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3,4-Dialkoxybenzoyl substituted derivatives of hexahydro-1,3,5-triazine with hexagonal columnar mesophases

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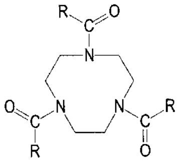
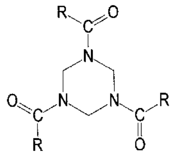
The synthesis of a homologous series of amidic derivatives of azacyclic compounds, i.e. 3,4-dialkoxybenzoyl ('two chain') N,N',N''-substituted hexahydro-1,3,5-triazines with alkoxy chains $-OC_nH_{2n+1}$ having $n=5$, 6, 8–14 and 16 carbon atoms, and of one corresponding amine derivative, i.e. 1,3,5-tris(3,4-didecyloxybenzyl)hexahydro-1,3,5-triazine, is described. The thermal behaviour of the compounds is characterized by means of polarizing microscopy and differential scanning calorimetry. The amide with $n=6$ is a monotropic liquid crystalline material, whereas the amides with $n=8$–14 and 16 exhibit enantiotropic mesomorphism. The amine derivative with $n=10$ is not a thermotropic liquid crystalline compound. The optical textures of the mesogenic compounds are spherulitic. X-ray diffraction measurements for the amides with $n=8$, 10, 12, 13 and 16 show evidence of a hexagonal columnar structure (Col_h) in the mesophase. The lattice constants of the mesophase are compared with the values from CPK models.

1. Introduction

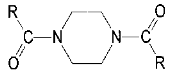
Several acylated macrocyclic polyamine derivatives of [18]aneN$_6$ (1,4,7,10,13,16-hexa-azacyclo-octadecane, hexacyclen) and larger ring homologues have been reported by Lehn and coworkers to form columnar mesophases [1, 2]. The amines have been substituted by 4-dodecyloxybenzoyl or 4-octyloxybenzoyl groups. Other publications describe further liquid crystalline benzoyl and cinnamoyl substituted derivatives of [18]aneN$_6$ [3–8]. So, 4-alkoxybenzoyl and 4-alkoxycinnamoyl groups were able to induce mesomorphism with [18]aneN$_6$, but not with the smaller azacycle [14]aneN$_4$ (1,4,8,11-tetra-azacyclotetradecane, cyclam) [3]. With both [18]aneN$_6$ and [14]aneN$_4$, further use of 3,4,5-trialkoxybenzoyl and 3,5-dialkoxybenzoyl substituents also did not lead to mesomorphism. However, a liquid crystalline derivative of [14]aneN$_4$ exists with the 3,4-didecyloxybenzoyl ('two chain') group [9]. Apparently not only the number of alkoxy chains, but also the substitution position at the benzene ring of the substituent, i.e. the effective space filling of the molecular outer sphere, is very important for the formation of the mesophase. With 'two chain' substituents, mesomorphism was likewise induced successfully in [18]aneN$_6$ [5], [12]aneN$_4$ (1,4,7,10-tetra-azacyclododecane, cyclen) [10] and the triazacycles [12]aneN$_3$ (1,5,9-triazacyclododecane) and [9]aneN$_3$ (1,4,7-triazacyclononane) **1a**–**1e** [5, 11]. The enantiotropic liquid crystalline behaviour of the [9]aneN$_3$ derivatives with alkoxy chains having $n=5$, 6, 8, 10 and 12 carbon atoms is summarized in table 1.



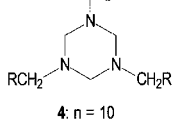
1a: n = 5
1b: n = 6
1c: n = 8
1d: n = 10
1e: n = 12



2a: n = 5	**2f**: n = 11
2b: n = 6	**2g**: n = 12
2c: n = 8	**2h**: n = 13
2d: n = 9	**2i**: n = 14
2e: n = 10	**2k**: n = 16



3: n = 10



4: n = 10

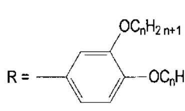


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Table 1. Transition temperatures (°C) and, in brackets, transition enthalpies (kJ mol^{-1}), glass transition temperatures T_g/°C and isobaric heat capacities ΔC_p/kJ K^{-1} mol^{-1} of freeze-dried **1a**–**1e**; heating rate 10°C min^{-1} [5, 11]. Cr crystalline phase, M mesophases, I isotropic phase.

Compound	*n*	$T_g/\Delta C_p$	Cr		M_1		M_2		I
1a	5	31/0·58	—		—		•	54·0 (3·54)	•
1b	6	28/0·38	•	74·0[a]	—		•	55·5 (2·87)	•
1c	8	26/0·32	—		—		•	57·0 (1·92)	•
1d	10	32/—	•	42·5[a] (17·66)	•	43·5 (1·55)	•	66·0 (2·55)	•
1e	12	38/—	•	52·0[a] (66·04)	•	48·5	•	75·5 (4·08)	•

[a] Only on first heating.

We wanted to know how the mesomorphism is influenced by a smaller cyclic core, but with the same number (three) of nitrogen atoms, i.e. the six membered hexahydro-1,3,5-triazine. On the other hand, 3,4-didecyloxybenzoyl substituted piperazine **3**, with only two nitrogen atoms in the six membered ring, exhibits only monotropic mesomorphism (clearing temperature 32·5°C, melting temperature 102·0°C) [11, 12]. Here we report the synthesis, the thermotropic liquid crystalline behaviour and the structure of the mesophase of a series of 'two chain' substituted hexahydro-1,3,5-triazines **2a**–**2k** with $n = 5$, 6, 8–14 and 16 carbon atoms in the alkoxy chains. In order to check the importance of the rigid benzamide group with respect to mesophase formation, we reduced the amide **2e** to the corresponding amine **4**.

2. Experimental

2.1. *Methods of characterization*

Infrared spectra were recorded with a Digilab FTS-40 FTIR spectrometer using pellets of sample (1 mg) dispersed in potassium bromide (500 mg). NMR spectra were recorded from solutions in deuteriochloroform on a Bruker AC-250 spectrometer. EI mass spectrometry (MS) was performed with a Finnigan MAT-8500 spectrometer with an ionization energy of 70 eV. Elemental analysis was carried out by Mikroanalytisches Labor Ilse Beetz, Kronach, Germany. Size exclusion chromatography (SEC) was performed using two polystyrene gel columns (600 × 8 mm, 5 μm particle size) of 100 and 500 Å pore size (Polymer Laboratories, PL gel columns) with tetrahydrofuran as eluent at 0·5 ml min^{-1}. The chromatograms were monitored with a Waters 440 absorbance detector at 245 nm and, at 30°C, with a Waters 410 differential refractometer. Thermal transitions were investigated with a Leitz Labolux 12-Pol polarizing microscope equipped with a Mettler FP 82 hot stage and FP 80 processing unit. Transition temperatures and enthalpies were recorded with a Perkin Elmer DSC 7 differential scanning calorimeter (heating rate 10 K min^{-1}). X-ray diffraction measurements for the mesophases were carried out with a Huber Guinier camera and Huber Guinier goniometer system with a copper anode (CuK_α radiation, $\lambda = 0{\cdot}154$ nm). The samples were prepared on a copper grid; lead nitrate was used for calibration.

2.2. *Materials*

Argon was dried and purified first over molecular sieves (3 Å) and then with potassium dispersed on aluminium oxide. Hexamethylenetetramine (HMTA), 4-*N*,*N*-dimethylaminopyridine (DMAP), powdered lithium aluminium hydride (95%) and absolute sulphuric acid (100%) were purchased from Aldrich. HMTA and DMAP were dried and purified by vacuum sublimation (10^{-3} mbar) and kept under an inert gas atmosphere. 1,4-Dioxan and tetrahydrofuran (THF) were distilled over potassium. Acetone was distilled over calcium chloride and stored over molecular sieves (3 Å). Preparative adsorption chromatography was carried out on silica gel, mesh 60 (Merck).

The 3,4-dialkoxybenzoyl chlorides were prepared according to the literature [13]. All acid chlorides were recrystallized from acetone, freeze-dried from benzene solution and kept under an inert gas atmosphere.

2.3. *Synthesis of the amides* **2a–2k**

The syntheses were carried out under anhydrous conditions and in an argon atmosphere. 6·36 mmol of 3,4-dialkoxybenzoyl chloride were dissolved in 50 ml of 1,4-dioxan at 60°C. An equimolar amount (6·36 mmol) of DMAP was added to the solution in one portion. After the formation of a white precipitate, 1·59 mmol of HMTA were added in one portion at 90°C; the mixture was stirred for 20 h at 100°C. The resulting white precipitate of DMAP hydrochloride was filtered off at room temperature. The filtrate was evaporated, the residue dissolved in 100 ml of diethyl ether, and the solution washed with a half saturated solution of sodium chloride in water, dried over sodium sulphate and evaporated. The residue (except in the case of **2a**) was recrystallized three times from THF/methanol/water, then further purified by adsorption chromatography on silica gel with hexane/ethyl acetate as eluent and finally freeze-dried from benzene solution (see table 2 for solvent

Table 2. Solvent mixtures for recrystallization, eluents for adsorption chromatography on silica gel, SEC elution volumes V_e and yields.

Compound	Recrystallization THF/methanol/water	Adsorption chromatography hexane/ethyl acetate	SEC V_e/ml	Yield/%
2a	—	2:1	25·9	74
2b	2:5:2	1:1	25·8	82
2c	1:10:0	2:1	25·3	79
2d	1:8:0	2:1	25·4	77
2e	1:5:0	2:1	25·4	75
2f	3:10:10	2:1	25·0	71
2g	3:10:0	2:1	23·9	69
2h	1:2:0	2:1	24·2	78
2i	1:2:0	2:1	24·3	85
2k	1:2:0	2:1	23·4	83

compositions). The purity of the white crystalline compounds was checked by SEC; elution volumes and yields are listed in table 2. The spectral data (IR, ^{1}H NMR, ^{13}C NMR and MS) confirm the structures.

2a: $C_{54}H_{81}N_3O_9$ (916·25). IR (KBr): ν (cm^{-1}) = 2957, 2935, 2872, 1662, 1600, 1583, 1516, 1468, 1430, 1394, 1267, 1231, 1142. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0·85 (t, 18 H, CH_3), 1·30–1·50 (m, 24 H, alkoxy), 1·70–1·85 (m, 12 H, OCH_2CH_2), 3·95 (t, 12 H, OCH_2), 5·35 (s, 6 H, NCH_2N), 6·75 (d, 3H, aromatic), 6·98 (d, 3H, aromatic), 7·05 (s, 3H, aromatic). ^{13}C NMR ($CDCl_3$): δ (ppm) = 13·8 (CH_3), 22·3, 28·1, 28·9 (alkoxy), 59·0 (br, NCH_2N), 69·2, 69·5 (OCH_2), 112·8, 114·1, 121·2, 125·7, 149·2, 151·9 (aromatic), 170·4 ($C{=}O$). MS (m/z) = 915 ($M^{\bullet +}$, 6%), 277 (100%).

2b: $C_{60}H_{93}N_3O_9$ (1000·41). IR (KBr) similar to **2a**. ^{1}H NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 1·30–1·50 (m, 36 H, alkoxy). ^{13}C NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 22·5, 25·6, 29·0, 29·1, 31·5 (alkoxy). MS (m/z) = 1000 $[M+H]^{\bullet +}$, 2%), 305 (100%).

2c: $C_{72}H_{117}N_3O_9$ (1168·74). IR (KBr) similar to **2a**. ^{1}H NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 1·30–1·50 (m, 60 H, alkoxy). ^{13}C NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 22·6, 25·9, 29·2, 29·3, 31·7 (alkoxy). MS (m/z) = 1167 ($M^{\bullet +}$, 42%), 768 (100%).

2d: $C_{78}H_{129}N_3O_9$ (1252·90). IR (KBr) similar to **2a**. ^{1}H NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 1·30–1·50 (m, 72 H, alkoxy). ^{13}C NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 22·6, 26·0, 29·2, 29·3, 29·4, 29·6, 31·9 (alkoxy). MS (m/z) = 1251 ($M^{\bullet +}$, 75%), 821 (100%).

2e: $C_{84}H_{141}N_3O_9$ (1337·06). IR (KBr) similar to **2a**. ^{1}H NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 1·30–1·50 (m, 84 H, alkoxy). ^{13}C NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 22·7, 26·0, 29·1, 29·2, 29·3, 29·4, 29·6, 29·7 (alkoxy). MS (m/z) = 1337 $[M+2H]^{\bullet +}$, 1%), 417 (100%). Elemental analysis: calculated C 75·53, H 10·63, N 3·14, O 10·70; found C 75·13, H 10·60, N 3·12, O 11·15%.

2f: $C_{90}H_{153}N_3O_9$ (1421·22). IR (KBr) similar to **2a**. ^{1}H NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 1·30–1·50 (m, 96 H, alkoxy). ^{13}C NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 22·7, 26·0, 29·1, 29·2, 29·3, 29·4, 29·5, 29·6, 31·9 (alkoxy). MS (m/z) = 1419 ($M^{\bullet +}$, 5%), 933 (100%).

2g: $C_{96}H_{165}N_3O_9$ (1505·38). IR (KBr) similar to **2a**. ^{1}H NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 1·30–1·50 (m, 108 H, alkoxy). ^{13}C NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 22·6, 25·9, 29·1, 29·2, 29·3, 29·4, 29·6, 30·5, 31·7 (alkoxy). MS (m/z) = 473 (100%).

2h: $C_{102}H_{177}N_3O_9$ (1589·54). IR (KBr) similar to **2a**. ^{1}H NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 1·30–1·50 (m, 120 H, alkoxy). ^{13}C NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 22·6, 25·9, 29·1, 29·2, 29·3, 29·4, 29·6, 29·8, 30·5, 31·7 (alkoxy). MS (m/z) = 989 (100%).

2i: $C_{108}H_{189}N_3O_9$ (1673·70). IR (KBr) similar to **2a**. ^{1}H NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 1·30–1·50 (m, 132 H, alkoxy). ^{13}C NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 22·7, 26·0, 29·2, 29·3, 29·4, 29·5, 29·8, 29·9, 31·9 (alkoxy). MS (m/z) = 1671 ($M^{\bullet +}$, 1%), 1100 (100%).

2k: $C_{120}H_{213}N_3O_9$ (1842·03). IR (KBr) similar to **2a**. ^{1}H NMR ($CDCl_3$) similar to **2a**, variations: δ (ppm) = 1·30–1·50 (m, 156 H, alkoxy). ^{13}C NMR ($CDCl_3$) similar to **2i**. MS (m/z) = 826 (100%).

2.4. *Reduction of the amide* **2e** *to the amine* **4**

The reaction was carried out under dry conditions and an argon atmosphere. A solution of aluminium hydride in THF was freshly prepared by a literature method [14, 15] by dropwise addition of 4·00 mmol of sulphuric acid (100%) to 8·0 mmol of lithium aluminium hydride dispersed in 30 ml of THF at 0°C. The suspension was stirred for 1 h at room temperature. The reduction of 2·00 mmol of the amide **2e** in 40 ml of THF to the amine **4** was performed according to the literature [16]. The product was recrystallized twice from acetone and subsequently freeze-dried from benzene solution (yield 74%). The purity of the white crystalline compound was checked by SEC (elution volume 24·6 ml) and elemental analysis. $C_{84}H_{147}N_3O_6$ (1295·11): calculated C 77·94, H 11·40, N 3·22, O 7·44; found C 78·01, H 11·29, N 3·20, O 7·50%. The spectral data (IR, ^{1}H NMR, ^{13}C NMR and MS) confirm the structure. IR (KBr): ν (cm^{-1}) = 2956, 2922, 2851, 1592, 1517, 1468, 1426, 1360, 1261, 1232, 1171, 1139, 898. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0·85 (t, 18 H, CH_3), 1·20–1·50 (m, 84 H, alkoxy), 1·70–1·85 (m, 12 H, OCH_2CH_2), 3·35 (br, 6 H, NCH_2N), 3·55 (s, 6 H, benzyl), 3·95 (t, 12 H, OCH_2), 6·75 (d, 6 H, aromatic), 6·85 (s, 3 H, aromatic). ^{13}C NMR ($CDCl_3$): δ (ppm) = 14·0 (CH_3), 22·6, 26·1, 29·3, 29·4, 29·5, 29·6, 29·7, 31·9 (alkoxy), 56·8 (benzyl), 69·2, 69·5 (OCH_2), 73·7 (NCH_2N), 113·5, 114·5, 121·2, 131·0, 148·2, 149·1 (aromatic). MS (m/z) = 403 (100%).

3. Results and discussion

3.1. *Synthesis of 'two chain' substituted hexahydro-1,3,5-triazines*

The acylation of hexahydro-1,3,5-triazine with a 3,4-dialkoxybenzoyl acid chloride by the same method as that used for [9]aneN_3 and larger azamacrocycles [3, 5] is not possible due to the instability of the cyclic aminal structure of hexahydro-1,3,5-triazine under the acidic reaction conditions. Attempts to form 'two chain' substituted hexahydro-1,3,5-triazines by the reaction of acid chlorides with formaldehyde and ammonia [17] or of nitriles with 1,3,5-trioxane [18, 19] failed in the case of substituents with alkoxy groups larger than methoxy. However, we were able to prepare successfully the compounds **2a**–**2k** by a heterogenous reaction of hexamethylenetetramine (HMTA) with four equivalents of 3,4-dialkoxybenzoyl chloride per HMTA in 1,4-dioxan in the presence of one equivalent *N*,*N*-dimethylaminopyridine (DMAP) per acid chloride at 100°C. We took into account reports on the cleavage of HMTA with acetic anhydride [20, 21]. Water causes byproducts in considerable amounts, formed by partial or total hydrolysis of HMTA and the subsequent acylation of the resulting amines. Consequently, we found the corresponding bis(3,4-dialkoxybenzoyl)diaminomethane as a byproduct. According to the literature, lower reaction temperatures favour the formation of the corresponding 3,7-bisacyl-1,3,5,7-tetra-azabicyclo[3.3.1]nonane [20, 21]. To optimize the yields of 1,3,5-tris(3,4-dialkoxybenzoyl)-hexahydro-1,3,5-triazines **2a**–**2k** (69–85% after purification, table 2), it is very important to carry out the reaction under thoroughly dry conditions at temperatures between 90 and 100°C with purified and dried educt materials. Thus, we used sublimed HMTA and DMAP, and acid chlorides freshly recrystallized from dry acetone and freeze dried from benzene solution.

The structures of the compounds **2a**–**2k** were confirmed by spectral data (IR, ^{1}H NMR, ^{13}C NMR and MS, see experimental part). The ^{1}H NMR spectra of all homologues exhibit one characteristic sharp singlet at 5·35 ppm corresponding to the methylene protons of the azacycle (NCH_2N).

3.2. *Thermal characterization*

The thermal behaviour of the freeze-dried amides **2a**–**2k** was determined by polarizing microscopy and DSC using a heating rate of 10 K min^{-1}. The results are summarized in table 3. The compounds **2b**–**2k** with hexyloxy or longer side chains show thermotropic mesomorphism. Compound **2b** ($n = 6$) is monotropic liquid crystalline, whereas **2c**–**2k** ($n = 8$–14 and 16) exhibit enantiotropic mesomorphism. All of the liquid crystalline

Table 3. Transition temperatures (°C) and, in brackets, transition enthalpies (kJ mol^{-1}), glass transition temperatures T_g/°C and isobaric heat capacities ΔC_p/kJ K^{-1} mol^{-1} of freeze-dried **2a**–**2k**; heating rate 10°C min^{-1}. Cr crystalline phases, Col_h hexagonal columnar mesophase, I isotropic phase, **[ ]** monotropic mesophase.

Compound	n	$T_g/\Delta C_p$	Cr_1		Cr_2		Col_h		I
2a	5	19/0·35	•	48·5 (3·77)[b]	•	70·0 (20·03)[a]	—		•
2b	6	—	•	57·0 (1·67)	•	73·0 (18·67)	•	[65·5] (4·92)	•
2c	8	—	•	34·5 (4·76)	•	75·5 (3·78)	•	84·5 (2·10)	•
2d	9	—	•	48·5 (23·44)	•	69·0 (10·28)	•	85·0 (3·77)	•
2e	10	—	•	50·5 (9·71)	•	61·5 (2·59)	•	88·0 (2·78)	•
2f	11	—[c]	•	45·5[a]	•	55·0[a]	•	86·0 (3·00)	•
2g	12	—	•	41·0[a]	•	57·0 (8·80)	•	88·0 (1·48)	•
2h	13	−4/0·55	—		•	53·0 (19·51)[a]	•	73·0 (0·86)	•
2i	14	—	•	31·0	•	45·0 (32·60)	•	86·5 (1·97)	•
2k	16	—	•	58·0	•	68·5	•	81·0 (4·81)	•

[a] Only on first heating.
[b] On heating after recrystallization.
[c] Not detectable by DSC.

compounds exhibit at least one thermodynamically stable crystalline phase, except **2f** and **2h** ($n=11$ and 13). Unlike the other compounds, **2f** and **2h** form mesophases which can be cooled below room temperature to an anisotropic glassy state without recrystallization.

With respect to the [9]aneN$_3$ compounds **1**, the analogous liquid crystalline hexahydro-1,3,5-triazine derivatives **2b**, **2c**, **2e** and **2f** with $n=6$, 8, 10 and 12 exhibit, after second and further heating, thermodynamically stable crystalline phases and only one mesophase with a higher clearing temperature. In contrast to the enantiotropic LC behaviour of **1a** and **1b**, that of **2b** is monotropic and **2a** exhibits only crystalline phases. We conclude that these systematic differences between the 'two chain' [9]aneN$_3$ and hexahydro-1,3,5-triazine derivatives are caused by the different sizes of the saturated azacyclic cores. The less flexible hexahydro-1,3,5-triazine core is assumed to enhance the stability and, hence, the transition temperatures of both the crystalline phase and the mesophase. On the other hand compound **3** with only two 3,4-didecyloxybenzoyl substituents is monotropic liquid crystalline [11, 12], whereas **2e** exhibits enantiotropic mesomorphism. With respect to almost the same size of their cyclic cores, the thermodynamic stability of the mesophase of **2e** is due to the additional rigid benzamide group at the core and the higher number of decyloxy side chains, which are believed to create a more effective space filling of the outer molecular sphere.

The textures of the liquid crystalline 'two chain' substituted hexahydro-1,3,5-triazines, observed by polarizing microscopy, are of the spherulitic or pseudo-focal-conic type, typical for columnar structures. Only the textures of **2h** and **2i** are small-sized and non-specific. As an example figure 1 shows the texture of **2f** at 80·0°C.

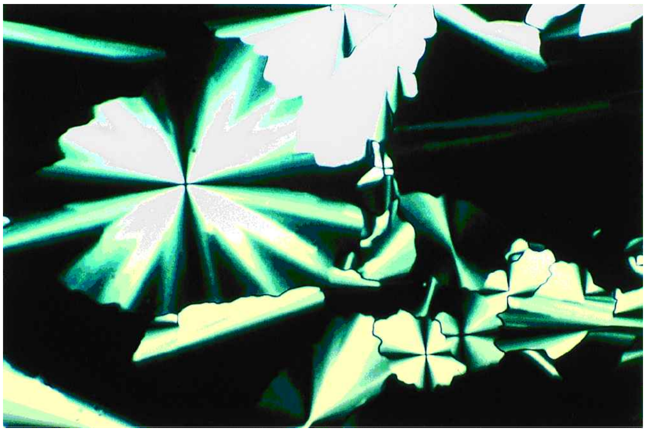


Figure 1. Texture of **2f** as seen by polarizing microscopy at 80·0°C, after cooling from the isotropic phase.

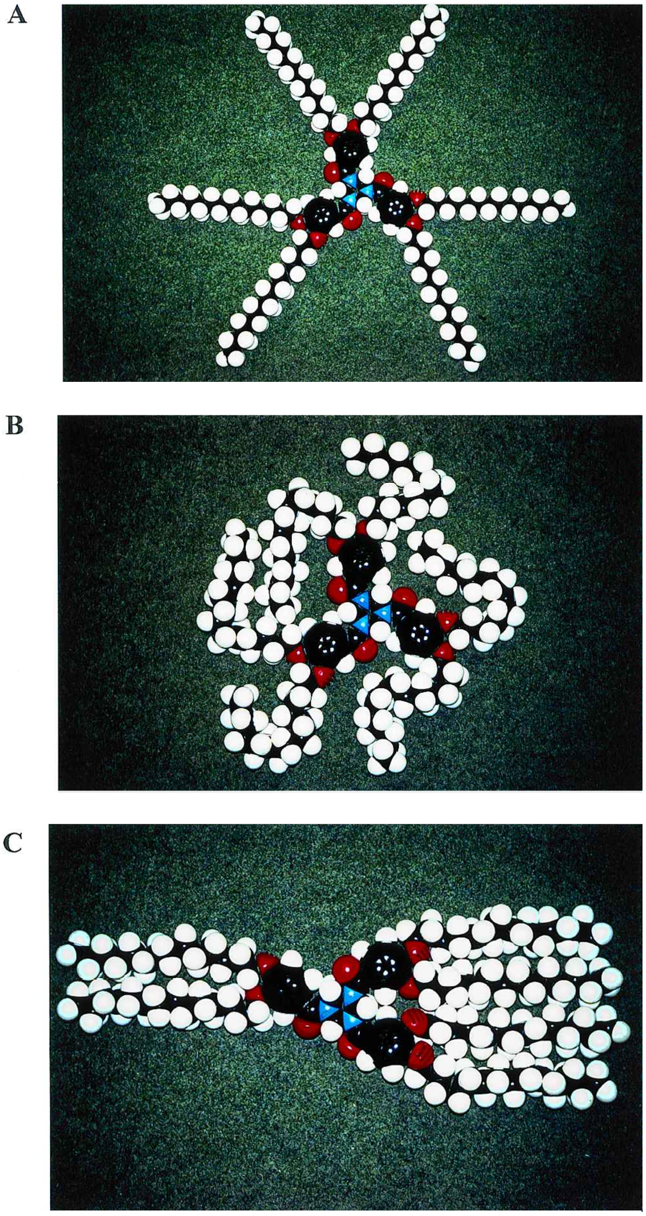


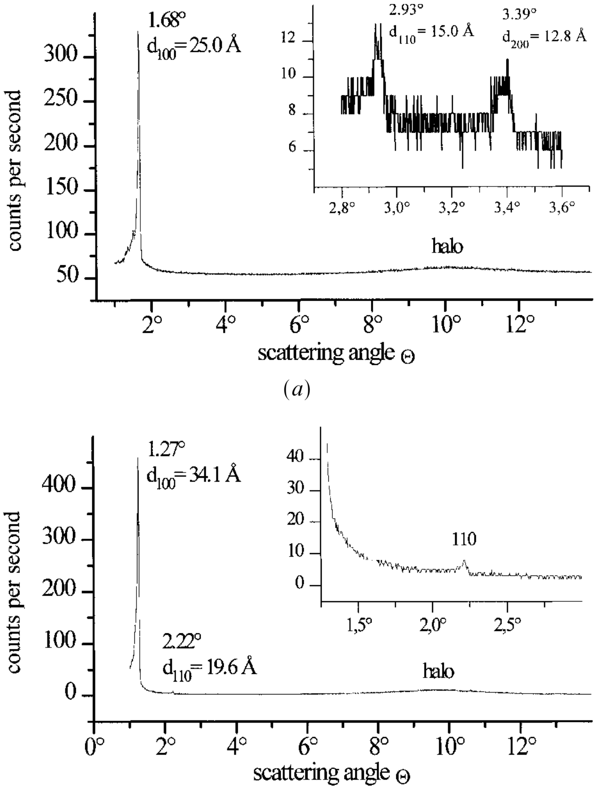
Figure 3. CPK models of two dimensional sterical conformers with a radial conformation and extended alkoxy chains (**A**), a radial conformation and optimal space filling chains (**B**) and a liner conformation with elongated chains (**C**).

3.3. *X-ray diffraction measurements*

The mesophases of hexahydro-1,3,5-triazine amide derivatives **2c**, **2e**, **2g**, **2h** and **2k** ($n=8$, 10, 12, 13 and 16) were investigated by means of X-ray diffraction measurements. The samples show distinct 1 0 0, 1 1 0 and 2 0 0 reflections at small angles, corresponding to lattice spacings $d_{100}:d_{110}:d_{200}=1:1/\sqrt{3}:1/2$ and a broad halo at $d_{\text{halo}} \sim 4{\cdot}5$ Å, characteristic for fluid alkyl chains. For $n=12$ and 13, the 1 1 0 and 2 0 0 reflections are very weak, so that they could only be detected with the

Guinier camera. The derivatives **2c** and **2k** ($n = 8$ and 16) exhibit 1 1 0 reflections with sufficient intensity to be recorded by the Guinier goniometer (figure 2). The investigations show evidence of a hexagonal columnar disordered structure (Col_h) in the mesophase. The lattice spacings and the evaluated lattice constants a_{hex} are listed in table 4.

We compared the lattice constants with the molecular diameters obtained from CPK models with different conformations for the 'two chain' substituted hexahydro-1,3,5-triazines. A 'closed', spheroidal arrangement of the flexible alkyl chains around the azacyclic core is not possible within the hexagonal columnar mesophase. Here, the formation of columns requires a two dimensional arrangement of the apolar alkyl chains between the staggered polar cores. In principle, three sterical conformers could be taken into consideration: a two dimensional radial conformation with extended alkoxy chains (**A**), another radial one with optimal space filling, 'fluid', alkoxy chains in the outer molecular sphere (**B**) and a linear conformation with elongated side chains (**C**) (figure 3). The molecular dimensions obtained from the CPK models are summarized in table 5. The values of the conformer **B** correspond best with the lattice constants from X-ray diffraction. The diameter of the 1,3,5-tris(3,4-dioxybenzoyl)hexahydro-1,3,5-triazine core without alkyl chains ($n = 0$) was evaluated by linear extrapolation of the lattice constants of **2c**, **2e**, **2g**, **2h** and **2k** ($n = 8$, 10, 12, 13 and 16) to $a_{hex,n=0}$ (figure 4). The value of $a_{hex,n=0} = 21$ Å is close to the diameter of 18 Å from the CPK model of the core. Therefore, we assume that the columns in the hexagonal mesophase are piled up from the polar cores of the molecules with an outer sphere of radially distributed, 'fluid', alkoxy chains (figure 5).



(*a*)

(*b*)

Figure 2. Guinier goniometer diffraction patterns of (*a*) **2c** ($n = 8$) at 70°C and (*b*) **2k** ($n = 16$) at 75°C.

3.4. *Reduction of **2e** to the cyclic aminal **4***

To investigate the influence of the rigid benzamide groups on the mesogenic behaviour, **2e** with decyloxy side chains was reduced with aluminium hydride to the corresponding 1,3,5-tris(3,4-didecyloxybenzyl)hexahydro-1,3,5-triazine **4**. Melting and decomposition occur at 56·6°C and 235°C, respectively. According to its aminal structure, **4** undergoes slow hydrolysis in air at room temperature, and this becomes much faster under acidic conditions. With respect to **2e**, the flexibility of the hexahydro-1,3,5-triazine core in **4** is increased and

Table 4. Results of X-ray diffraction measurements on the compounds **2c**, **2e**, **2g**, **2h** and **2k** and (in brackets) estimated relative intensities from reflections on the films: vs very strong, s strong, m medium, w weak, vw very weak.

			Lattice spacing d_{hk0}/Å				
Compound	n	T/°C	1 0 0	1 1 0	2 0 0	d_{halo}/Å	a_{hex}/Å
2c	8	65	26·2 (vs)	14·8 (w)	13·0 (m)	4·4 (s)	30·0
		70[a]	25·0[a]	15·0[a]	12·8[a]	4·3[a]	29·9[a]
2e	10	65	28·4 (vs)	16·6 (vs)	14·3 (w)	4·5 (s)	32·9
2g	12	75	30·2 (vs)	17·5 (vw)	—(vw)[b]	4·5 (s)	34·9
2h	13	50	31·3 (vs)	18·2 (vw)	—(vw)[b]	4·5 (s)	36·3
2k	16	70	34·3 (vs)	19·8 (s)	17·1 (w)	4·5 (s)	39·3
		75[a]	34·1[a]	19·6[a]	—	4·5[a]	39·4[a]

[a] Obtained by goniometer measurements.

[b] Not evaluable because reflection is too weak.

Table 5. Molecular dimensions of the different sterical conformers obtained from CPK models.

Compound	n	Diameters by CPK models/Å			Lattice constants by X-ray a_{hex}/Å
		A	**B**	**C**	
2c	8	37	29	35	30·0
2e	10	42	33	40	32·9
2g	12	47	34	46	34·9
2h	13	50	33	48	36·3
2k	16	57	36	51	39·3

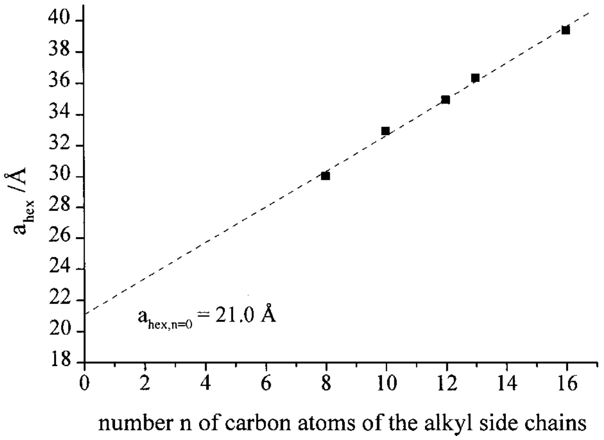


Figure 4. Linear extrapolation of the lattice constants of **2c**, **2e**, **2g**, **2h** and **2k** ($n = 8$, 10, 12, 13 and 16) to $a_{\text{hex},n=0}$ for the 1,3,5-tris(3,4-dioxybenzoyl)hexahydro-1,3,5-triazine core without alkyl chains ($n = 0$).

the geometry and electronic properties of the molecule are changed. As expected, and in analogy to former investigations on the reduction products of mesomorphic amides of [9]aneN_3 and piperazine [12], compound **4** is not a thermotropic liquid crystalline material.

4. Conclusion

It is possible to induce thermotropic mesomorphic behaviour in the small hexahydro-1,3,5-triazine cycle with 3,4-dialkoxybenzoyl (‘two chain’) substituents with hexyloxy or longer side chains. The higher melting temperatures compared to those of analogous 1,4,7-triazacyclononane derivatives and the appearance of stable crystalline phases are assumed to be due to the more rigid cyclic core. X-ray diffraction measurements of derivatives with $n = 8$, 10, 12, 13 and 16 show a hexagonal columnar (Col_h) structure for the mesophase. The observed spherulitic or pseudo-focal-conic textures correspond to the X-ray results. Comparison of the lattice constants (evaluated from the diffraction patterns) with the molecular dimensions, obtained from CPK models of different sterical conformers, lead us to believe that the columns in the mesophase are piled up from radial molecular mesogenic units with optimal space filling, ‘fluid’, alkoxy chains in their outer sphere. A similar formation of columnar structures was observed with a class of three chain substituted mesogens exhibiting a related molecular structure with respect to the trisubstituted core [22]. Reduction of the amide groups in the derivative with $n = 10$ leads to the corresponding non-mesogenic cyclic aminal compound.

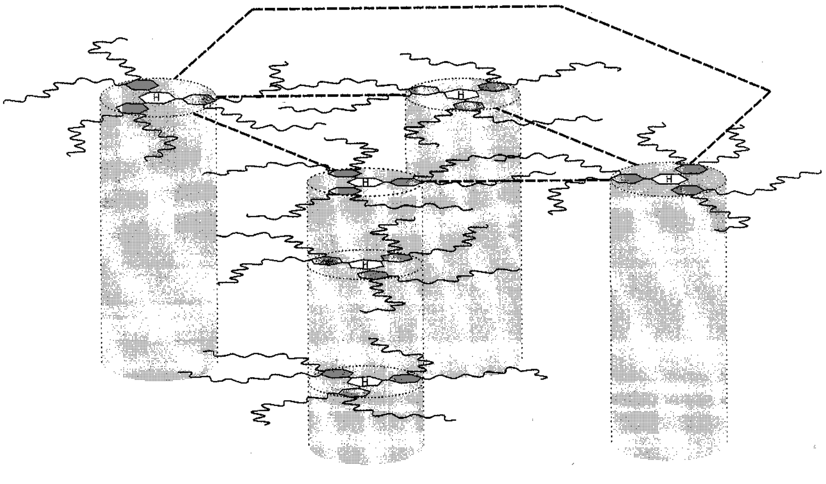


Figure 5. Schematic picture of the hexagonal columnar mesophase (Col_h) without amidic and ether linking groups.

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