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Structure and properties of new liquid crystalline cubane-1,4-dicarboxylic acid derivatives

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New symmetrical esters of cubane-1,4-dicarboxylic acid have been prepared. These compounds have the bulky cubane moiety as the central building block. Five classes of derivative have been synthesized: (a) bis[(4-alkyl)phenyl]cubane-1,4-dicarboxylates; (b) bis[(4-alkoxy)phenyl]cubane-1,4-dicarboxylates; (c) the two chiral derivatives bis(cholestenyl) cubane-1,4-dicarboxylate, and (*S*)-bis[4-(2-methylbutyloxycarbonyl)phenyl]cubane-1,4-dicarboxylate; (d) three members of the bis [4-(2,2-alkoxycarbonylvinyl)phenyl]cubane-1,4-dicarboxylates; and (e) bis[(4′-ethoxycarbonyl)-1,1′-biphenyl-4-yl]cubane-1,4-dicarboxylate. The shorter homologues of the alkoxyphenyl ester series exhibited a nematic (N) phase. No mesophase was observed for the pentyl derivative, while the higher homologues showed a smectic A (SmA) phase according to X-ray investigations. The 4-alkylphenyl and chiral derivatives showed only a melting point. The double swallow tailed bis[4-(2,2-alkoxycarbonylvinyl)phenyl)]cubane-1,4-dicarboxylates also exhibited no mesophase behaviour. On increasing the number of aromatic rings on both sides of the central cubane moiety, N and SmA phases appeared at higher temperatures. In binary mixtures of homologues of alkoxyphenylcubane esters, the temperature range of the SmA phase of the individual compounds became wider and enantiotropic in nature.

1. Introduction

Compounds containing the cubane skeleton have been known since 1964 [1, 2]. This highly stressed skeleton is thermodynamically and kinetically surprisingly stable. Over the past 20 years, cubane derivatives have been extensively investigated for military and medical applications because of their unique properties and application potential.

For more than a century of liquid crystal research, a great number of calamitic liquid crystals have been prepared [3]. Not only aromatic moieties but also numerous cyclohexane [4] bicyclohexane [5], bicyclo-[2,2,2]-octane [6], carborane [7] and bridged [8] compounds have been synthesized exhibiting liquid crystallinity. Of these liquid crystals, however only few have incorporated the cubane moiety in their molecular architectures. These include several cubane-1,4-dicarboxylic acid derivatives with enantiotropic or monotropic nematic phase [9, 10] which were reported in the early 1980s. Recently some new tetra-substituted cubane derivatives were synthesized, and their glass-forming ability was compared with other volume-excluding systems [11].

It is well known that not only the structural aspects (molecular anisotropy), but also delocalization plays an important role in mesophase formation. Compounds cited in, for example, ref. [4–8] provide evidence that limited delocalization of the π electrons neither promotes nor hinders the appearance of mesomorphism.

A new sub-field of liquid crystal research involves the investigation of banana-shaped (bent-core) liquid crystals [12]. The *meta*-substitution in the central ring of the bent-core structure disrupts the delocalization in the molecule and therefore the 'arms' connected to the central ring should consist of a minimum of two

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aromatic rings to introduce liquid crystal behaviour. A recent review summarizes these new architectures and the associated new mesophases [13]. In the core systems of these new architectures delocalization is also limited [14].

Cubane-1,4-dicarboxylic acid is a unique substitute for the aromatic ring in conventional liquid crystals, which also prevents the delocalization of the π electrons along the molecular core. Our aim is to investigate the liquid crystallinity of compounds that contain the cubane moiety in their molecular architecture. By changing the length to breadth ratio of the molecules we have synthesized new model compounds to elucidate their mesomorphic properties. Furthermore the mesomorphic properties and miscibility of these new compounds were investigated in binary mixtures.

2. Experimental

Gas chromatographic analyses were carried out on a Hewlett Packard 5890 series II system, equipped with a 50 m PONA column, using a H_2 gas flow of 1 ml min^{-1} and a flame ionization detector. ^1H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 499.803 MHz and were referenced to $SiMe_4$, the relaxation delay was set to 10 s. $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 125.687 MHz and were referenced to $SiMe_4$. IR spectra were recorded on a Perkin–Elmer spectrophotometer, Spectrum One. Samples were measured as films on NaCl disks. The thermal behaviour of the polymers was determined by 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. Polarizing optical microscopy (POM) measurements were carried out with an Amplival POL-U polarizing microscope equipped with a Boetius hot stage. The phase diagrams of binary mixtures were determined using first the contact method [15] and finally by determination of the transition temperatures of selected mixtures of known composition.

2.1. *Synthesis*

4-Propyloxyphenol, 4-pentyloxyphenol, 4-hexyloxyphenol, 4-heptyloxyphenol and 4-octylphenol were purchased from Acros, 4-nonylphenol from Lancaster and all used without further purification. 4-*n*-Octyloxyphenol was prepared according to the literature [16]. The synthetic procedure described earlier [17–19] for the preparation of cubane 1,4-dicarboxylic acid has been modified in the steps obtaining compounds 8 and 9. 2,2,5-Tribromocyclopentanone ethylene ketal (4), endo-2,4-dibromodicyclopentqadiene-1,8-dion-bis (ethylene ketal) (6), endo-2,4-dibromodicyclopentadiene-1,8-dion-8-ethylene ketal (7), cubane-1,4-dicarboxylic acid (10) and cubane-1,4-dicarboxylic dichloride (11) were prepared according to the literature [1, 2, 17, 18].

2.1.1. Cyclopentanone ethylene ketal (3). This was prepared according to the literature [17,18]. The purity of the obtained transparent oil was 99% by GC analysis. GC parameters: 80°C for 10 min, heating rate 10°C min^{-1}, then 200°C for 10 min, retention time 12.85 min, $C_7H_{12}O_2$=128.17. ^1H NMR (δ, $CDCl_3$):3,88 (s, 4H); 1.57–1.80 (m, 8H).

2.1.2. 5,9-Dibromopentecyclo-[5,3,0,$0^{2,5}$,$0^{3,9}$,$0^{4,8}$]-deka-6,10-dion-6-ethylene ketal (8). In a 4l reactor, equipped with a non-cooled 400 W UV lamp compound 7 (90,5 g, 0,25 mol) was dissolved in warm methanol (3400 ml and 100 ml benzene). The solution was illuminated for 9 h, the non–cooled lamp kept the methanol boiling. The reaction mixture was then evaporated under reduced pressure to 150 ml, and added dropwise to 1 l of water at 70–80°C. A viscous brown oil separated, which was discarded, and white crystals solidified from the remaining water solution. After filtration the crystals were washed with water; yield 74 g (82%), m.p. 149–150°C, $C_{12}H_{10}Br_2O_3$=362,02. ^1H NMR: (δ, $CDCl_3$): 4.30–3.91 (m, 4H); 3.34–3.21 (m, 4H); 3.00 (s, 1H); 2.90–2.84 (m, 1H); 2.75 (s, 1H); 2.72–2.64 (m, 1H). ^{13}C NMR: 120.17; 107.13; 66.48; 66.23; 65.76; 61.86; 50.50; 50.17; 48.47; 46.34; 45.51; 43.35.

2.1.3. 5,9-Dibromo-pentecyclo-[5,3,0,$0^{2,5}$,$0^{3,9}$,$0^{4,8}$]-deka-6,10-dion (9). Compound **8** (60.1 g, 0.17 mol) was dissolved in warm concentrated HBr (48%) solution and allowed to react at 100–110°C for 3 h. After cooling, the reaction mixture was neutralized with solid $NaHCO_3$. The precipitate formed after two days was filtered off and dried *in vacuo* at 60°C. The organic material was extracted with ethyl acetate, then the solution was evaporated to dryness. The crude product (45.7 g) was crystallized from water (350 ml), with decolorization with charcoal. The crystals formed during cooling were discarded; the mother liqour was then evaporated. If necessary, the crystals thus obtained were recrystallized from water. The purity was controlled by thin layer chromatography using Kieselgel 60 plates developed with *n*-hexane/ethyl acetate 1/1, and detected by spraying with 5% sulphuric acid in methanol solution. R_f.: 0.14–0.19 for product **10**, 0.36–0.45 for monoketal (**5**), 0.73–0.82 for byproduct; yield 44.9g (85%), m.p. 231–232°C, $C_{10}H_6Br_2O_2$=317.97. ^1H NMR (δ, DMSO-d6)

5.99 (d, 4H, J=21,9); 3.04–2.90 (m, 4H); 2.58–2.51 (m, 2H). ^{13}C NMR: 105.95; 67.23; 50.73; 49.07; 43.79.

2.1.4. General procedure for the preparation of bis[4′-(alkoxyphenyl)]cubane-1,4-dicarboxylates (Ia–Ie). Cubane-1,4-dicarboxylic dichloride (**11**) (0.96 g, 5 mmol) was dissolved in dichloromethane (10 ml) and added to a stirred mixture of the appropriate phenol derivative (10 mmol) and triethylamine (1.5 ml) in dichloromethane (45 ml). The reaction mixture was stirred for 24 h at room temperature and afterwards extracted with water (3 × 10 ml). The organic layer was dried over sodium sulphate, and evaporated to dryness. The residue was purified by flash chromatography on Kieselgel (0.063–0.02 mm) with elution by chloroform. The appropriate fractions were collected and evaporated to dryness. The residue was crystallized from hexane, ethyl acetate or a chloroform/acetone mixture. The final products were obtained in 40–85% yield. Phase transition data and melting points are summarized in table 1. Representation preparative details are given below.

2.1.4.1. *Bis[4′-(propyloxyphenyl)]cubane-1,4-dicarboxylate (***Ia***).* Compound **11** (0.69 g, 3.0 mmol) in dichloromethane (10 ml) was reacted with 4-*n*-propyloxyphenol (0.912 g, 6.0 mmol) dissolved in dichloromethane (25 ml) in the presence of triethylamine (1.2 ml). Crystallization was from ethyl acetate; yield 1.15 g, (83.02 %), $C_{28}H_{28}O_6$= 460.53. IR: 3004 (w), 2972 (w), 2955 (m), 2922 (m), 2872 (w), 1735 (s), 1603 (w), 1507 (s), 1474 (m), 1391 (w), 1322 (m), 1254 (m), 1204 (s), 1197 (s), 1183 (s), 1111 (m), 1103 (m), 1064 (s), 1010 (m), 980 (m), 940 (w), 913 (w), 860 (m), 898 (w), 741 (m). ^{1}H NMR (δ, 20°C, $CDCl_3$, 500 MHz): 7.01 (m, 4H, $Ph^{2,6}$), 6.90 (m, 4H, $Ph^{3,5}$), 4.45 (s, 6H, cubane), 3.91 (t, 4H, OCH_2), 1.80 (m, 4H, OCH_2CH_2), 1.04 (t, 6H, CH_3). ^{13}C NMR (δ, 20°C, $CDCl_3$, 125 MHz): 170.4 (2C, COO), 157.0 (2C, Ph^4), 143.9 (2C, Ph^1), 122.3 (4C, $Ph^{2,6}$), 115.2 (4C,

Table 1. Transition temperature (°C) and associated enthalpies (kJ mol^{-1}) for the cubane-based materials. Also listed are the molecule dimensions (Å).

Compound	Substituent	Cr_1	T, [ΔH]	SmX	T, [ΔH]	SmA	T, [ΔH]	N	T, [ΔH]	I	Length	Width	Length/ width
See [8]	**CH_3O**	•	175.1	—	—	—	—	•	179.7	•	21	2.7	7.8
Ia	**C_3H_7O**	•	180.7 [56.83]	—	—	—	—	(•)	(140.5)[b]	•	26	2.7	9.6
See [8]	**C_4H_7O**	•	150.0	—	—	—	—	(•)	(133.0)[c]	•	29	2.7	10.7
Ib	**$C_5H_{11}O$**		124.7 [7.85]	•	138.9 [34.56]	—	—	—	—	•	31	2.7	11.4
Ic	**$C_6H_{13}O$**	•	126.3 [12.52]	•	133.5 [34.31]	(•)	(123.0) [5.08]	—	—	•	34	2.7	12.6
Id	**$C_7H_{15}O$**	•	72.1 [3.91]	•	121.6 [10.82]	•	135.8 [41.24]	—	—	•	36	2.7	13.3
Ie	**$C_8H_{17}O$**	•	120.3 [11.59]	•	130.9 [39.65]	•	134.8[b]	—	—	•	39	2.7	14.4
IIa	**C_8H_{17}**	•	105.5 [35.72]	—	—	—	—	—	—	•	36	2.7	13.3
IIb	**C_9H_{19}**	•	108.9[b]	•	127.8 [38.38]	—	—	—	—	•	39	2.7	14.4
IIIa	**(S)-2MeBuOOC**	•	130.4 [42.83]	—	—	—	—	—	—	•	31	2.7	11.5
IIIb	**Cholestenyl**	•	245[cd]	—	—	—	—	—	—	•	45	4.1	11.0
IVa	**Octyl**	•	68.08 [68.67]	—	—	—	—	—	—	•	45	43	1.0
IVb	**Decyl**	•	70.15 [135.46]	—	—	—	—	—	—	•	52	45	1.2
IVc	**Hexadecyl**	•	92.84 [159.05]	—	—	—	—	—	—	•	70	57	1.2
V	**C_2H_5COO phenyl**	•	219.6 [15.89]	—	—	—	234.3[d] [31.64]	•	—	•	34	2.7	12.6

[a]( ) Denotes monotropic transitions.
[b]Enthalpy could not be resolved.
[c]POM observation.
[d]Decomposition.

$Ph^{3,5}$), 70.0 (2C, OCH_2), 56.0 (2C, cubane), 47.5 (6C, cubane), 22.7 (2C, CH_2), 10.7 (2C, CH_3).

2.1.5. Bis[4′-(octylphenyl)]cubane-1,4-dicarboxylate (IIa). Compound **11** (1.15 g, 5.0 mmol) in dichloromethane (15 ml) was reacted with 4-*n*-octylphenol (2.06 g, 10.0 mmol) dissolved in dichloromethane (45 ml) in the presence of triethylamine (1.5 ml). The crude product was recrystallized from hexane; yield 1.42 g, (49.92 %), $C_{38}H_{40}O_4$=568.8 IR: 2955 (m), 2920 (s), 2850 (s), 1740 (s), 1594 (w), 1504 (m), 1465 (m), 1316 (m), 1265 (m), 1214 (s), 1189 (s), 1162 (m), 1111 (w), 1058 (s), 1015 (m), 909 (s), 866 (m), 736 (s), 650 (m). ^{1}H NMR (δ, 20°C, $CDCl_3$, 500 MHz): 7.18 (m, 4H, $Ph^{3,5}$), 7.01 (m, 4H, $Ph^{2,6}$), 4.45 (s, 6H, cubane), 2.60 (t, 4H, $PhCH_2$), 1.61 (m, 4H, $PhCH_2CH_2$), 1.33–1.24 (m, 20H, CH_2), 0.88 (t, 6H, CH_3). ^{13}C NMR (δ, 20°C, $CDCl_3$, 125 MHz): 170.1 (2C, COO), 148.5 (2C, Ph^1), 140.7 (2C, Ph^4), 129.4 (4C, $Ph^{3,5}$), 121.2 (2C, $Ph^{2,6}$), 56.0 (2C, cubane), 47.5 (6C, cubane), 35.5, 32.0, 31.6, 29.6, 29.44, 29.40, 22.8 (7C, CH_2), 14.3 (2C, CH_3).

2.1.6. (S)-Bis{4′-[(2-methylbutyl)oxycarbonyl]phenyl} cubane-1,4-dicarboxylate (IIIa). Compound **11** (0.46 g, 2.0 mmol) in dichloromethane (10 ml) was reacted with (*S*)-4-(2-methylbutyloxycarbonyl)phenol (0.846 g, 4.0 mmol) dissolved in dichloromethane (25 ml) in the presence of triethylamine (1.0 ml). The crude product was recrystallized from hexane and ethyl acetate; yield 0.53 g, (46.28%), $C_{34}H_{35}O_9$=572.66. IR: 3006 (w), 2963 (m), 1741 (s), 1710 (s), 1602 (m), 1503 (w), 1463 (m), 1410 (w), 1329 (m), 1306 (w), 1275 (s), 1204 (m), 1192 (m), 1158 (m), 1108 (m), 1095 (m), 1050 (m), 1023 (w), 1013 (w), 877 (m), 756 (m), 691 (w). ^{1}H NMR (δ, 20°C, $CDCl_3$, 500 MHz): 8.10 (m, 4H, $Ph^{2,6}$), 7.21 (m, 4H, $Ph^{3,5}$), 4.50 (s, 6H, cubane), 4.21 (m, 2H, OCH_2), 4.13 (m, 2H, OCH_2), 1.85 (m, 2H, OCH_2CH), 1.53 (m, 2H, $CHCH_2$), 1.28 (m, 2H, $CHCH_2$), 1.01 (d, 6H, $CHCH_3$), 0.96 (t, 6H, CH_2CH_3). ^{13}C NMR (δ, 20°C, $CDCl_3$, 125 MHz): 169.2 (2C, cubane–COO), 166.0 (2C, C^1COO), 157.4 (2C, Ph^4), 131.3 (4C, $Ph^{2,6}$), 128.3 (2C, Ph^1), 121.7 (4C, $Ph^{3,5}$), 69.8 (2C, OCH_2), 55.9 (2C, cubane), 47.6 (6C, cubane), 34.4 (2C OCH_2CH), 26.3 (2C, CH_2CH_3), 16.7 (2C, $CHCH_3$), 11.4 (2C, CH_2CH_3).

2.1.7. Bis(cholestenyl)cubane-1,4-dicarboxylate (IIIb). Compound **11** (0.80 g, 3.5 mmol) in dichloromethane (17 ml) was reacted with 4-*n*-octyloxyphenol (2.707 g, 7.0 mmol) dissolved in dichloromethane (25 ml) in the presence of triethylamine (1.3 ml). The crude product was recrystallized from chloroform/acetone mixture; yield 0.55 g, (16.91%), $C_{64}H_{96}O_4$=929,48. IR: 2934 (s), 2867 (m), 2849 (m), 1717 (s), 1466 (m), 1371 (m), 1356 (m), 1326 (s), 1217 (s), 1199 (m), 1083 (s), 994 (m), 924 (m), 839 (w), 734 (m), 666 (m). ^{1}H NMR (δ, 20°C, $CDCl_3$, 500 MHz): 5.37 (m, 2H, H^6), 4.64 (m, 2H, H^3), 4.19 (s, 6H, cubane), 2.32 (m, 4H, H^4), 2.04–1.94 (m, 4H, H^7), 1.88–0.92(m, 30H), 0.92 (d, 6H, H^{21}), 0.87–0.85 (m, 12H, H^{26}, H^{27}), 0.67 (s, 6H, H^{19}). ^{13}C NMR (δ, 20°C, $CDCl_3$, 125 MHz): 171.4 (2C, COO), 139.8 (2C, C^5), 122.8 (2C, C^6), 74.0 (2C, C^3), 56.8, 56.2, 56.1, 50.1, 47.1 (6C, cubane), 42.4, 39.9, 39.6, 38.3, 37.2, 36.7, 36.3, 36.0, 32.1, 32.0, 28.4, 28.2, 27.9, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0 (see figure 1)

2.1.8. General procedure for the preparation of bis[4-(2,2-alkoxycarbonylvinyl)phenyl)]cubane-1,4-dicarboxylate (IVa–IVc). Cubane-1,4-dicarboxylic dichloride (**11**) (1 mmol) and 4-(hydroxy)dialkylbenzal malonate (2 mmol) were dissolved in 2-butanone in the presence of triethylamine (3 ml) and stirred for 48 h at room temperature. After adding 20 ml of water, the phases were separated; the organic layer was washed with 3 × 20 ml of water, dried over magnesium sulphate and evaporated. The crude product was purified either by column or by flash chromatography on a Kieselgel column eluted with a solvent or solvent system varied for individual compounds. The appropriate fractions were evaporated and recrystallized from hexane.

2.1.8.1. *Bis[4 -(2,2-octyloxycarbonylvinyl)phenyl)] cubane-1,4 -dicarboxylate (***IVa***).* Quantities: compound (**11**) (0.27 g, 1.2 mmol), 4-(hydroxy)dioctylbenzal malonate (1.03 g, 2.38 mmol), triethylamine (0.3 ml), in 2-butanone (20 ml). Purification on Kieselgel 60 column

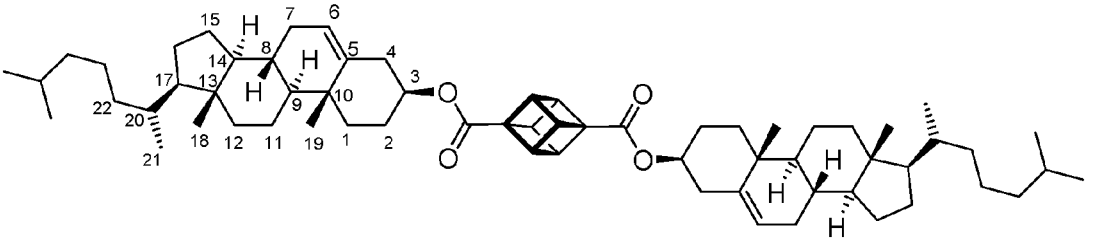

Figure 1. NMR assignments of **IIIb**.

(0.063–0.2 mm) eluted with a mixture of ethyl acetate/*n*-hexane: 2/3; yield 0.723 (54%), $C_{62}H_{84}O_{12}$=1021.35. IR (films on NaCl from $CDCl_3$ solution): 2955 (m), 2926 (s), 2855 (m), 1729 (s), 1631 (w), 1602 (w), 1507 (m), 1467 (w), 1394 (w), 1314 (m), 1260 (s), 1192 (s), 1167 (s), 1110 (w), 1056 (m), 940 (w), 842 (w), 721 (w). ^{1}H NMR (δ, 20°C, $CDCl_3$, 500 MHz): 7.70 (s, 2H, =CH), 7.49 (d, $^3J_{HH}$=8.8 Hz, 4H, $Ph^{3,5}$), 7.15 (d, $^3J_{HH}$=8.8 Hz, 4H, $Ph^{2,6}$), 4.47 (s, 6H, cubane), 4.24 (vq, 8H, OCH_2), 1.67 (m, 8H, OCH_2CH_2), 1.4–1.2 (m, 40H, CH_2), 0.87 (m, 12H, CH_3). ^{13}C NMR (δ, 20°C, $CDCl_3$, 125 MHz): 169.3 (2C, cubane–*C*OO), 166.9, 164.2 (4C, =C*C*OOCH$_2$), 152.2 (2C, Ph^1), 141.0 (2C, =*C*H), 130.9 (4C, $Ph^{3,5}$), 130.8 (2C, Ph^4), 126.6 (2C, =*C*COOCH$_2$), 122.1 (4C, $Ph^{2,6}$), 66.2, 66.0 (4C, O*C*H$_2$), 55.9 (2C, cubane), 47.5 (6C, cubane), 31.9 (4C, *C*H$_2$CH$_3$), 29.33, 29.03, 28.6, 28.5, 26.0, 22.79, 22.77 (20C, *C*H$_2$), 14.2 (4C, CH*C*H$_3$).

2.1.9. Bis[(4′-ethoxycarbonyl)-1,1′-biphenyl-4-yl]cubane-1,4-dicaboxylate (V). Compound **11** (0.60 g, 2.65 mmol) in dichloromethane (12.5 ml) was reacted with ethyl 4-hydroxybiphenylcarboxylate (1.27 g, 5.25 mmol) in dichloromethane (35 ml) in the presence of triethylamine (1 ml). Crystallization was from chloroform/diethyl ether mixture; yield 1.39 g (83.11%), $C_{40}H_{32}O_8$=640.70. IR: 2991 (m), 2919 (w), 2848 (w), 1736 (s), 1712 (m), 1606 (w), 1491 (w), 1396 (w), 1368 (w), 1276 (m), 1213 (m), 1202 (m), 1186 (m), 1099 (m), 1066 (m), 1005 (w), 846 (m), 769 (m), 761 (m). ^{1}H NMR (*δ*, 20°C, $CDCl_3$, 500 MHz): 8.11 (m, 4H, $Ph^{3',5'}$), 7.65–7.63 (m, 8H, $Ph^{2',6'}$, $Ph^{2,6}$), 7.24 (m, 4H, $Ph^{3,5}$), 4.52 (s, 6H, cubane), 4.00 (q, 4H, OCH_2), 1.42 (t, 6H, CH_3). ^{13}C NMR (*δ*, 20°C, $CDCl_3$, 125 MHz): 169.8 (2C, cubaneCOO), 166.6 (2C, $COOCH_2$), 150.7 (2C, Ph^4), 144.7 (2C, Ph^1), 137.9 (2C, $Ph^{1'}$), 130.3 (4C, $Ph^{3',5'}$), 129.5 (2C, $Ph^{4'}$), 128.5 (4C, $Ph^{2,6}$), 127.1 (4C, $Ph^{2',6'}$), 122.2 (4C, $Ph^{3,5}$), 61.2 (2C, OCH_2), 56.0 (2C, cubane), 47.6 (6C, cubane), 14.5 (2C, CH_3).

3. Results

3.1. *Synthesis*

The documented synthetic procedure [1, 2, 17–19] for the preparation of 1,4-cubanedicarboxylic acid was scaled up and improved giving higher yields and allowing for a more straightforward purification of the intermediates. In this route (figure 2) first the cyclopentanon ethylene ketal (**3**) was prepared and brominated in 1,4-dioxane with its bromo complex. The obtained tribromo derivative (**4**) was then hydrolysed in alkaline conditions yielding **5**. This compound dimerized in a Diels–Alder reaction, and the endo-2,4-dibromodicyclopentadiene-1,8-dion-8-ethylene ketal (**6**) was isolated. After removal of one protecting group in acidic conditions, the obtained **7** was transformed in a [2+2] photocyclization reaction giving 5,9-dibromopentecyclo-[5,3,0,$0^{2,5}$,$0^{3,9}$,$0^{4,8}$]-deka-6,10-dion (**8**). The removal of the second ketal group [20] and a double Favorskii rearrangement [21] led to the key intermediate, the cubane 1,4-dicarbolyxic acid (**10**). The synthetic route is shown in figure 2.

In some steps the recrystallization of the intermediates (compounds **4, 6** and **7**) was unecessary as they were obtained in high purity. The cubane ester derivatives **Ia-V** were prepared in the usual manner using the appropriate acid chloride. The new compounds are in figure 3.

3.2. *Mesophase behaviour*

The thermal behaviour of these new ester derivatives of cubane-1,4-dicarboxylic acid was investigated by POM and DSC and is summarized in the table. Among the alkoxyphenyl ester (**Ia–Ie**) homologues, a stronger tendency towards mesophase formation was observed, than with the alkylphenyl (**IIa, IIb**) esters. For the shorter homologues a nematic phase appeared. Only the methoxyphenyl derivative has an enantiotropic nematic phase according to the literature [8, 9]. On increasing the alkyloxy chain length, the nematic phase formation ability was slowly depressed, becoming monotropic for the propyloxyphenyl (**Ia**) and butyloxyphenyl esters [8, 9]. This mesophase completely disappeared at the pentyloxyphenyl ester (**Ib**). By neither DSC nor POM measurement was a mesophase observed. It is very unusual, that in a homologous series mesophase formation is extinguished at a member in the middle of the series. On further increase in the length of the chains, a monotropic smectic A phase appeared at the hexyloxy (**Ic**) analogue; this phase became enantiotropic at the heptyloxyphenyl (**Id**), and octyloxyphenyl (**Ie**) derivatives. For those compounds (**Ic–Ie**) exhibiting a smectic A phase at higher temperatures, a more ordered phase is also observed at lower temperature, and these are currently under investigation by XRD. The alkyl-substituted phenolesters bis[4′-(*n*-octyl)phenyl]cubane-1,4-dicarboxylate (**IIa**) and the 4′-(*n*-nonyl)phenyl analogue **IIb** did not show liquid crystallinity. However, the length to width ratio of **IIa** and **IIb** is similar to that of **Id** and **Ie**, i.e. even with similar long chains, the former did not show liquid crystallinity. Most likely the bond angle connecting the alkoxy and alkyl tails to the aromatic ring is more favorable in the case of the alkoxy compound. The chiral derivatives

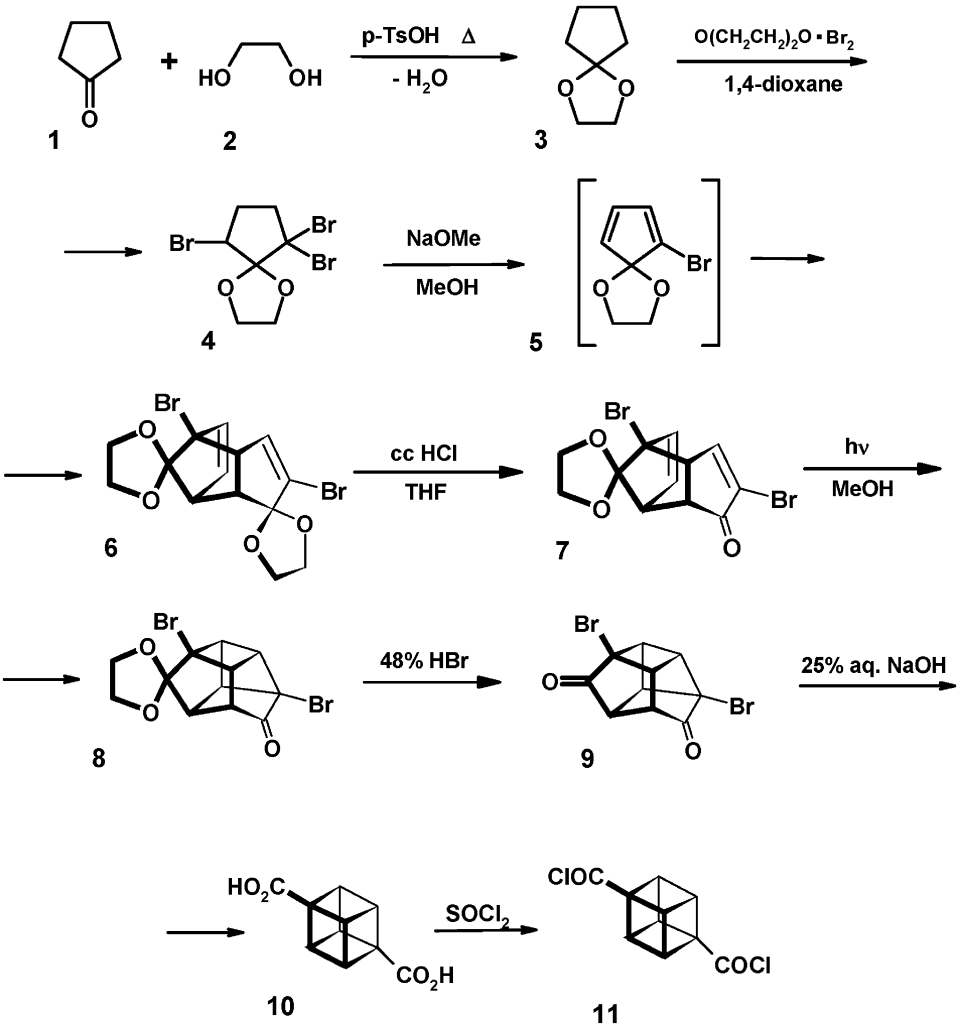

Figure 2. Synthetic pathway for the preparation of cubane 1,4-dicarboxylates.

IIIa and **IIIb** do not form a mesophase. We suspect, that in the case of **IIIa** the branched (*S*)-2-methylbutyl substituents are too short, resulting in a disadvantageous change of the length to breadth ratio. In the case of **IIIb** the cholesterol substituents are too bulky, which hinders the stacking of the molecules. Increasing the length of terminal chains in the swallow-tailed compounds **IVa–IVc** did not promote liquid crystalline behaviour. On increasing the number of the aromatic rings, the tendency to exhibit mesophase formation is again increased as is seen in compound **V** (see table 1).

3.3. *Binary mixtures of cubane derivatives*

These cubane derivatives are new and have a unique architecture, they exhibit a rich polymorphism in the crystalline phase, but only a few of them are actually liquid crystalline. According to previous investigations on calamitic compounds, the latent mesomorphic properties may be revealed in mixtures [22–25]. Thus we have investigated their mesophase formation ability in binary mixtures.

Two series of mixtures were prepared, mixing two members of the same homologous series of the bis(alkoxyphenyl)-cubane-1,4-dicarboxylates. In the first series compound **Ia** exhibiting a monotropic nematic phase was mixed with **Ie** showing an enantiotropic smectic A phase. Preliminary experiments were carried out on a contact preparation using the Koffler method. On heating, both the melting and clearing temperatures were lower in the mixtures than in the individual compounds. Figure 4 shows the texture of the preparation at 134°C on cooling. The growth of the SmA phase of **Ie** (K68) is seen at the right hand side.

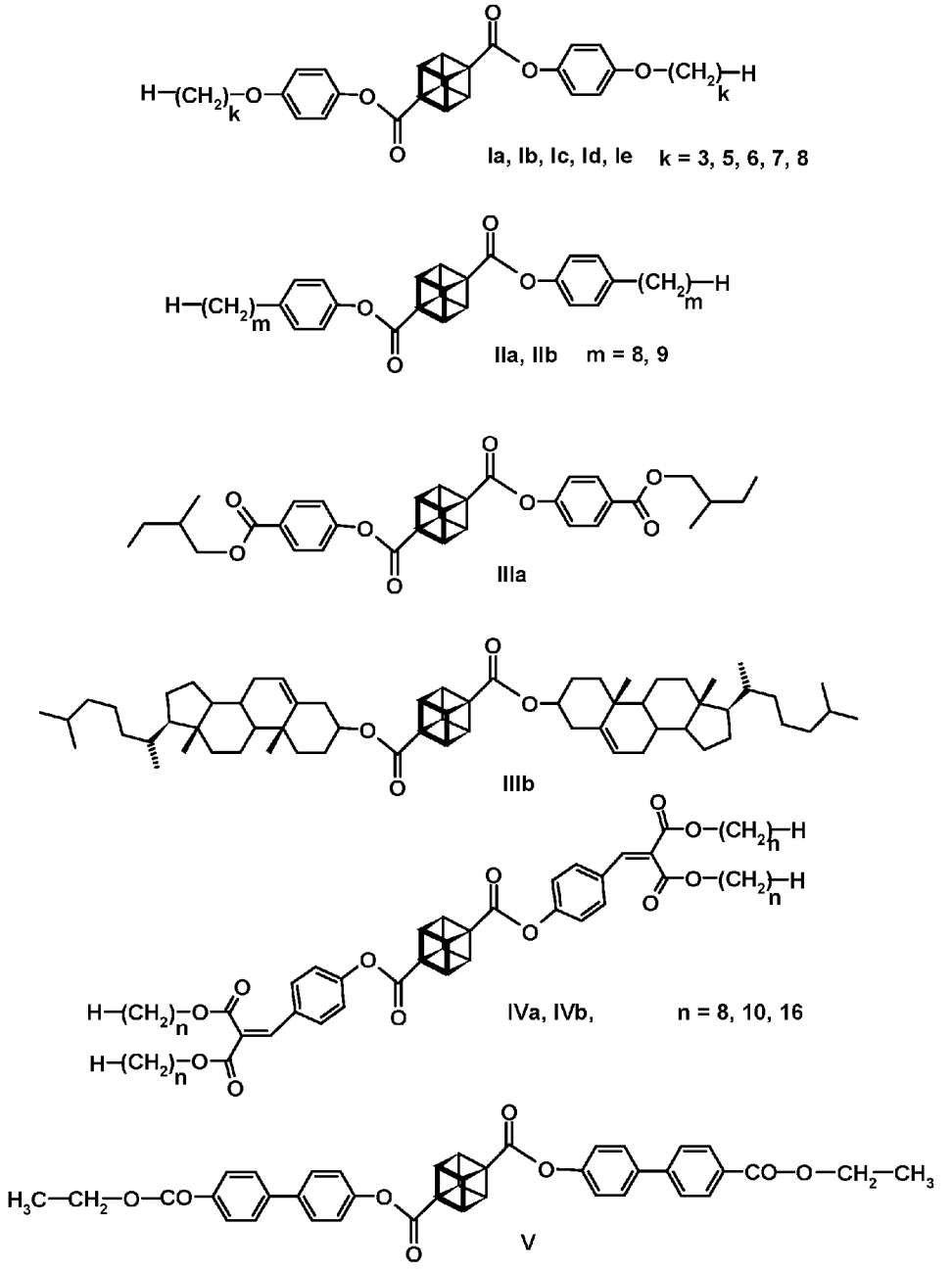

Figure 3. New cubane-1,4-dicarboxylate derivatives.

The thin black region in the middle of the preparation is the isotropic phase, while on the left hand side **Ia** (K65) is already in one of its crystalline modifications.

On the basis of these results, mixtures of known compositions were prepared. On heating, no mesophase could be observed at low concentrations of **Ie**, while a SmA phase was the only mesophase observed at concentrations of **Ie** at and above 50%, figure 5 (*a*). The mixture containing a 1:1 ratio of the components exhibited the lowest melting point of all the mixtures. On cooling, at low concentrations of **Ie** a monotropic nematic phase appeared. The presence of **Ie** at 20 wt % was already sufficient to give rise to the appearance of the SmA phase, figure 5 (*b*). The widest temperature range of the SmA phase was observed at the ratio of 1:1 of the individual compounds.

The other series of binary mixtures contained the hexyloxyphenyl (**Ic**) and octyloxyphenyl (**Ie**) derivatives exhibiting monotropic and enantiotropic SmA phases, respectively. Adding **Ie** to **Ic** in increasing

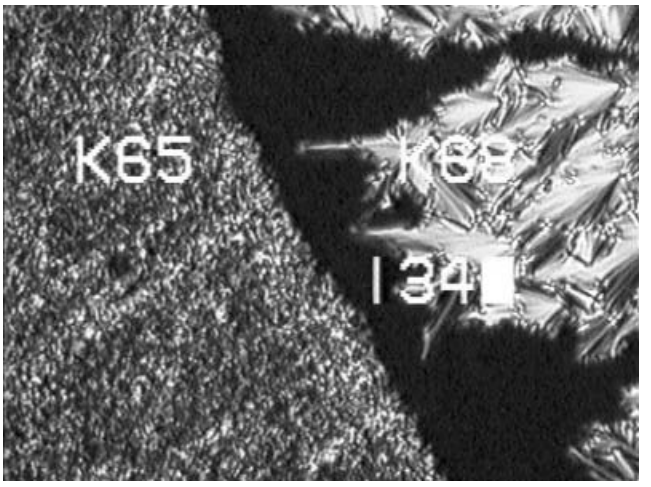

Figure 4. Contact preparation of **Ia** (K65) and **Ie** (K68) on cooling at 134°C.

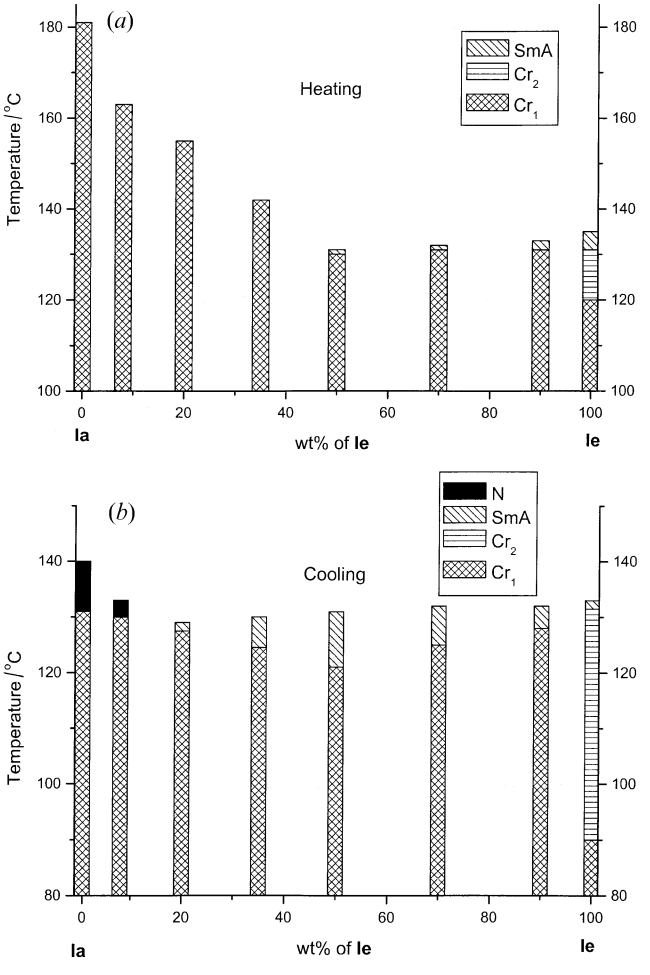

Figure 5. Transition temperatures of binary systems composed of **Ia** and **Ie:** (*a*) heating, (*b*) cooling.

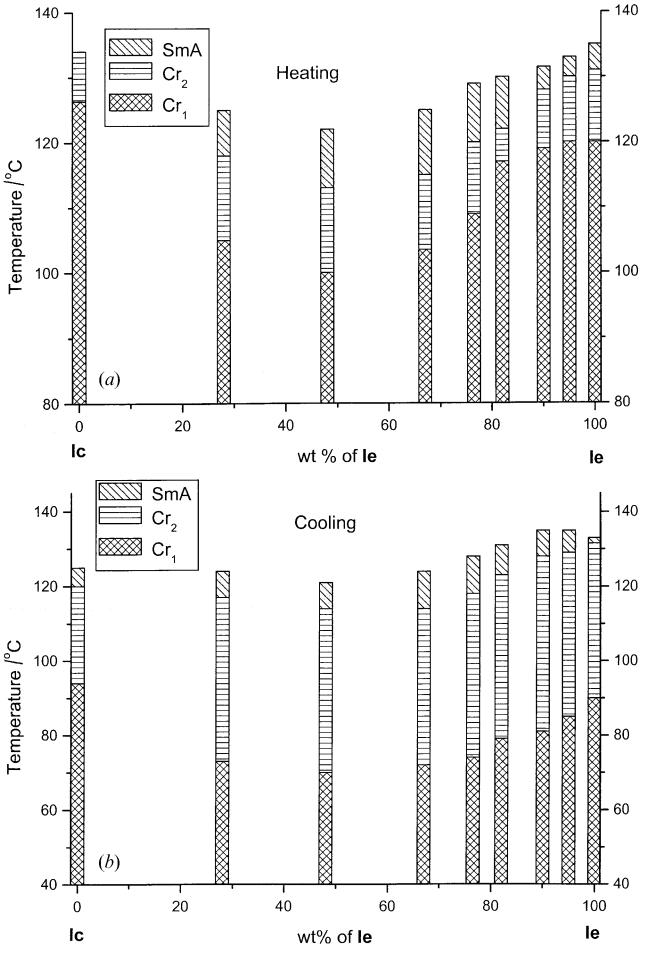

Figure 6. Transition temperatures of binary system composed of **Ic** and **Ie:** (*a*) heating, (*b*) cooling.

concentrations (28–82 wt %), the SmA phase became enantiotropic and the temperature range broadened compared with that of the individual compounds, figure 6 (*a*).

A melting point depression was observed in all the mixtures investigated. In the contact preparation of **Ic** (K62) and **Ie** (K68), figure 7 (*a*), the mixtures around the 1:1 ratio of the components also showed lower clearing temperatures. On both sides of the photomicrograph the crystalline phases of **Ic** (K62) and **Ie** (K68) are seen. The contact method helped in the detection of a 2°C induction effect on the isotropic–SmA phase transition on cooling, in mixtures containing 90–95 wt % of **Ie**, figures 6 (*b*) and 7 (*b*). It is worth noting that not only the melting points but the temperatures of the crystalline modification (Cr_2) have broadened and become much more supercoolable in these mixtures compared with the individual components, figure 6 (*b*).

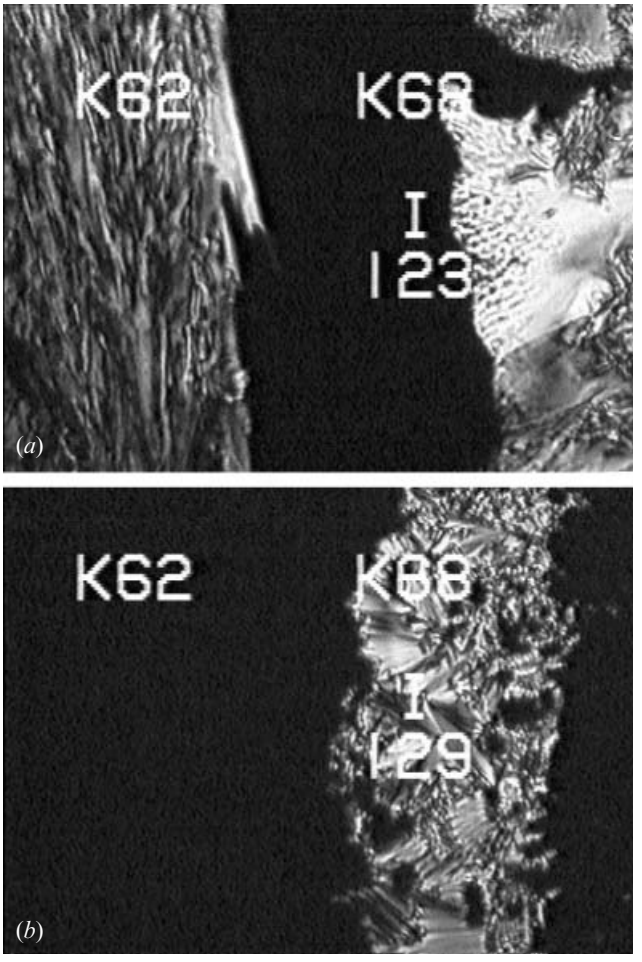

Figure 7. Contact preparation of **Ic** (K62) and **Ie** (K68): (*a*) heating, (*b*) cooling.

4. Conclusions

The preparation of cubane-1,4-dicarboxylic acid has been modified and scaled up, improving the yield and purity of the intermediates. Five main groups of cubane-1,4-dicarboxylates were prepared. Higher members of the homologous series of 4-alkoxyphenyl-cubane-1,4-dicarboxylates exhibited nematic and smectic A phases. The melting points and the mesophase temperatures were shifted to lower temperatures with increasing chain length as commonly observed, but the mesophase formation was extinguished at compound **Ib**. The 4-alkylphenyl esters showed no liquid crystallinity. The delocalization of the π electrons in this series is shorter than that in the alkoxy derivatives, and probably this accounts for the absence of liquid crystallinity. The chiral derivatives showed no liquid crystal mesophases, most probably due to their unfavorable length to breadth ratio. Increasing the number of aromatic rings on both arms connected to the cubane moiety promotes polymorphism. In binary mixtures of cubane derivatives (**1c**–**1e** and **Ia**–**Ie**) an enhanced SmA mesophase formation was observed.

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