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Liquid Crystals

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First liquid crystalline cuneane-caged derivatives: a structure-property relationship study

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First liquid crystalline cuneane-caged derivatives: a structure–property relationship study

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The synthesis and phase behaviour of the first cuneane derivatives having 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 methods: either by isomerization of the previously prepared bis[4-(*n*-alkoxyphenyl)]cubane-1,4-dicarboxylates or by direct esterification of the cuneane-2,6-dicarboxylic acid. Enantiotropic nematic phases were observed for the first four homologues. The higher homologues exhibited enantiotropic smectic A phases. The bis[4-(*n*-octylphenyl]cuneane-2,6-dicarboxylate exhibited the SmA phase at a lower temperature than its octyloxy analogue. The mesophases were investigated and established by polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction. Quantum chemical calculations suggest elongated structure for these new liquid crystalline compounds.

1. Introduction

During more than one hundred years of liquid crystal research over a hundred thousand liquid crystals have been synthesized [1, 2]. These mainly contain aromatic moieties, but numerous cyclohexane [3], bicyclohexane [4], bicyclo-2,2,2[222]-octane [5], bridged–ring [6], and carborane [7] mesomorphic compounds have also been prepared. It is well known that not only morphological aspects, but also delocalization plays an important role in the mesophase formation. Recently a new field of liquid crystal research has developed focused on banana-shaped or bent-core molecules having a different molecular architecture compared with that of the conventional calamitic compounds [8–10]. Until now little work has been devoted to compounds containing a cubane moiety in their molecular architecture [11, 12]. A few cubane-1,4-dicarboxylic acid derivates have been reported [13, 14] with enantiotropic or monotropic nematic phases. Recently, however we reported numerous achiral and chiral cubane-1,4-dicarboxylate derivatives with liquid crystalline properties [15]. No literature references were found in which cuneane-2,6-dicarboxylates were used as the central unit of liquid crystal molecules. The cuneane skeleton (pentacyclo[$3.3.0.0^{2,4}.0^{3,7}.0^{6,8}$]octane) was first reported in 1968. The name 'cuneane' was adopted for simplicity and is derived from the Latin 'cuneus', meaning a wedge [16]. Comparing the cubane skeleton with the cunean-cage, it was shown, that cuneane should be 30–40 kcal mol^{-1} 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]; in this reaction silver(I) or palladium(I) salts were used as catalyst.

In this paper we report the quantitative isomerization of the mono- and di-methyl cubane-1,4-dicarboxylates 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 these were actually found.

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For example, dimethyl cubane-1,4-dicarboxylate was transformed into dimethyl cuneane-2,6-dicarboxylate and dimethyl cuneane-1,3-dicarboxylate in the ratio 20:1 [18].

Our aim was to investigate whether the previously 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 any mesomorphic properties.

2. Materials and methods

Dimethyl cubane-1,4-dicarboxylate (**2**) was prepared according to the method described earlier [9]. The synthesis of the bis[4-(*n*-alkoxyphenyl)]cubane-1,4-dicarboxylates was also described earlier [10]. 4-*n*-Alkoxyphenols as methoxy-, ethoxy- propoxy-, butoxy-, hexyloxy- and heptyloxy-phenols 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 ^{1}H NMR and ^{13}C NMR spectroscopy. The spectra were taken with a 250 MHz Bruker spectrometer at 20°C in $CDCl_3$ solution. The numbering system for the assignment of the NMR signals is shown in figure 1.

Gas chromatographic analyses were carried out on a Chrompack CP 9001 system equipped with a 25 m CP Sil 13CB column, using a H_2 gas flow (5 ml min^{-1}) and flame ionization detector. High performance liquid chromatographic analyses was performed using a Merck Hitachi LaChrom HPLC system with L-7450 diode array detector, L-7100 pump, L-7200 autosampler and L-7614 degasser. A LiChrospher 100 RP-8 column (150 × 4 mm ID, 5 μm particle size) was eluted by water/acetonitrile mixture using the elution program: initial 95% water and 5% acetonitrile, followed by a linear gradient elution with 100% acetonitrile for 20 min, finally an isocratic elution for more than 15 min. The flow rate was 1.0 ml min^{-1}. Chromatographic data were collected by HSM software; the chromatogram type was fixed WL at 215 nm.

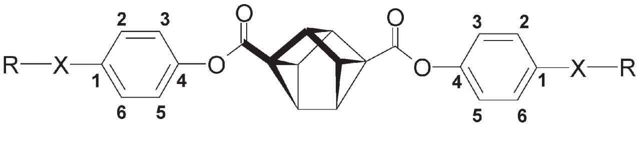


Figure 1. Numbering system used in the assignment of the NMR spectrum.

The thermal behaviour of the compounds was studied by polarizing optical microscopy (POM) with an Amplival POL U instrument 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^{-1}.

X-ray diffraction experiments were performed using Cu K_α radiation (λ=1.5418 Å) from a fine focus sealed-tube generator in conjunction with double-mirror focusing optics, which provided 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 × 100 μm^2.

3. Synthesis

3.1. *Dimethyl cuneane-2,6-dicarboxylate (3)*

Silver perchlorate (6.2 g, 30 mmol) was freshly dried over phosphorus pentoxide *in vacuo* at 120°C for 10 h and added under argon to a stirred solution of methylcubane-1,4-dicarboxylate (**2**) (10 g, 45.5 mmol) in anhydrous, thiophene-free benzene (200 ml), while the solution became red. The reaction proceeded under argon at 60°C in a stirred sealed flask for 5 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 a silver halogenide test were negative, and then dried over Na_2SO_4. 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), 6.1 g (61%) of dimethyl cuneane-2,6-dicarboxylate was obtained, 99.9% pure by GC analysis.

3.2. *Cuneane-2,6-dicarboxylic acid (4)*

A solution of sodium hydroxide (2.0 g, 50 mmol) in 40 ml methanol and 2 ml water was added to a stirred solution of **3** (3.52 g, 16 mmol) in methanol (100 ml) over a 5 min period. After 1 h the reaction mixture was heated at reflux for 5 h, and then stirred overnight at room temperature. The solvent was removed, and the white solid obtained dissolved in 14 ml water. The solution was acidified dropwise with 4.4 ml concentrated hydrochloric acid at 0°C. The white precipitate thus formed was collected, washed three times with 4 ml ice-cold water, and dried in vacuum to yield 3.01 g (98.0%) of product.

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

Method A. The 4-(*n*-alkyloxy)phenol (3.80 mmol) was added to a suspension of cuneane-2,6-dicarboxylic acid (360 mg, 1.88 mmol) in dichloromethane. The reaction mixture was cooled to 0°C and a solution of 4-(*N*,*N*-dimethylamino)pyridine (90 mg, 0.7 mmol, 1/5 equiv) in 10 ml dichloromethane added, followed by a solution of *N*,*N*-dicyclohexylcarbodiimid (860 mg 4.17 mmol, 1.1 equiv.) in 10 ml dichloromethane. Stirring was continued for 1 h at 0°C, and then overnight at room temperature. The reaction mixture was filtered on celite 545, and the solvent removed. The solid residue was dissolved in 5 ml dichloromethane, and purified by flash chromatography on a Kieselgel 60 (0.063–0.02 mm) column, eluting with dichloroethane/ethanol 10/1 mixture. The appropriate fractions were collected and evaporated *in vacuo*; the product was purified by crystallization from *n*-hexane/ethanol 5/1 to give a 60–80% yield. A selection of typical NMR characterization data is given below.

Bis[4-(methoxyphenyl)]cuneane-2,6-dicarboxylates (5a): yield 494 mg (65%), $C_{24}H_{20}O_6=404.42$. ^1H NMR (δ, 20°C, $CDCl_3$, 250 MHz), 6.97 (m, 4H, $Ph^{2,6}$), 6.86 (m, 4H, $Ph^{3,5}$), 3.78 (s, 6H, O*CH₃*), 3.36 (m, 2H, cuneane), 3.30 (m, 4H, cuneane). ^{13}C NMR (δ, 20°C, $CDCl_3$, 250 MHz), 169.3 (2C, COO), 157.6 (2C, Ph^4), 144.3 (2C, Ph^1), 122.7 (4C, $Ph^{2,6}$), 114.8 (4C, $Ph^{3,5}$), 56.0 (2C, OCH_3), 45.0 (2C, cuneane), 44.2 (2C, cuneane), 41.7 (2C, cuneane), 39.1 (2C, cuneane).

Bis[4-(ethoxyphenyl)]cuneane-2,6-dicarboxylates (5b): yield 937 mg (83%), $C_{38}H_{48}O_6=600.80$. ^1H NMR (δ, 20°C, $CDCl_3$, 250 MHz), 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), 3.30 (m, 4H, cuneane), 1.76 (m, 4H, OCH_2CH_2), 1.35 (m, 20H, $–(CH_2)_5–$), 0.89 (t, 6H, CH_3). ^{13}C NMR (δ, 20°C, $CDCl_3$, 250 MHz), 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), 32.2 (2C, OCH_2CH_2), 29.7, 29.6, 26.6, 26.4, 23.0 (10C, $–(CH_2)_5–$),14.5 (2C, CH_3).

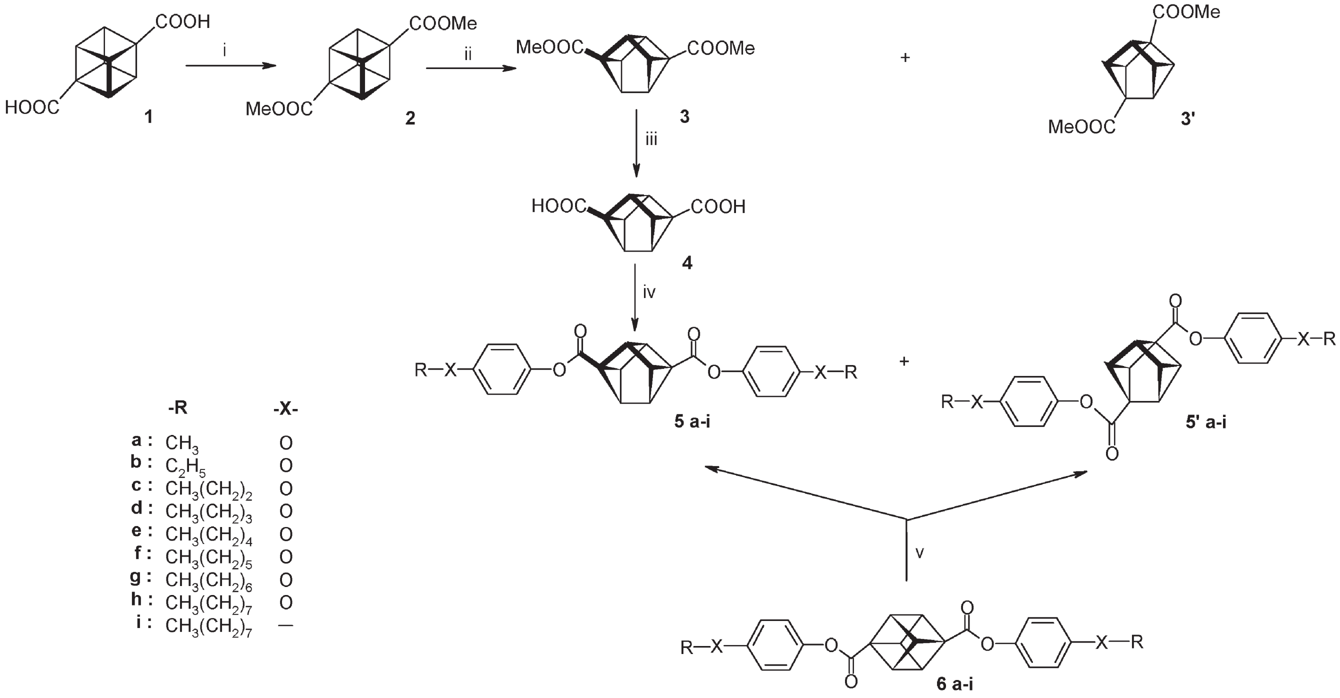
Bis[4-(n-octylphenyl)]cuneane-2,6-dicarboxylates (5i): yield 813 mg (76%), $C_{38}H_{48}O_4=568.80$. ^1H NMR (δ, 20°C, $CDCl_3$, 250 MHz), 7.15 (m, 4H, $Ph^{2,6}$), 6.95 (m, 4H, $Ph^{3,5}$), 3.37 (m, 2H, cuneane), 3.29 (m, 4H, cuneane), 2.58 (t, 4H, $Ph–CH_2$), 1.57 (m, 4H, $PhCH_2–CH_2$), 1.26 (m, 20H, $–(CH_2)_5–$), 0.88 (t, 6H, CH_3). ^{13}C NMR (δ, 20°C, $CDCl_3$, 250 MHz), 169.1 (2C, COO), 148.7 (2C, Ph^4), 140.8 (2C, Ph^1), 129.6 (4C, $Ph^{2,6}$), 121.5 (4C, $Ph^{3,5}$), 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, $PhCH_2–CH_2$), 31.8, 29.8, 29.7, 29.6, 23.1 (10C, $–(CH_2)_5–$),14.5 (2C, CH_3).

Method B. Bis[4-(*n*-alkyloxyphenyl)]cubane-1,4-dicarboxylate (0.7–0.8 mmol) was added in an argon atmosphere to a solution of freshly dried anhydrous silver perchlorate (200–250 mg, 0.96–1.20 mmol) in anhydrous, thiophene-free benzene (15 ml). The resulting yellow solution was protected from light in a sealed flask flushed with argon. After one week stirring at 70°C, the solution was allowed to cool to room temperature, quenched with water and extracted with dichloromethane. The combined organic extracts were washed with water, until a silver halogenide test was negative, then dried over Na_2SO_4, and evaporated. The crude product was purified by flash chromatography on a Kieselgel 60 (0.063–0.02 mm) column eluted with *n*-hexane/ethyl acetate 2/1 mixture. The appropriate fractions were collected, the solvents removed under vacuum, and the product purified by crystallization from *n*-heptane. The products were characterized as described for method A.

4. Results and discussion

The first liquid crystalline bis[4-(*n*-alkyloxyphenyl)]cuneane-2,6-dicarboxylates were prepared by 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 (**3a**) and dimethyl cuneane-1,3-dicarboxylate (**3′a**). Theoretically, ten differently disubstituted isomers could be formed, but only two were present in the reaction mixtures. This method gave the methyl esters in an isomer ratio **3a**:**3′a**=20:1. After hydrolysis of the dimethyl cuneane-2,6-dicarboxylate, the acid so obtained was reacted with the appropriately substituted 4-(*n*-alkoxy)phenol derivatives (scheme 1). These new compounds were prepared by a direct ester formation.

In method B a rearrangement reaction was carried out on the previously synthesized bis[4-(*n*-alkoxyphenyl)]cubane-1,4-dicarboxylates (**6a**–**i**) (scheme 1) with silver(I) catalysis. The new liquid crystalline cuneane-cage derivatives (**5a**–**i**) exhibited liquid crystalline mesophases, but the transition temperatures were not sharp, even after four repeated crystallizations from different solvents. The phase transition temperatures were observed over large temperature intervals (5–10°C). However, by thin layer chromatography only one spot was detected; it was postulated that the isomer ratio was less advantageous than that obtained in the rearrangement reaction of the simple dimethyl cubane-1,4-dicarboxylate. The isomers could not be resolved by 600 MHz NMR spectroscopy either. Finally, high performance liquid chromatography provided evidence that isomers of compounds **5a**–**i** and **5′a**–**i** were present



Scheme 1. Reaction pathway for the preparation of bis[4-(*n*-alkoxyphenyl)]cuneane-2,6-dicarboxylates: i: Dowex-50 resin H^+ form, MeOH, reflux, 3 h; ii: $AgClO_4$, benzene, 70°C, 5 days; iii: NaOH, MeOH, H_2O, 3 h; iv: DCC, DMAP, DCM, RT; v: $AgClO_4$, benzene, 70°C, 5 days.

in 9:1 ratio. It should be noted that compounds **5′a–i** are the phenylester derivatives of the 1,3-substituted cuneanes. Despite this less advantageous isomer ratio, we can establish that the liquid crystalline bis[4-(*n*-alkoxyphenyl)]cubane-1,4-dicarboxylates could have been isomerized with no unexpected degradation or other side reactions into cuneane-caged derivatives. Indeed, studies of the phase behaviour of the materials synthesized show relatively wide mesophase ranges, as listed 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 using the software CAChe/PM5 [19].

The first four members of the homologous series exhibit a nematic (N) phase. The first compound **5a** has only a 40°C wide monotropic N phase, see figure 2 (*a*), which may be observed only on cooling to almost 50°C below the temperature at which the material melts on heating. This indicates that **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**. Compound **5d** has both nematic and smectic A phases, see figures 2 (*b*, *c*). The higher homologues exhibit only an enantiotropic SmA phase, see for example figure 2 (*d*). Compounds **5e–g** 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 analogue. This behaviour is similar to that observed for the conventional aromatic liquid crystals.

The largest nematic phase temperature range may be observed for the ethoxy derivative **5b**, and exists over about 80°C on cooling. Among compounds **5f**, **5g**, **5h** the SmA phase of the hexyloxy derivative has the largest range during the cooling cycle. However the temperature range of the **5i** N phase is the lowest, its interval is also the shortest.

5. X-ray investigations

Observations were carried out on unoriented samples filled into 1 mm diameter Lindemann capillaries. The spacing corresponding to the layer thickness (*d*) was determined by fitting the peak profiles at low angles in the one-dimensional intensity vs. diffraction angle data extracted from the diffraction patterns. 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 lengths of the molecules in their

Table 1. Phase transition temperatures (°C), enthalpies (ΔH kcal mol) in parentheses, and calculated molecular length (*L*), of bis[4-(*n*-alkyloxyphenyl)]cuneane-2,6-dicarboxylatesoxylates. Cr=crystalline, SmA=smectic A, N=nematic, I=isotropic liquid; H (C) denotes heating (cooling) cycle.

Compound		Cr1	Cr2	SmA		N		I	*L*/Å
5a	H	•	170.5 (9.53)					•	23.7
	C	•	81.7 (0.23)			•	121.6 (0.16)	•	
5b	H	•	144.3 (9.16)			•	180.3 (0.30)	•	25.65
	C	•	93.3 (3.98)			•	174.5 (0.27)	•	
5c	H	•	128.9 (9.12)			•	148.3 (0.18)	•	28.95
	C	•	128.3 (0.21)			•	141.2 (0.18)	•	
5d	H	•	120.0 (8.87)	•	121 [a]	•	146.2 (0.22)	•	31.24
	C	•	79.15 (3.28)	•		•	146 [a]	•	
5e	H	•	115.0 (7.90)	•	136.80 [a]	•	136.8 (1.91)	•	33.69
	C	•	79.9 (2.44)	•	108.1 [a]		135.5 (2.74)	•	
5f	H	•	101.1 (8.73)			•	145.5 (1.67)	•	36.34
	C	•	72.1 (0.27)	•	74.8 (3.64)	•	142.2 (1.39)	•	
5g	H	•	96.0 (9.71)			•	145.5 (1.90)	•	38.93
	C	•	85.6 (2.79)	•	91 [a]	•	143.9 (2.75)	•	
5h	H	•	94.7 (6.36)	•	98.2 (0.21)	•	146.7 (2.24)	•	41.34
	C	•	85.7 (6.18)			•	145.2 (2.76)	•	
5i	H	•	79.3 (11.24)			•	95.6 (1.83)	•	38.27
	C	•	74.8 (3.00)			•	95.1 (3.04)	•	

[a] No data available.

most stable conformation, i.e. with the extended form of the alkyl chains, were calculated by the CAChe/PM5 [19] software. Table 1 shows the calculated molecular length (*L*) and table 2 the measured X-ray spacings, *d*. Generally, the X-ray spacings are observed to be smaller than the molecular lengths. In reality, the molecules are 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

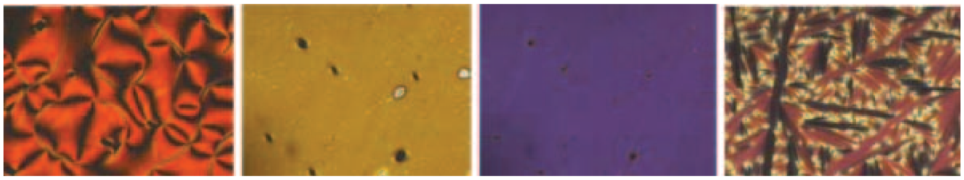

(*a*) (*b*) (*c*) (*d*)

Figure 2. Typical textures of 5 µm 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.

Table 2. X-ray data: d=layer spacing, D=intermolecular distance.

Compound	Temp./°C	Phase	d/Å	D/Å
5c	116	N	23.6[a]	4.741[a]
5f	120	SmA	32.034 15.843	4.712
5g	120	SmA	34.040	4.737

[a] Statistical value.

have more possibilities for *gauche* conformations (table 1). Actually, this is not the case. Indeed, the difference increases: 2.05, 4.31 and 4.89 Å for **5c** **5f** and **5g**, respectively. However there can be other reasons for the differences, such as interpenetrating molecules, or uncorrelated tilting of the molecules giving what are known as 'de Vries' smectics [20].

The low and wide angle periodicities d (layer spacing) and D (intermolecular distance), determined by X-ray measurements for selected cuneane derivatives are shown in table 2. For **5f** and **5g** with a 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.

6. Quantum chemical calculations

Quantum chemical calculations were 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 mol^{-1} (143.67 kJ mol^{-1}) is within the expectation of the cited literature [19].

For further quantum chemical calculations with the semiempirical method CAChe/PM5, bis[4-ethoxyphenyl]cuneane-2,6-dicarboxylate was chosen as a model compound. The compound is shown in figure 3, in three different styles showing exactly the same projection of the molecule. The simple skeleton of the upper part nicely shows the cuneane cage in the middle. Here the most stable conformation of **5b** is depicted with heat of formation −97.80 kcal mol^{-1}. It is surprising that this

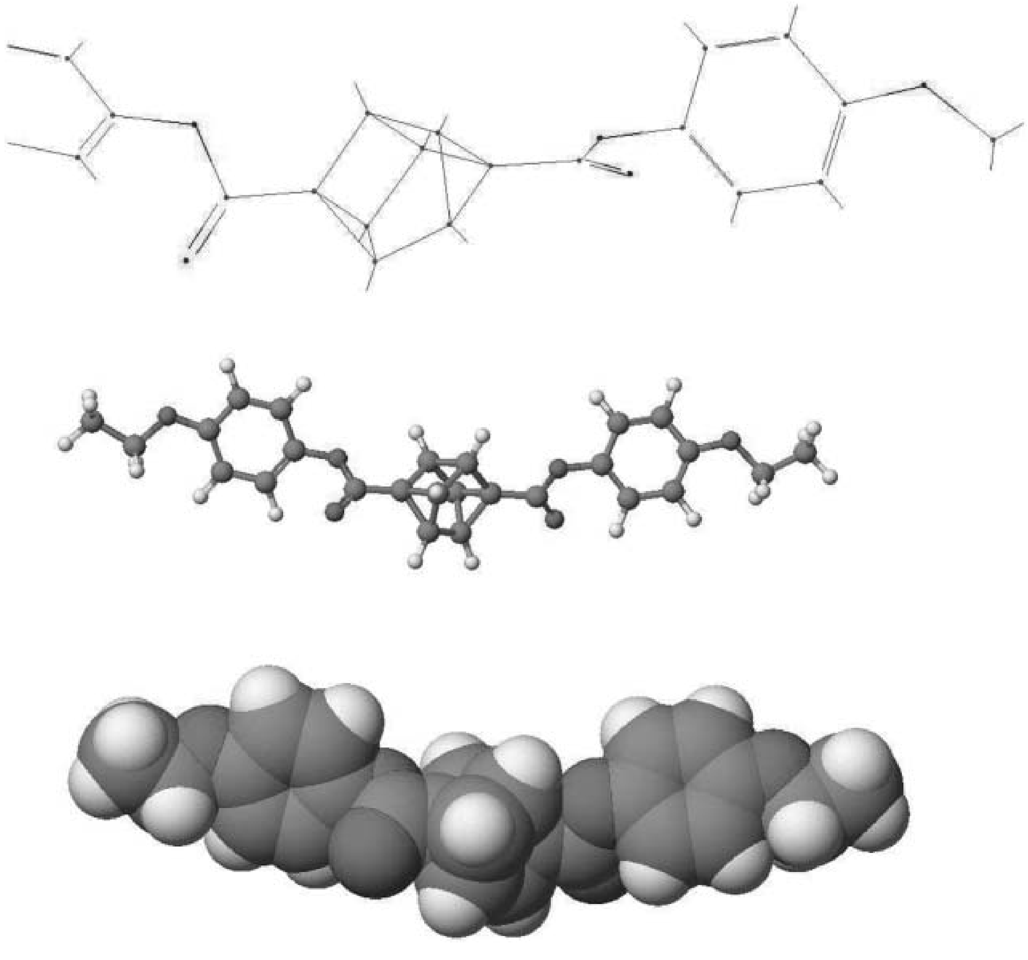


Figure 3. Chemical structure of bis[4-(ethoxyphenyl)]cuneane-2,6-dicarboxylate.

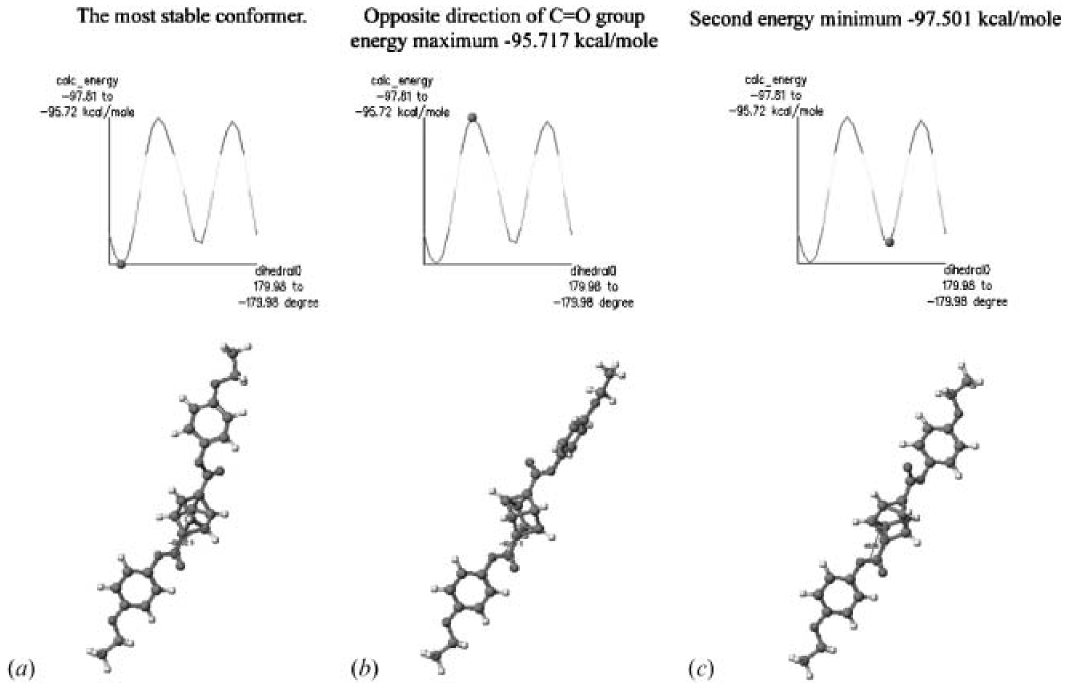


Figure 4. Quantum chemical calculations on the most stable conformers of bis[4-(ethoxyphenyl)]cuneane-2,6-dicarboxylate.

conformation does not have a symmetry centre. The planes of the benzene rings are mutually twisted by 30°. The C=O groups are not pointing in opposite directions, but instead 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 representative of the most stable conformation, the energy map of the rotation of the left-hand C_2H_5–C_6H_4–COO– around the cuneane–O bond was calculated, figure 4 (*a*): two minima and two maxima were found. The lower minimum corresponds to the most stable conformer, shown in figure 4 (*a*) (it is the same as in figure 3.) The maxima correspond to activation energies of about 2 kcal mol^{-1}, which are quite low.

Figure 4 (*b*) shows the situation where the two C=O groups are oriented antiparallel. Figure 4 (*c*) 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 in the first minimum corresponding to figure 4 (*a*). Note that all conformers of the cuneanes considered here are considerably elongated and should have some mesogenic potential.

7. Conclusions

New bis[4-(*n*-alkoxyphenyl)]cuneane-2,6-dicarboxylates have been prepared by two methods. 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-dicarboxylates was different in the two reaction pathways. These new compounds with unusual molecular architecture exhibited nematic and smectic A phases. Quantum chemical calculations showed that the most stable conformer has an alongated structure, and the molecular length was correlated with the X-ray results.

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