2$), 0.97 (t, 6H, CH_3). ^{13}C - NMR (δ , 20°C, $CDCl_3$, 250MHz), 169.3 (2C, COO), 157.2 (2C, Ph^4), 144.1 (2C, Ph^1), 122.6 (4C, $Ph^{2,6}$), 115.4 (4C, $Ph^{3,5}$), 68.5 (2C, OCH_2), 44.9 (2C, cuneane), 44.2 (2C, cuneane), 41.7 (2C, cuneane), 39.1 (2C, cuneane), 31.7 (2C, OCH_2CH_2), 19.6 (2C, $OCH_2CH_2-CH_2$), 14.2 (2C, CH_3).

Bis[4-(n-pentyloxyphenyl)]cuneane-2,6-dicarboxylates (5e): 4-(n-pentyloxy)phenol 684mg, (3.80mmol), other reagents as given above. **5e:** 709mg, (73%), $C_{32}H_{36}O_6=516.64$

1H -NMR (δ , 20°C, $CDCl_3$, 250MHz), 6.95 (m, 4H, $Ph^{2,6}$), 6.85 (m, 4H, $Ph^{3,5}$), 3.92 (t, 4H, OCH_2), 3.36 (m, 2H, cuneane), 3.29 (m, 4H, cuneane), 1.77 (m, 4H, OCH_2CH_2), 1.40 (m, 8H, $-(CH_2)_2-$), 0.93 (t, 6H, CH_3). ^{13}C - NMR (δ , 20°C, $CDCl_3$, 250MHz), 169.3 (2C, COO), 157.2 (2C, Ph^4), 144.1 (2C, Ph^1), 122.6 (4C, $Ph^{2,6}$), 115.4 (4C, $Ph^{3,5}$), 68.8 (2C, OCH_2), 44.9 (2C, cuneane), 44.2 (2C, cuneane), 41.7 (2C, cuneane), 39.1 (2C, cuneane), 29.4 (2C, OCH_2CH_2), 28.6, 22.8 (4C, $-(CH_2)_2-$), 14.4 (2C, CH_3).

Bis[4-(n-hexyloxyphenyl)]cuneane-2,6-dicarboxylates (5f): 4-(n-hexyloxy)phenol 738mg, (3.80mmol), other reagents as given above. **5f:** 706mg, (69%), $C_{34}H_{40}O_6=544.69$

1H -NMR (δ , 20°C, $CDCl_3$, 250MHz), 6.95 (m, 4H, $Ph^{2,6}$), 6.85 (m, 4H, $Ph^{3,5}$), 3.92 (t, 4H, OCH_2), 3.37 (m, 2H, cuneane), 3.29 (m, 4H, cuneane), 1.76 (m, 4H, OCH_2CH_2), 1.4 (m, 12H, $-(CH_2)_3-$), 0.90 (t, 6H, CH_3). ^{13}C - NMR (δ , 20°C, $CDCl_3$, 250MHz), 169.3 (2C, COO), 157.2 (2C, Ph^4), 144.1 (2C, Ph^1), 122.6 (4C, $Ph^{2,6}$), 115.4 (4C, $Ph^{3,5}$), 68.8 (2C, OCH_2), 44.9 (2C, cuneane), 44.2 (2C, cuneane), 41.7 (2C, cuneane), 39.1 (2C, cuneane), 32.0 (2C, OCH_2CH_2), 29.6, 26.1, 23.0 (6C, $-(CH_2)_3-$), 14.4 (2C, CH_3).

Bis[4-(n-heptyloxyphenyl)]cuneane-2,6-dicarboxylates (5g): 4-(n-heptyloxy)phenol 791mg, (3.80mmol), other reagents as given above. **5g:** 678mg, (63%), $C_{36}H_{44}O_6=572.75$

$^1\text{H-NMR}$ (δ , 20°C , CDCl_3 , 250MHz), 6.95 (m, 4H, $\text{Ph}^{2,6}$), 6.85 (m, 4H, $\text{Ph}^{3,5}$), 3.92 (t, 4H, OCH_2), 3.36 (m, 2H, cuneane), 3.30 (m, 4H, cuneane), 1.76 (m, 4H, OCH_2CH_2), 1.35 (m, 16H, $-(\text{CH}_2)_4-$), 0.89 (t, 6H, CH_3). $^{13}\text{C-NMR}$ (δ , 20°C , CDCl_3 , 250MHz), 169.3 (2C, COO), 157.2 (2C, Ph^4), 144.1 (2C, Ph^1), 122.6 (4C, $\text{Ph}^{2,6}$), 115.4 (4C, $\text{Ph}^{3,5}$), 68.8 (2C, OCH_2), 44.9 (2C, cuneane), 44.2 (2C, cuneane), 41.7 (2C, cuneane), 39.1 (2C, cuneane), 32.2 (2C, OCH_2CH_2), 29.7, 29.4, 26.4, 23.0 (8C, $-(\text{CH}_2)_4-$), 14.5 (2C, CH_3).

Bis[4-(n-octyloxyphenyl)]cuneane-2,6-dicarboxylates (5h): 4-(n-octyloxy)phenol 845mg, (3.80mmol), other reagents as given above. **5h:** 937mg, (83%), $\text{C}_{38}\text{H}_{48}\text{O}_6=600.80$

$^1\text{H-NMR}$ (δ , 20°C , CDCl_3 , 250MHz), 6.95 (m, 4H, $\text{Ph}^{2,6}$), 6.85 (m, 4H, $\text{Ph}^{3,5}$), 3.92 (t, 4H, OCH_2), 3.36 (m, 2H, cuneane), 3.30 (m, 4H, cuneane), 1.76 (m, 4H, OCH_2CH_2), 1.35 (m, 20H, $-(\text{CH}_2)_5-$), 0.89 (t, 6H, CH_3). $^{13}\text{C-NMR}$ (δ , 20°C , CDCl_3 , 250MHz), 169.3 (2C, COO), 157.2 (2C, Ph^4), 144.1 (2C, Ph^1), 122.6 (4C, $\text{Ph}^{2,6}$), 115.4 (4C, $\text{Ph}^{3,5}$), 68.8 (2C, OCH_2), 44.9 (2C, cuneane), 44.2 (2C, cuneane), 41.7 (2C, cuneane), 39.1 (2C, cuneane), 32.2 (2C, OCH_2CH_2), 29.7, 29.6, 26.6, 26.4, 23.0 (10C, $-(\text{CH}_2)_5-$), 14.5 (2C, CH_3).

Bis[4-(n-octylphenyl)]cuneane-2,6-dicarboxylates (5i): 4-n-(octyl)phenol 784mg, (3,80mmol), other reagents as given above. **5i:** 813mg, (76%), $\text{C}_{38}\text{H}_{48}\text{O}_4=568.80$

$^1\text{H-NMR}$ (δ , 20°C , CDCl_3 , 250MHz), 7.15 (m, 4H, $\text{Ph}^{2,6}$), 6.95 (m, 4H, $\text{Ph}^{3,5}$), 3.37 (m, 2H, cuneane), 3.29 (m, 4H, cuneane), 2.58 (t, 4H, Ph-CH_2), 1.57 (m, 4H, $\text{PhCH}_2\text{-CH}_2$), 1.26 (m, 20H, $-(\text{CH}_2)_5-$), 0.88 (t, 6H, CH_3). $^{13}\text{C-NMR}$ (δ , 20°C , CDCl_3 , 250MHz), 169.1 (2C, COO), 148.7 (2C, Ph^4), 140.8 (2C, Ph^1), 129.6 (4C, $\text{Ph}^{2,6}$), 121.5 (4C, $\text{Ph}^{3,5}$), 45.0 (2C, cuneane), 44.2 (2C, cuneane), 41.7 (2C, cuneane), 39.1 (2C, cuneane), 35.7 (2C, Ph-CH_2), 32.3 (2C, $\text{PhCH}_2\text{-CH}_2$), 31.8, 29.8, 29.7, 29.6, 23.1 (10C, $-(\text{CH}_2)_5-$), 14.5 (2C, CH_3).

Method B.

Bis[4-(n-alkyloxyphenyl)]cuneane-2,6-dicarboxylates (5a-i)

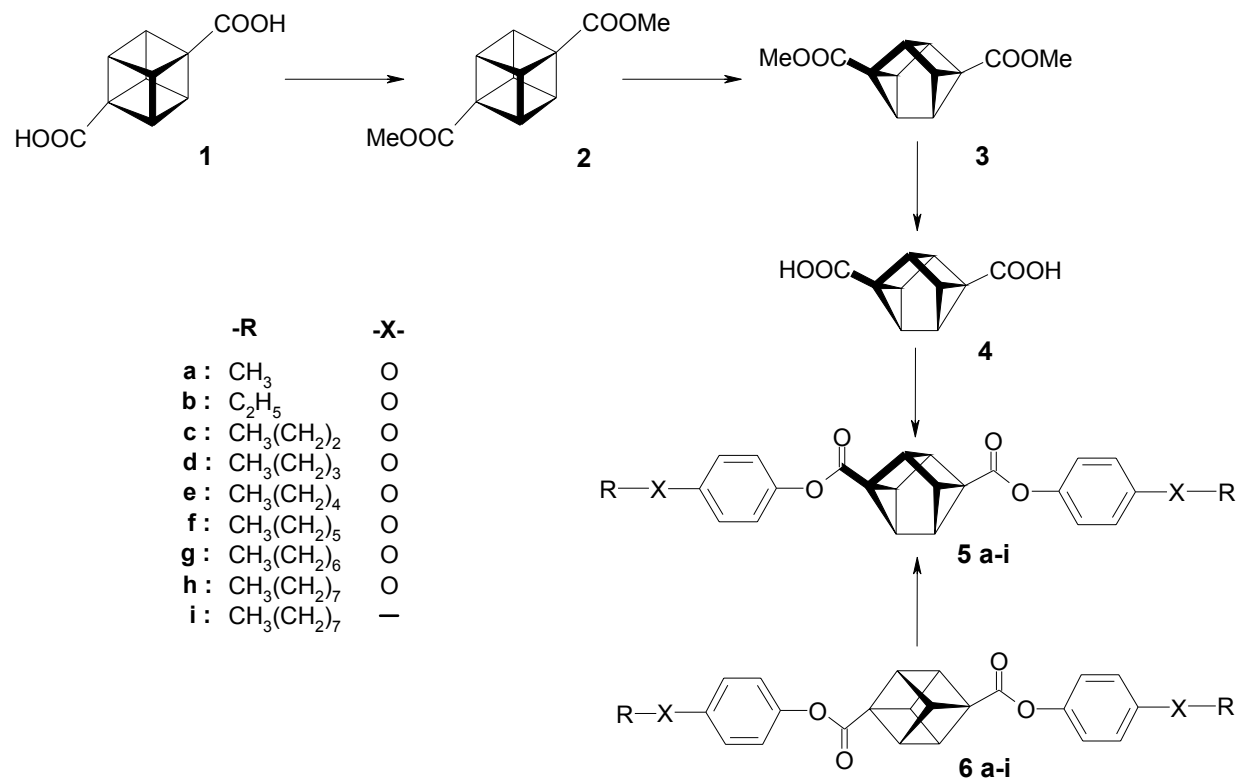
Bis[4-(n-alkyloxyphenyl)]cubane-1,4-dicarboxylates (0.7-0.8mmol) was added in argon atmosphere to a solution of the freshly dried anhydrous silver perchlorate (200-250mg, 0.96-1.20mmol) in anhydrous, thiophene free 15mL benzene. The yellow solution obtained this way was protected from light in a sealed bottle rinsed with argon. After one week stirring at 70°C , the solution was allowed to cool down to room temperature, quenched with water and extracted with dichloromethane. The combined organic extracts were washed with water, until the silver halogenide test become negative, then dried over Na_2SO_4 , and evaporated. The crude material was cleaned by flash-chromatography on Kieselgel 60 (0.063-0.02mm) column eluted with n-hexane/ethyl acetate 2:1 mixture. The appropriate fractions were collected, the solvents removed in vacuum, and the product was purified by crystallization from n-heptane.

The characterization of the products was as described above under Method A.

Results and Discussion

The first liquid crystalline bis[4-(n-alkyloxyphenyl)]cuneane-2,6-dicarboxylates were prepared by both methods A and B. In Method A, following the literature, the dimethyl cubane-1,4-dicarboxylate was isomerized to the appropriate dimethyl cuneane-2,6-dicarboxylate (**a**) and dimethyl cuneane-1,3-dicarboxylate (**b**). Theoretically ten differently disubstituted isomers could have been formed, but only two of them were present in the reactions mixtures. This method gave the methyl esters in an isomer ratio as **a:b=20:1**. After hydrolysis of the dimethyl cuneane-

2,6-dicarboxylate, the acid obtained was reacted with the appropriate substituted 4-(n-alkoxy)phenol derivatives (Scheme 1). These new compounds have been prepared by a direct ester formation.



Scheme 1.

Reaction pathway for preparation of bis[4-(n-alkoxyphenyl)]cuneane-2,6-dicarboxylates

According to the other possibility (Method B) the rearrangement reaction was carried out on the formerly synthesized bis[4-(n-alkoxyphenyl)]cubane-1,4-dicarboxylates (**6a-i**) (Scheme 1.) with silver (I) catalysis. The new liquid crystalline cuneane-caged derivatives (**5a-i**) exhibited liquid crystalline mesophases, but the transition temperatures were not sharp. These phase transition temperatures were observable in large temperature interval (5-10 degrees). By thin-layer chromatography the compounds were clean, so it was postulated, that the isomer ratio was not so advantageous than that obtained in the rearrangement reaction of the simple dimethyl cubane-1,4-dicarboxylate. By high performance liquid chromatography, the formed isomers could be separated. This method gave the evidence that **a:b** isomers were present in ratio 9:1. In spite of this less advantageous isomer ratio, we can establish, that the liquid crystalline cubane-1,4-dicarboxylates could have been isomerized without any unexpected degradation or other side reactions.

Quantum chemical calculations have been performed with the software CAChe [19], using different methods. The energy difference between cubane and cuneane was calculated by

use of the DFT method CAChe DGauss B88-LYP. The result of 34.34 kcal/mole (143.67 kJ/mole) is within the expectation of the cited literature [19].

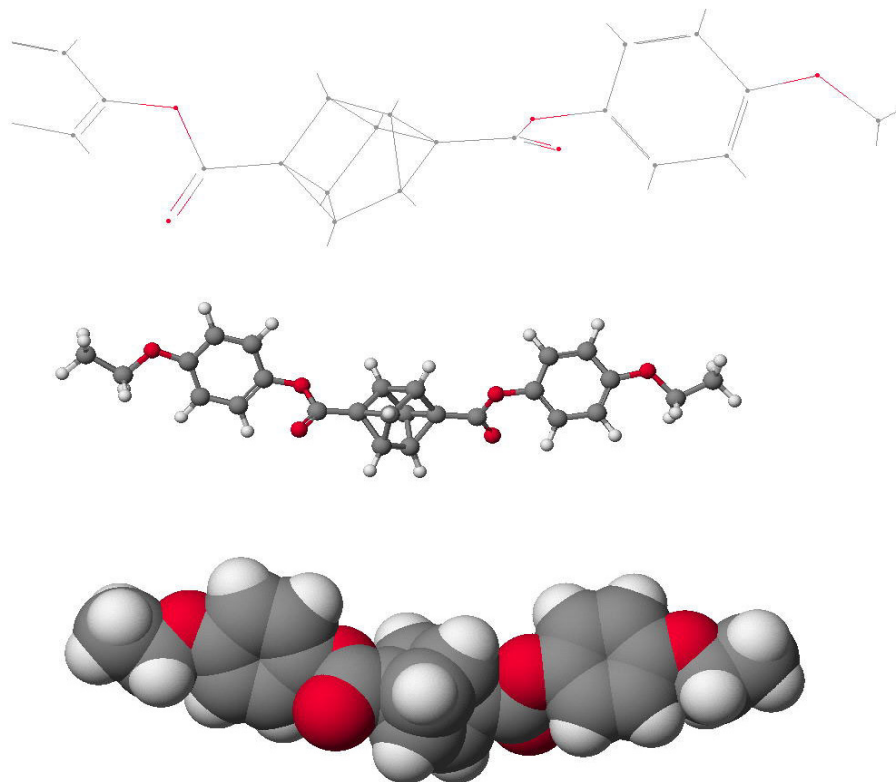


Figure 1. Chemical structure of bis[4-(ethoxyphenyl)]cuneane-2,6-dicarboxylate

For further quantum chemical calculations with the semiempirical method CAChe/PM5 bis[4-ethoxyphenyl]cuneane-2,6-dicarboxylate was chosen as model compound. The compound is shown in **Figure 1** in 3 different models, showing exactly the same projection of the molecule. The simple skeleton on the upper part shows nicely the cuneane cage in the middle. Here the most stable conformation of **5b** is depicted with heat of formation -97.8 kcal/mole. It is surprising that this conformation does not have a symmetry center. The planes of the benzene rings are mutually twisted by 30° . The C=O groups are not oppositely directed, but their directions make an angle of less than 90° . The molecule has an elongated shape, with a slight bend. To prove that the energy minimum found is really the most stable conformation, the energy map of the rotation of the left $\text{C}_2\text{H}_5\text{-C}_6\text{H}_4\text{-COO-}$ around the cuneane-O bond was calculated (**Figure 2a**): 2 minima and 2 maxima have been found. The lower minimum corresponds to the most stable conformer, shown in the figure 2a (it is the same as the conformation shown in **Figure 1**). The maxima correspond to activation energies of about 2kcal/mole, which are quite low.

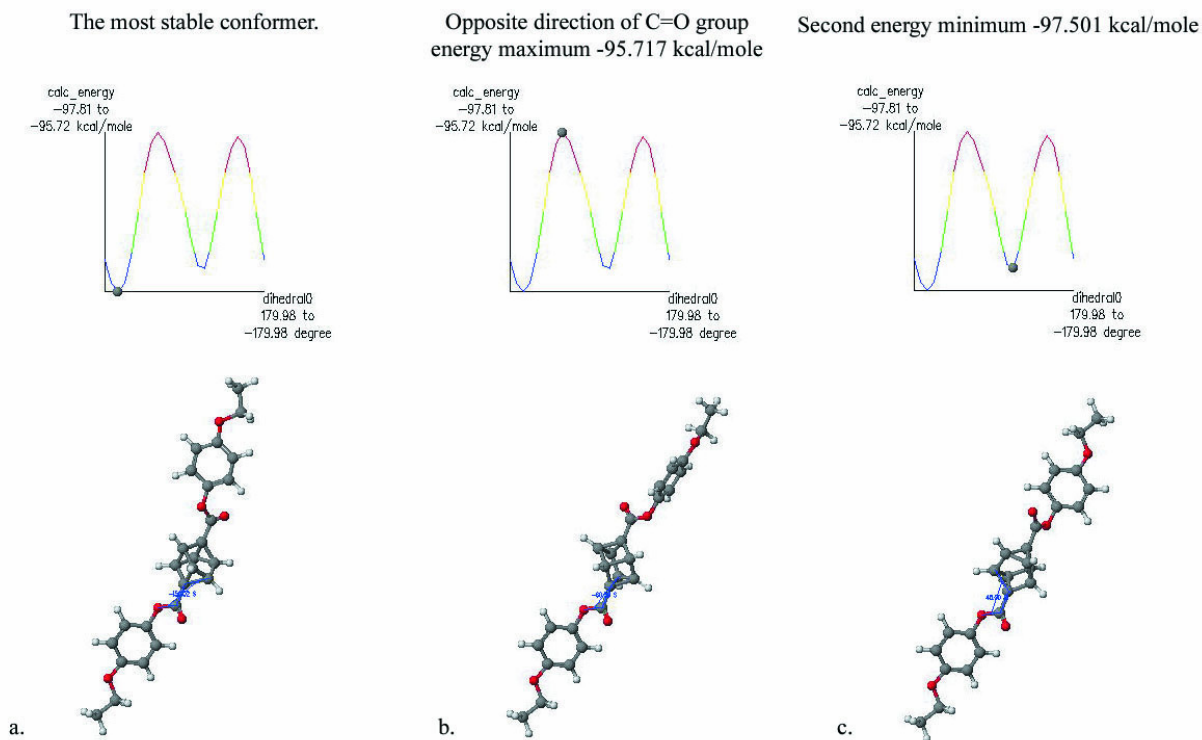


Figure 2: Quantum chemical calculations on the most stable conformers of bis[4-(ethoxyphenyl)]cuneane-2,6-dicarboxylate

Figure 2b shows the situation where the two C=O groups are oriented antiparallel. **Figure 2c** shows the conformation of the second minimum, where the planes of the benzene rings are twisted by 30° , and the directions of the C=O groups make an angle of less than 90° . This is not very different from the situation of the first minimum corresponding to **Figure 2a**. Note that all conformers of the cuneane considered here are quite nicely elongated and should have some mesogenic potential.

Indeed studies of the phase behavior of the materials synthesized show relatively wide mesophase ranges as shown in **Table 1**. In the last column of this table we also show the lengths of the molecules in their most stable conformation, i.e. with the extended form of the alkyl chains, as calculated by the software CAChe/PM5 [19].

The first four members of the homologous series exhibit nematic (N) phase. The very first compound **5a** has only 40 degrees wide monotropic N phase (see **Figure 3a**), which can be observed only on cooling at almost 50 degrees below the temperature where the material melts in heating. This indicates that the **5a** has a very stable crystal modification, which hinders the observation of the N phase on heating. The N phase is more stable in compounds **5b** and **5c**. **5d** has both nematic and smectic A phases (see **Figure 3b** and c). The higher homologues exhibit only enantiotropic SmA phase (see e.g. **Figure 3d**). **5e-5g** have two crystalline phase modifications on cooling. Comparing the octyloxyphenyl- (**5h**) and the octylphenyl (**5i**) derivatives (see **Table 1**), we see that the alkyl analogue has lower melting and phase transition temperatures than its alkoxy one. This behavior is similar to the usual aromatic liquid crystals.

Code	Cr1	$^{\circ}\text{C}$, [$\Delta\text{H}/\text{kcal}/\text{mol}$]	Cr2	$^{\circ}\text{C}$, [$\Delta\text{H}/\text{kcal}/\text{mol}$]	SmA	$^{\circ}\text{C}$, [$\Delta\text{H}/\text{kcal}/\text{mol}$]	N	$^{\circ}\text{C}$, [$\Delta\text{H}/\text{kcal}/\text{mol}$]	I	L (\AA)
5a	+	170.5 [9.53]	-	-	-	-			+	23.17
	+	81.7 [0.23] ↓	-	-	-	-	(+)	121.6 [0.16] ↓	+	
5b	+	144.3 [9.16]	-	-	-	-	+	180.3 [0.30]	+	25.65
	+	93.3 [3.98] ↓	-	-			+	174.5 [0.27] ↓	+	
5c	+	128.9 [9.12]	-	-	-	-	+	148.3 [0.18]	+	28.95
	+	128.3 [0.21] ↓	-	-	-	-	+	141.2 [0.18] ↓	+	
5d	+	120.0 [8.87]	-	-	+	121 [n.d.]	+	146.2 [0.22]	+	31.24
	+	79.15 [3.28] ↓	-	-	+	120 [n.d.] ↓	+	146 [n.d.] ↓	+	
5e	+	115.0 [7.90]		-	+	136.8 [1.91]	-	-	+	33.69
	+	79.9 [2.44] ↓	+	108.1 [n.d.] ↓	+	135.5 [2.47] ↓	-	-	+	
5f	+	101.1 [8.73] ↓	-	-	+	145.5 [1.67]	-	-	+	36.34
	+	72.1 [0.27]	+	74.8 [3.64] ↓	+	142.2 [1.39] ↓	-	-	+	
5g	+	96.0 [9.71]	-	-	+	145.5 [1.90]	-	-	+	38.93
	+	85.6 [2.79] ↓	+	91 [n.d.] ↓	+	143.9 [2.75] ↓	-	-	+	
5h	+	94.7 [6.36]	+	98.2 [0.21]	+	146.7 [2.24]	-	-	+	41.34
	+	85.7 [6.18] ↓	-	-	+	145.2 [2.76] ↓	-	-	+	
5i	+	81.7 [11.24]	-	-	+	96.3 [1.83]	-	-	+	38.27
	+	74.8 [3.00] ↓	-	-	+	95.1 [3.04] ↓	-	-	+	

Table 1: Phase transition temperatures ($^{\circ}\text{C}$), enthalpies [$\Delta\text{H}/\text{kcal}/\text{mol}$], and calculated molecular lengths of bis[4-(*n*-alkyloxyphenyl)]cuneane-2,6-dicarboxylates. Cr: crystalline, SmA: smectic-A, N: nematic, I: isotropic liquid, ↓: cooling cycles, n.d.: no data, +: phase exists, -: phase does not exist, () : monotropic phase.

The typical textures observed in polarizing microscope are shown in **Figure 3**.

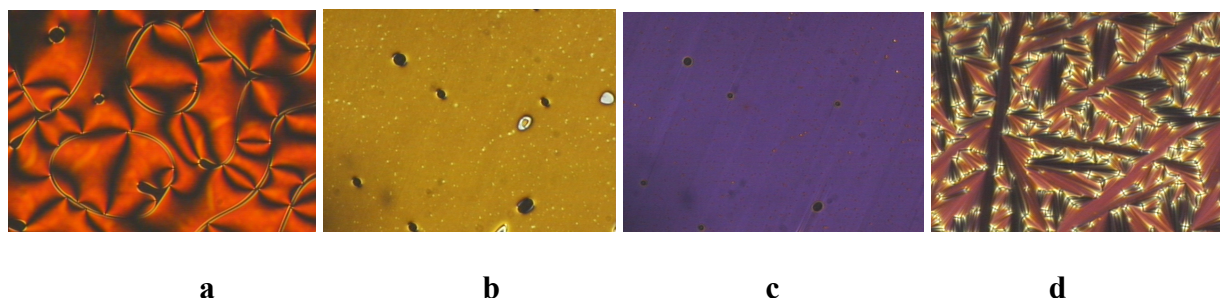


Figure 3: Typical textures of $5\ \mu\text{m}$ films with planar unidirectionally rubbed polyimide surfaces. (a) 5a at 129°C ; (b) 5d at 133°C in the nematic phase; (c) 5d at 105°C in the SmA phase; (d) 5e at 128.2°C at SmA phase.

A representative DSC curve of 5i is shown in Figure 4.

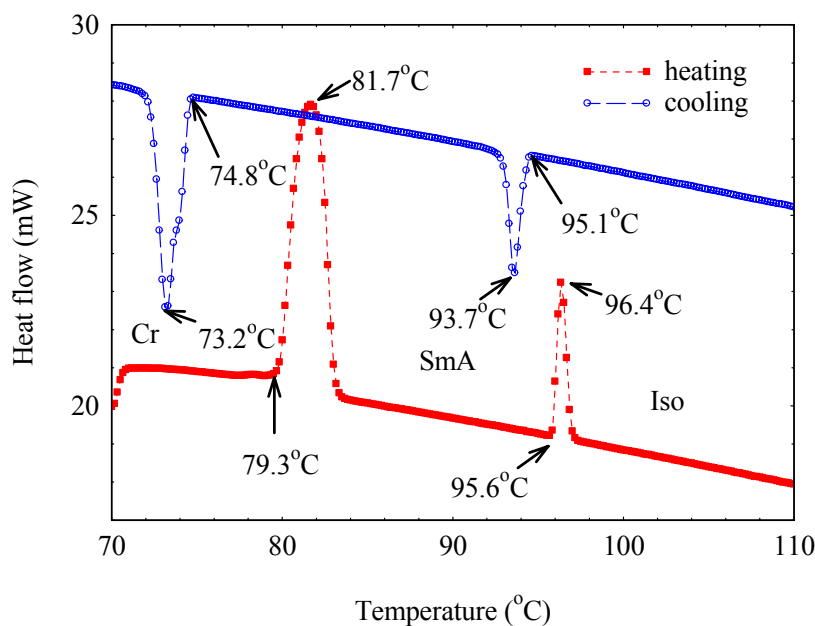


Figure 4: DSC curve of compound 5i.

The phase transitions of the new cuneane derivatives are graphically presented in **Figure 5**. The largest temperature range of the nematic phase can be observed on the ethoxy- derivative **5b**. This phase exists over about 80 degrees. The SmA phase of the hexyloxy derivative is the largest in the cooling cycle for the compounds 5f-g.

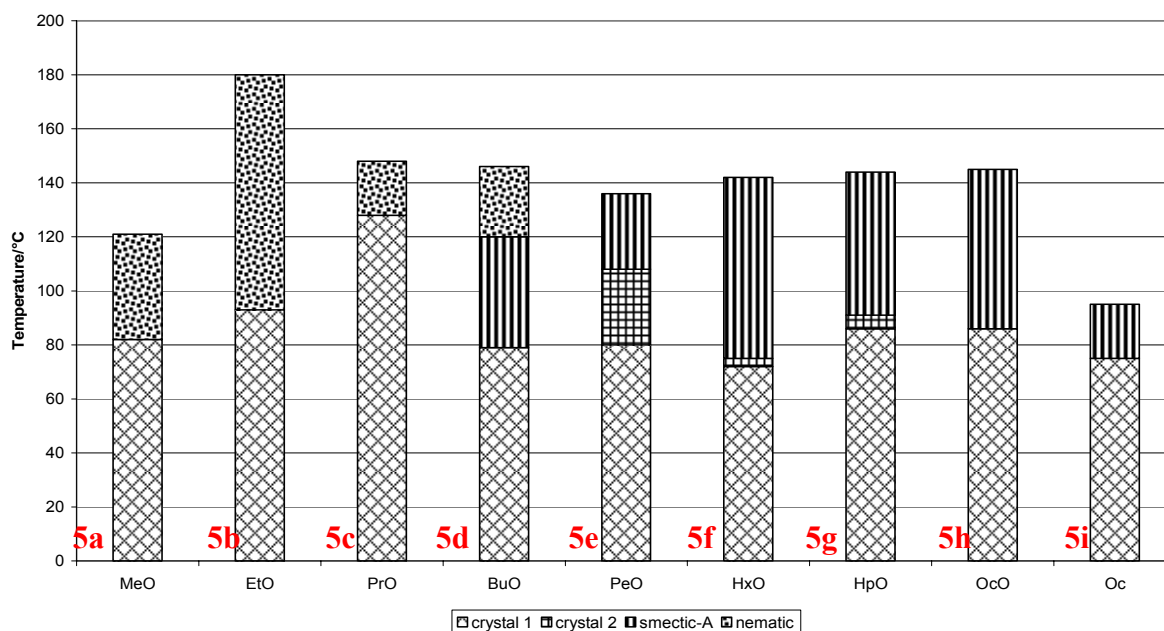


Figure 5. Phase transition temperatures of cuneane esters on cooling.

X-ray investigations were carried out on unoriented samples filled in Lindemann capillaries of 1 mm diameter. The layer thickness (d) was determined from the low angle diffraction patterns show that the layer periodicity is generally smaller than the molecular lengths (compare **Table 1** and **Table 2**). In reality, the molecules are not completely extended due to gauche conformations in the alkyl chains. In this case the difference between X-ray spacing and molecular length should increase with increasing molecular length, because longer alkyl chains have more possibilities for gauche conformations (**Table 1**).

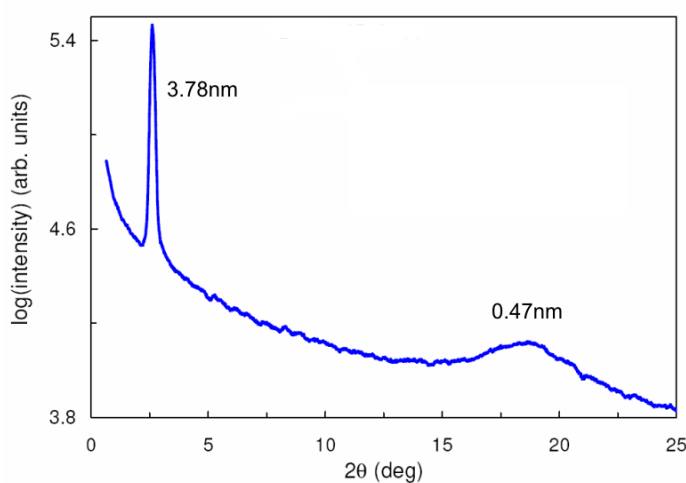


Figure 6. X-ray diffraction profile of **5f** at 122°C.

The difference is indeed increasing: 2.05 Å, 4.306 Å, and 4.89 Å for **5c**, **f** and **g**, respectively. However there can be other reasons for the differences, such as interpenetrating molecules, or uncorrelated tilting of the molecules known as „de Vries“ smectics [20].

In all the materials the mesophases exhibited a broad and diffuse peak at wide angles suggesting liquid-like arrangement in a plane normal to the director direction. The magnitude of the average separation between the molecules (D) in this plane was extracted from such diffuse maxima. The X-ray diffraction profile of **5f**. is depicted in figure 6.

Code	Temp.	Phase	d (Å)	D (Å)
5c	116°C	N	23.6*	4.74*
5f	120°C	SmA	32.03	4.71
5g	120°C	SmA	34.04	4.74

* corresponds to the periodicity of layer fluctuations

Table 2: The low and wide angle periodicities d and D, respectively determined by X-ray measurements for selected cuneane derivatives. For 5f and 5g with smectic A phase the low angle periodicity corresponds to the smectic layer spacing, whereas for the nematic phase of 5c it indicates the layer periodicity of the smectic cybotactic groups.

Conclusions

New bis[4-(n-alkoxyphenyl)]cuneane-2,6-dicarboxylates have been prepared by two different ways. The longer reaction route, where first the cubane skeleton was isomerized to the cuneane-cage, led to liquid crystalline materials with higher purity. The isomer ratio of cuneane-2,6- and cuneane-1,3-dicarboxylate was different in the two reaction pathways. The new compounds with unusual molecular architecture exhibited nematic and smectic A phases.

The quantum chemical calculation showed the most stable conformer has an elongated structure, and the molecular length was correlated with the X-ray results.

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