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Mesomorphic property of 2,5-dibenzoyloxy-, 5-benzoylamino-2-benzoyloxy-, and 2,5-dibenzoylamino-tropones with mono-, di-, and tri-alkoxyl groups on the benzoyl groups and their benzenoid derivatives

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Mesomorphic property of 2,5-dibenzoyloxy-, 5-benzoylamino-2-benzoyloxy-, and 2,5-dibenzoylamino-tropones with mono-, di-, and tri-alkoxyl groups on the benzoyl groups and their benzenoid derivatives

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Mesomorphic properties of three-ring systems such as 2,5-dibenzoyloxytropones, 5-benzoylamino-2-benzoyloxytropones and 2,5-dibenzoylaminotropones with 4-alkoxy, 3,4-dialkoxy, and 3,4,5-trialkoxy groups on the benzoyl groups were investigated together with those of the corresponding benzenoids. Derivatives with two monoalkoxybenzoyl groups showed nematic and smectic A and C phases. Troponoid tetracatenars with two dialkoxybenzoyl groups had hexagonal columnar phases except for troponoids with two ester-connecting groups, whereas the corresponding benzenoids with two dialkoxybenzoyl groups were non-mesomorphic. All troponoid hexacatenars with two trialkoxybenzoyl groups formed hexagonal columnar phases. With the exception of benzenoid hexacatenars with two ester-connecting groups, the benzenoid hexacatenars showed hexagonal and tetragonal columnar phases. These mesomorphic properties were discussed from the standpoint of the difference of the core structure and the connecting group, where the amide-connecting group played a role to induce and enhance mesomorphic properties through hydrogen bonding.

Keywords: troponoid liquid crystals; [1,9]-sigmatropy; three-ring polycatenars; hexagonal and tetragonal columnar phases; hydrogen bonding

1. Introduction

The development of new types of liquid crystals is an important and challenging subject from theoretical and practical points of view, because liquid crystalline materials are widely applied in communication and information processing systems. Generally, the fundamental structure of the conventional rod-like liquid crystals consists of a rigid core with flexible side chains at the terminals of the core [1]. The former core induces orientational order and the latter side chains fluidity. The incompatibility between the flexible chains and the rigid core might also give rise to positional ordering.

In most conventional rod-like liquid crystals, one chain is attached to each end of the rigid core. Such materials can organise to nematic phases with only orientational order or layer structures in which the aromatic cores are organised to be parallel within layers to form smectic liquid crystalline phases. When the number of the side chains is increased, the mesomorphic property is changed. An elongated, strictly linear, and mostly polyaromatic core, which is terminated by three to six flexible chains, is called a polycatenar mesogen [2, 3]. The increase in the number of chains disturbs the organisation of the rigid cores in infinite layers and gives rise to a change of the mesophase type from smectic to columnar via cubic phases. In the columnar phases the rod-like cores are organised in columns and the disruption of the layers induces ribbons, which are surrounded by the fluid chains. It was also recognised that in order to keep the mesomorphic properties in such polycatenar mesogens, the core length has to be increased as the number of the side chains is increased [2, 3]. Hence, it was generally reported that four rings ($k = 2$) are the minimum number of rings in the rigid cores of tetracatenar mesogens ($m+n = 2$) and at least five rings ($k = 3$) are required in penta- ($m+n = 3$) and hexacatenar ($m+n = 4$) mesogens to induce columnar mesophases. Penta- and hexa-catenar mesogens with only three ($k = 1$) or four ($k = 2$) rings can also form liquid crystalline phases, but they show exclusively nematic and in a few cases also smectic phases [2, 3]. When additional structural modifications such as introduction of hydrogen bonding groups, however, were added into molecules, they are able to form

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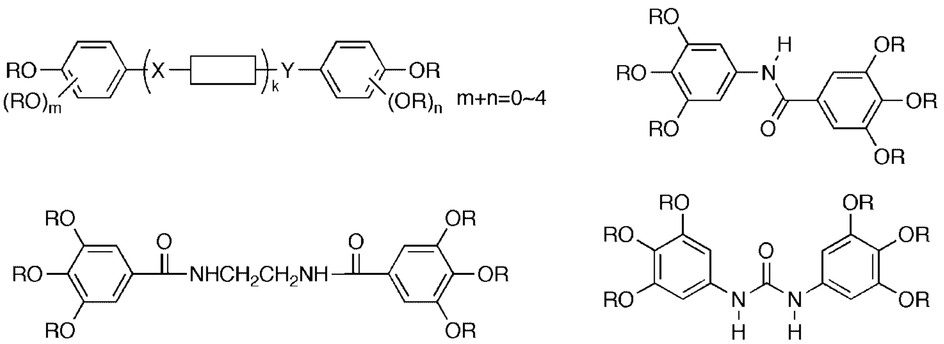
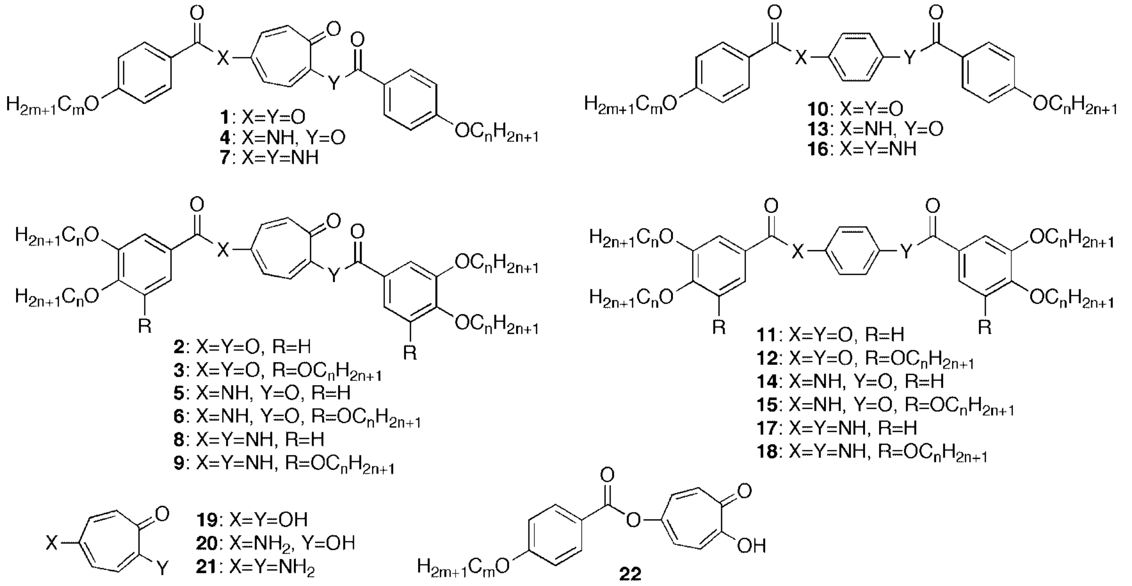


Scheme 1. Examples of polycatenars.



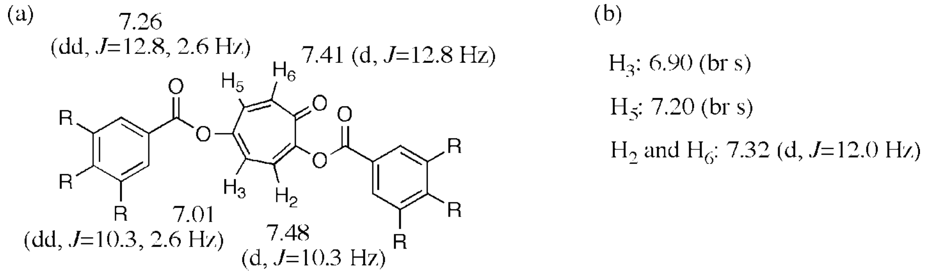
Scheme 2. Compounds under investigation.

columnar phases although they have only a two-ring core structure as shown in Scheme 1 [4–6].

In this paper, we synthesise 2,5-dibenzoyloxytropones (**1**–**3**), 5-benzoylamino-2-benzoyloxytropones (**4**–**6**), and 2,5-dibenzoylaminotropones (**7**–**9**) with mono-, di-, and tri-alkoxy groups on the benzoyl group and the corresponding benzenoids (**10**–**18**) to discuss the difference in mesomorphic properties depending on the core structures as well as the connecting groups.

2. Synthesis

Troponoids **1**–**9** were synthesised by benzoylation of 5-hydroxytropolone (**19**), 5-aminotropolone (**20**), and 2,5-diaminotropone (**21**). 2,5-Di(4-alkoxybenzoyloxy) tropones (**1**) with the different length of the alkoxyl groups were synthesised by reactions of 5-(4-alkoxybenzoyloxy)tropolones (**22**) [7] and 4-alkoxybenzoyl chlorides. The corresponding benzenoids were similarly synthesised (Scheme 2). The nuclear magnetic resonance (NMR) spectra of troponoids **1**–**6** with a benzoyloxy group at the C-2 position are characteristic as observed in 2-acyloxytropones [8–12]. The patterns of the NMR spectra are largely dependent on the measuring temperature. For example, the selected ^{1}H NMR data of **3d** measured at –59.9°C and 18.4°C are shown in Scheme 3. The assignment of the data was based on the fact that the coupling constants between the protons across the olefinic double bond are larger than those across the olefinic single bond [13]. At 18.4°C, protons H_2 and H_6, which appear as a doublet at δ 7.48 ($J = 10.3$ Hz) and 7.41 ($J = 12.8$ Hz) at –59.9°C, are coalesced to become a doublet



Scheme 3. ^{1}H NMR spectra of **3d** (R=$OC_{10}H_{21}$) in $CDCl_3$ (a) at –59.9°C and (b) at 18.4°C.

(J = 12.0 Hz) at δ 7.32, whereas protons H_3 and H_5 were observed as the broad signals at δ 6.90 and 7.20, respectively. These behaviours are explained by the migration of the benzoyl group at the C-2 position between the oxygen atom and the tropone carbonyl group, so-called [1,9]-sigmatropy [7]. Other troponoids (**1**, **2**, **4**–**6**) with a benzoyloxy group at the C-2 position behaved similarly.

3. Results and discussion

3.1 Mesomorphic properties of troponoids and benzenoids with two monoalkoxylated benzoyl groups

The transition temperatures were determined by a differential scanning calorimeter (DSC). The appearance of the mesophases was identified on the basis of the observed microscopic texture and X-ray diffraction (XRD) observation. The phase transition temperatures of troponoids (**1**, **4**, **7**) and benzenoids (**10**, **13**, **16**) with two monoalkoxylated benzoyl groups are summarised in Tables 1–4. They show nematic (N), smectic A (SmA), and C (SmC) phases depending on the length of the side chains. As shown in Tables 2 and 4, the amide-connecting groups enhanced thermal stability of the mesophases, as well as melting points. This should be due to hydrogen bonding between the amide groups. Next, we compared the transition temperatures of troponoids and benzenoids with two monoalkoxylated benzoyl groups, summarised in Tables 2 and 4. The thermal stability of the SmC phases of troponoids **1** and **4** increased more than that of benzenoids **10** and **13**, respectively, and that of the N phases of troponoids **1** and **4** decreased more than that of benzenoids **10** and **13**, whereas the thermal stability of both N and SmC phases of troponoid **7** decreased more than that of benzenoid **16**. It is reported that benzenoid **10** has a planar structure with maximum overlap of the π orbitals [14]. As discussed above, the troponoid with a benzoyloxy group at the C-2 position has a [1,9]-sigmatropic system, where the benzoyl group is migrating between the oxygen atom at the C-2 position and the carbonyl oxygen atom in a mesophase (SmC) phase, as observed in the ^{13}C cross polarisation magic angle spinning (CPMAS) spectra of 5-dodecyloxy-2-(4-dodecyloxybenzoyloxy)tropone [9]. In order to operate the [1,9]-sigmatropy, the C-O bond between the oxygen atom at the C-2 position and the benzoyl carbonyl carbon atom has to be nearly parallel to the π orbital of the tropone ring. Therefore, the mutual conjugation along the entire molecule should be reduced to decrease the overlap of the π orbital of the whole molecule, and the shape of molecules becomes more bent than that of benzenoid **10**. The bent molecules should be more likely to form lamellar structures than straight molecules, because the bent molecules can pack more efficiently in layer

Table 1. Transition temperatures (°C) of troponoid **1** with two monoalkoxylated benzoyl groups.

1	m	n	Cr		SmC		SmA		N		Iso
a	1	1	·	152					·	245[Dec]	
b	4	4	·	130					·	210	·
c	4	6	·	116					·	189	·
d	4	8	·	110					·	188	·
e	4	10	·	105			·	(99)[a]	·	180	·
f	4	12	·	100	·	131	·	153	·	175	·
g	6	4	·	121					·	192	·
h	6	6	·	125					·	188	·
i	6	10	·	112	·	130			·	177	·
j	6	12	·	107	·	142	·	150	·	173	·
k	8	4	·	116	·	(113)[a]			·	185	·
l	8	5	·	124	·	137			·	184	·
m	8	6	·	119	·	141			·	181	·
n	8	8	·	111	·	154			·	177	·
o	8	10	·	106	·	163			·	177	·
p	8	12	·	102	·	176					·
q	10	4	·	107	·	137			·	179	·
r	10	6	·	107	·	151			·	177	·
s	10	8	·	108	·	165			·	175	·
t	10	10	·	104	·	171			·	175	·
u	10	12	·	100	·	175					·
v	12	6	·	103	·	154			·	169	·
w	12	10	·	96					·	175	·
x	12	12	·	99	·	173					·

Note: [a]Data in parentheses are monotropic transition temperatures.

Table 2. Transition temperatures (°C) of troponoids **1, 4,** and **7** with two monoalkoxylated benzoyl groups.

n	**1**	X=Y=O	**4**	X=NH, Y=O	**7**	X=Y=NH
1	**a**	Cr·152·N·245·Dec	**a**	Cr·223·N·240·Dec	**a**	Cr·221·N·298·Dec
4	**b**	Cr·130·N·210·Iso	**b**	Cr·197·SmC·223·Dec	**b**	Cr·225·N·269·Dec
6	**h**	Cr·125·N·188·Iso	**c**	Cr·172·SmC·226·Dec	**c**	Cr·197·SmC·219·N·239·Iso
8	**n**	Cr·111·SmC·154·N·177·Iso	**d**	Cr·153·SmC·232·Dec	**d**	Cr·190·SmC·239·N·242·Iso
10	**t**	Cr·104·SmC·171·N·175·Iso	**e**	Cr·146·SmC·229·Dec	**e**	Cr·180·SmC·233·Iso
12	**x**	Cr·99·SmC·173·Iso	**f**	Cr·136·SmC·222·Dec	**f**	Cr·175·SmC·232·Iso
14	**y**	Cr·96·SmC·171·Iso	**g**	Cr·132·SmC·218·Dec	**g**	Cr·170·SmC·225·Iso

Table 3. Transition temperatures (°C) of benzenoid **10** with two monoalkoxylated benzoyl groups.

10	m	n	Cr		SmC		SmA	N		Iso
a[a]	1	1	·	222				·	300	·
b[b]	4	4	·	153				·	241	·
c[b]	4	6	·	117				·	226	·
d[b]	4	8	·	121				·	214	·
e[b]	6	6	·	124				·	213	·
f[c]	8	8	·	122	·	126		·	195	·
g[c]	10	10	·	127	·	147	·		182	·
h[c]	12	12	·	109	·	156		·	172	·

Notes: [a]M. J. S. Dewar and J. P. Schröder. *J. Org. Chem.*, **30**, 2296–2300 (1965). [b]S. A. Haut, D. C. Schröder, and J. P. Schröder, *J. Org. Chem.*, **37**, 1425–1428 (1972). [c]S. L. Arora, J. L. Fergason and T. R. Taylor, *J. Org. Chem.*, 1970, **35**, 4055–4058.

structures than the straight molecules [15], which should be more likely to form N phases. The relationship between troponoid **4** and benzenoid **13** is similar to that between **1** and **10**. Furthermore, troponoids with the more polar core structure than benzenoids should be more likely to form layer structures through microphase segregation. Therefore there was a greater increase in thermal stability of the SmC phases of troponoids than that of the benzenoids.

The thermal behaviour between troponoid **7** and benzenoid **16** with two amide groups is different from those with monoalkoxybenzoyl groups. The thermal stability of the SmC phases of benzenoid **16** is higher than that of troponoid **7**. Both have two amide groups, which contribute to play a role in the formation of mesophases through hydrogen bonds. In the ^{1}H NMR spectra of compound **7b**, the amide proton at the C-2 position and the ring proton at the C-3 position of compound **7b** appeared at δ 10.2 as a singlet and 9.22 as a doublet ($J = 11.2$ Hz), respectively. Since the amide proton at the C-5 position appeared at δ 7.84, the amide proton at the C-2 position was observed at the lower magnetic field due to intramolecular hydrogen bonding between the tropone carbonyl group, which made the structure of the tropone and the benzoylamide group coplanar. This result is supported by the observation of the lower chemical shift (δ 9.22) for the ring proton at the C-3 position, which is due to the anisotropy of the benzoylamide carbonyl group as shown in a reference compound [16, 17] in Scheme 4. On the other hand, since benzenoid **16** forms intermolecular hydrogen bonds at the C-2 and C-5 positions, they should form a thermally more stable SmC phase by making more tight lamellar structures than troponoid **7**.

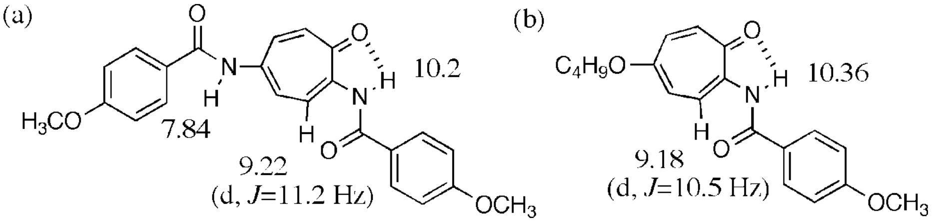
3.2 Mesomorphic properties of troponoid and benzenoid tetracatenars

An alkoxyl group was added at the C-3 position of the two benzoyl groups of the monoalkoxylated molecules. The transition temperatures of troponoids (**5**, **8**) are summarised in Table 5. Although troponoid tetracatenar **2** with two ester-connecting groups and

Table 4. Transition temperatures (°C) of benzenoids **10**, **13**, and **16** with two monoalkoxylated benzoyl groups.

n	**10**	X=Y=O	**13**	X=NH,Y=O	**16**	X=Y=NH
1	**a**	Cr·222·N·300·Iso	**a**[a]	Cr·255·N·303·Iso	**a**	Cr·335·Iso
4	**b**	Cr·153·N·241·Iso	**b**[a]	Cr·229·N·254·Iso	**b**	Cr·313·Iso
6	**e**	Cr·124·N·213·Iso	**c**	Cr·190·SmC·198·N·230·Iso	**c**	Cr·293·(N·288·)[b]Iso
8	**f**	Cr·122·SmC·126·N·195·Iso	**d**	Cr·185·SmC·220·N·222·Iso	**d**	Cr·289·(SmC·287·)[b]Iso
10	**h**	Cr·127·SmC·147·N·182·Iso	**e**	Cr·175·SmC·220·Iso	**e**	Cr·279·SmC·282·Iso
12	**j**	Cr·109·SmC·156·N·172·Iso	**f**	Cr·168·SmC·216·Iso	**f**	Cr·272·SmC·274·Iso
14	**m**	Cr·105·SmC·157·N·163·Iso	**g**	Cr·162·SmC·211·Iso	**g**	Cr·270·(SmC·270·)[b]Iso

Notes: [a]V. Kalyvas and J.E. McIntyre, *Mol. Cryst. Liq. Cryst.*, **80**, 105–118 (1982). [b]Data in parentheses are monotropic transition temperatures.



Scheme 4. ^{1}H NMR spectra of **7b** (a) and a reference compound (b) in CDCl$_3$.

Table 5. Transition temperatures (°C) of troponoids **5** and **8** with two dialkoxylated benzoyl groups.

n	5	X=NH,Y=O	8	X=Y=NH
4	**a**	Cr·121·Iso	**a**	Cr·174·Iso
6	**b**	Cr·89·Iso	**b**	Cr·157·Iso
8	**c**	Cr·97·Col$_h$·102·Iso	**c**	Cr·154·(Col$_h$·131·)^{a}Iso
10	**d**	Cr·105·Col$_h$·114·Iso	**d**	Cr·150·(Col$_h$·142·)^{a}Iso
12	**e**	Cr·111·Col$_h$·127·Iso	**e**	Cr·146·(Col$_h$·146·)^{a}Iso
14	**f**	Cr·111·Col$_h$·129·Iso	**f**	Cr·139·Col$_h$·146·Iso
16	**g**	Cr·113·Col$_h$·128·Iso	**g**	Cr·134·Col$_h$·139·Iso

[a]Data in parentheses are monotropic transition temperatures.

benzenoid tetracatenars (**11**, **14**, **17**) are not mesomorphic, troponoids **5** and **8** with at least one amide-connecting group showed a hexagonal columnar (Col$_h$) phase. The typical texture and XRD pattern of the Col$_h$ phase of aligned **8f** (a_{hex} = 36.4 Å) at 142°C are shown in Figure 1. The XRD data showed a sixfold symmetry to identify the Col$_h$ phase. Here the number of molecules[1] in a hypothetical disk was calculated to be three from a thickness of 5.0 Å (see [18]).

Troponoid **5f** has the similar textures to the Col$_h$ phase of troponoid **8f**. Although the XRD study of non-aligned **5f** showed only one reflection at 31.9 Å in the small-angle region, which could be assigned to the (100) reflection of a Col$_h$ phase, troponoid **5f** has a Col$_h$ phase, from observation of the texture. From the lattice parameter (a_{hex} = 36.9 Å) and the height of the diffuse scattering at 4.9 Å at 115°C, the number of molecules in a disk was calculated to be three [18], which indicated that three compounds are found on the disk. The troponoid tetracatenars **2** with two ester groups are not mesomorphic, but the replacement of the ester groups by amide groups made it possible to form mesophases through hydrogen bonding.

Mesophase induction was not achieved by replacement of an ester group by an amide group in the benzenoid tetracatenars **14** and **17**. For these compounds, only an increase in the melting points was found due to intermolecular hydrogen bonding, and no liquid crystalline phase was detected.

3.3 Mesomorphic properties of troponoid and benzenoid hexacatenars

One more alkoxyl group was introduced at the C-5 position on two benzoyl groups. The transition temperatures are summarised in Tables 6 and 7. They show columnar phases except for benzenoid **12**. The troponoid hexacatenar **3f**, for example, shows a typical texture of a Col$_h$ phase when viewed through crossed polarisers as observed in **8f**. The powder XRD pattern of unaligned **3f** measured at 65°C shows only one sharp reflection corresponding to 30.7 Å, but the small-angle XRD pattern of aligned

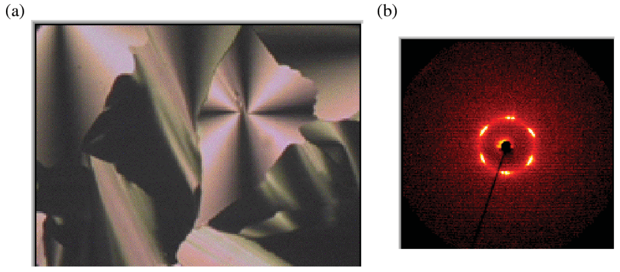


Figure 1. (a) Texture at 140°C on cooling process and (b) X-ray diffraction pattern of aligned **8f** (hexagonal lattice parameter: 36.4 Å). The alignment was obtained by slow cooling (0.01 K min^{-1}) of a droplet of the sample (diameter ca. 1 mm) on a glass plate. The incident X-ray beam was parallel to the substrate and the scattered intensity has been recorded using a 2D detector (HI-Star, Siemens, sample detector distance: 90 mm) (colour version online).

Table 6. Transition temperatures (°C) of troponoids **3**, **6**, and **9** with two trialkoxylated benzoyl groups.

n	3	X=Y=O	6	X=NH,Y=O	9	X=Y=NH
4	**a**	Cr·116·Iso	**a**	Cr·202·Iso	**a**	
6	**b**	Cr·41·Col$_h$·73·Iso	**b**	Cr·175·Iso	**b**	Cr·112·Col$_h$·123·Iso
8	**c**	Cr·78·(Col$_h$·78·)^{a}Iso	**c**	Cr·153·(Col$_h$·153·)^{a}Iso	**c**	Cr·89·Col$_h$·119·Iso
10	**d**	Cr·75·Col$_h$·80·Iso	**d**	Cr·145·(Col$_h$·144·)^{a}Iso	**d**	Cr·66·Col$_h$·108·Iso
12	**e**	Cr·63·Col$_h$·78·Iso	**e**	Cr·10·Col$_h$·141·Iso	**e**	
14	**f**	Cr·34·Col$_h$·74·Iso	**f**		**f**	Cr·29·Col$_h$·70·M^b·99·Iso
16	**g**	Cr·36·Col$_h$·74·Iso	**g**	Cr·48·Col$_h$·132·Iso	**g**	Cr·45·Col$_h$·48·M^b·93·Iso

Note: ^{a}Data in parentheses are monotropic transition temperatures.^{b}M: unidentified mesophase.

Table 7. Transition temperatures (°C) of benzenoids **15** and **18** with two trialkoxylated benzoyl groups.

n	15	X=NH,Y=O	18	X=Y=NH
4	**a**	Cr·105·Iso	**a**	Cr·232·Iso
6	**b**	Cr·78·(Col$_h$·48·)^{a}Iso	**b**	Cr·167·Iso
8	**c**	Cr·84·(Col$_h$·57·)^{a}Iso	**c**	Cr·168·Iso
10	**d**	Cr·84·(Col$_h$·63·)^{a}Iso	**d**	Cr·158·Iso
12	**e**	Cr·37·Col$_h$·66·Iso	**e**	Cr·156·Iso
14	**f**	Cr·34·Col$_h$·65·Iso	**f**	Cr·59·Col$_{tet}$·149·Iso
16	**g**	Cr·53·Col$_h$65·Iso	**g**	Cr·69·Col$_{tet}$·150·Iso

Note: ^{a}Data in parentheses are monotropic transition temperatures.

3f (65°C) clearly shows a sixfold symmetry, as observed in **8f**, which confirms a Col$_h$ phase with the lattice parameter $a_{hex} = 34.5$ Å. The number of molecules in a hypothetical slice of the columns with a thickness of 4.2 Å was calculated to be two [18], i.e. two molecules in a head-to-tail alignment arrange in the cross section of the columns.

The stability of the liquid crystalline phases of these troponoid hexacatenars can be further enhanced by replacement of the ester groups by amide groups. Troponoid **9d** has a Col$_h$ phase in a broad temperature region, whereas **9f** shows two types of liquid crystalline phases. A powder XRD study of the low-temperature mesophase of **9f** at 55°C showed a diffuse wide-angle scattering (4.2 Å) and three small-angle reflections corresponding to 33.5, 19.3, and 17.1 Å, which correspond to a ratio of their position of $1{:}1/\sqrt{3}{:}1/2$, suggesting a Col$_h$ phase. The texture supports the result. Only one reflection corresponding to 31.7 Å was found in an unidentified mesophase M at 85°C, together with a diffuse wide-angle scattering. On the basis of textural observations, a fluid smectic phase (SmA or SmC) can be excluded.

As mentioned above, all benzenoid tetracatenars (**11**, **14**, **17**) were non-mesomorphic. By further introduction of an alkoxy group on the benzoyl group of benzenoid tetracatenars, benzenoid hexacatenars **15** and **18** with an amide-connecting group showed columnar phases. The texture of benzenoid hexacatenar with an ester- and an amide-connecting group **15e** is shown in Figure 2a, which is the typical texture of a Col$_h$ phase. Although the XRD data showed one peak at 28.3 Å at 60°C in the small-angle region, we assigned it to be (100) reflection of the Col$_h$ phase ($a_{hex} = 32.7$ Å), where two molecules make a disk [18]. The texture of **18f** is shown in Figure 2b. The XRD data of benzenoid hexacatenar **18f** with two amide groups have two peaks at 41.0 and 30.1 Å at 130°C. They correspond to a ratio of their positions of $1{:}1/\sqrt{1.85} \approx 1{:}1/\sqrt{2}$, which suggested a Col$_{tet}$ phase.

In the derivatives with two monoalkoxylated benzoyl groups, both troponoids and benzenoids have the N, SmA, and SmC phases where benzenoids have an N phase with higher thermal stability than the troponoids, and the troponoids have a more thermally stable SmC phase than the benzenoids. As discussed above, the effect of the connecting group on thermal stability is observed to be as follows: diester < ester and amide < diamide. Hydrogen bonding of the amide group plays a role in enhancing the thermal stability of the mesophases.

In the polycatenars, the troponoid core enhanced the thermal stability of the Col$_h$ phase, as shown in the results of troponoid **6** and benzenoid **15** in Tables 6 and 7. It is thought that mesophase formation in the troponoid polycatenar series is dependent on the fact that the troponoid core has the large dipole moment [19]. This enhances attractive core–core interactions by

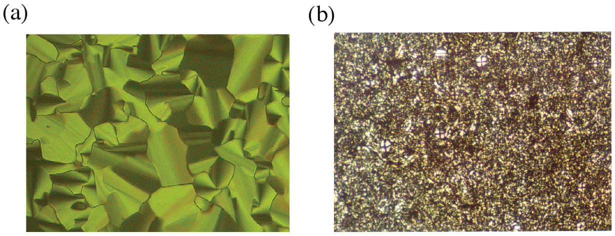


Figure 2. (a) Textures of **15e** at 62°C and (b) **18f** at 136°C (colour version online).

forming a head-to-tail alignment, and increases the incompatibility of the core region with the non-polar aliphatic chains. A related inducing effect of the mesophase in the troponoid core has been previously found in calamitic monocyclic 2-acyloxy-5-alkoxytropones [20, 21], where they form SmA phases, whereas the related benzenoid derivatives are non-mesomorphic [22].

In the troponoid tetracatenars series, replacement of the ester group by the amide group can be successfully used to stabilise or induce liquid crystalline phases, due to the additional lateral attractive forces provided by hydrogen bonding, whereas in the related benzenoid tetracatenars only a very strong enhancement of the melting points is observed. Troponoid tetracatenars with two amide-connecting groups have the $\mathrm{Col_h}$ with the highest thermal stability in the troponoid polycatenars, which is due to intramolecular hydrogen bonding between the amide group and the tropone carbonyl group, which contributes to a flattening of the 2-benzoylaminotropone structure. The flat molecule enables a more effective packing of these cores within the columns, which enhances the formation of liquid crystalline states [16, 23]. Furthermore, intramolecular hydrogen bonding between the tropone carbonyl and the adjacent amide group reduces the number of sites for intermolecular hydrogen bonding when compared with the benzenoids; this might be one of the reasons for displaying the rather low melting points.

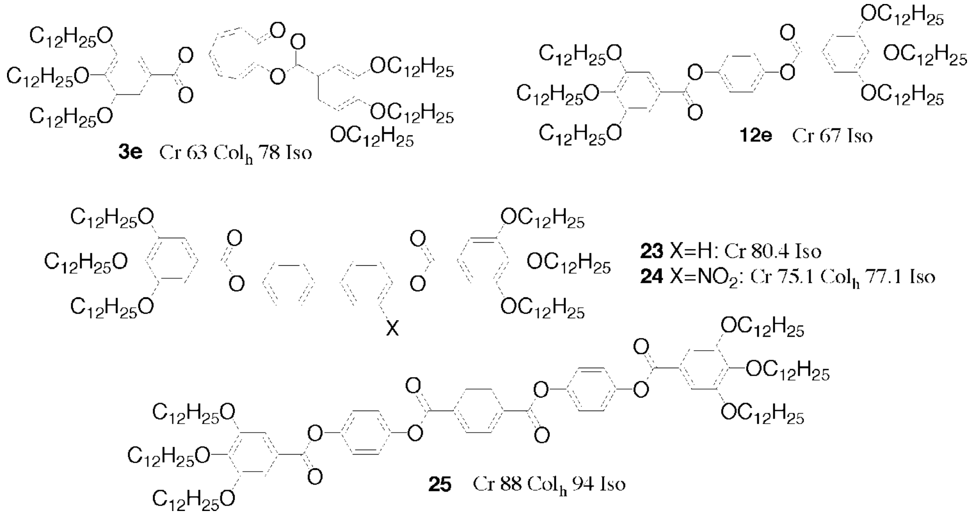
In the hexacatenars, the thermal stability of the $\mathrm{Col_h}$ phase of **9** with two amide groups was decreased more than that of **6** with an ester and amide group. While tetracatenars **8** with two amide groups had higher thermal stability than **5** with an ester and an amide group, the effect of the amide group at the C-2 position is not the same between tetracatenars and hexacatenars. When comparing the thermal stability between troponoid tetracatenars **8** and hexacatenars **9**, the former has the higher transition temperatures. The stacking force of the three-ring core system is not strong enough to form disks when the number of the side chain increases. The area balance between the core part and the four side chains should be best in the troponoid hexacatenars. The additional introduction of two side chains gave rise to a mismatch in the area size between the core part and the side chain in troponoid polycatenars, decreasing the thermal stability of the $\mathrm{Col_h}$ phases [24, 25]. In the benzenoid, although the mesophases of tetracatenars disappeared, benzenoid hexacatenars **15** and **18** showed columnar phases.

Finally, the attractive force of the tropone ring as a core structure of liquid crystals is estimated by comparing the thermal stability of troponoid **3** and benzenoid hexacatenars **12**. In order to delete additional interactions such as hydrogen bonding of amide groups, hexacatenars with two ester groups as connecting groups were selected. Previously, we have prepared four-ring hexacatenars (**23**, **24**) with a biphenyl ring, where the former **23** was not mesomorphic and the latter **24** with a nitro group showed a $\mathrm{Col_h}$ phase. It was concluded that the nitro group acted as a polar substituent to enhance the lateral molecular interaction [26]. Since the thermal stability of the $\mathrm{Col_h}$ phase of **24** is almost the same as that of troponoid **3e**, it could be estimated that the attractive force of a tropone ring corresponds to that of the nitrobiphenyl ring. Furthermore, it is reported that five-ring benzenoid hexacatenar **25** [27] with a terephthaloyloxy structure as the central core showed a $\mathrm{Col_h}$ phase with similar thermal stability to **3e**. From these results, the attractive force of the tropone ring is estimated to correspond to that of three benzene ring systems (Scheme 5).

In conclusion, we observed the columnar liquid crystalline phases induced by tetra- and hexacatenar mesogens with a three-ring central core by modifying the core structure and the connecting group. The polarity of the troponoid ring increases microsegregation and core–core interaction by forming head-to-tail alignments. The replacement of the ester group by the amide group enhances the lateral interaction through intermolecular hydrogen bonding, and makes the core structure flat through intramolecular hydrogen bonding with the neighbouring tropone carbonyl group. This allows a decrease of the number of rings in the rigid core of tetra- and hexa-catenar mesogens.

4. Experimental details

Elemental analyses were performed at the elemental analysis laboratory of Kyushu University. NMR spectra were measured on JEOL GSX 270H, LA 400, and LA 600 spectrometers in $CDCl_3$; the chemical shifts are expressed in δ units. Infrared (IR) spectra were recorded using a JASCO IR Report 100 spectrometer with KBr disks. The stationary phase for column chromatography was Wako gel C-300 and the eluant was a mixture of ethyl acetate, chloroform, and hexane. Transition temperatures were measured using a DSC (Seiko DSC 200, heating and cooling rate was $5^\circ\mathrm{C\ min^{-1}}$) and the mesomorphic phase was observed with a polarising microscope (Olympus BHSP BH-2) equipped with a hot stage (Linkam TH-600RMS). X-ray powder diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-Kα radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.



Scheme 5. Estimation of effects of the core structure.

4.1 Synthesis of 2,5-di(4-butoxybenzoyloxy)-tropone (1b)

A thionyl chloride solution (1 ml) of 4-butoxybenzoic acid (93.2 mg, 0.48 mmol) and a drop of DMF were refluxed for 5 h. After excess thionyl chloride was removed under reduced pressure at 40–50°C, 5 ml of pyridine, 27.7 mg (0.2 mmol) of 5-hydroxytropolone, and a catalytic amount of DMAP were added to the above residue. After the reaction mixture was stirred at room temperature for 12 h, the mixture was poured into 2 M HCl solution at 0°C and extracted with AcOEt. The organic layer was washed with water, dried on $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on a silica-gel column to give **1b** (90 mg, 92%), ^{1}H NMR δ 0.99 (3H, t, $J = 7.0$ Hz), 1.00 (3H, t, $J = 7.0$ Hz), 1.45–1.60 (4H, m), 1.75–1.90 (4H, m), 4.05 (2H, t, $J = 6.5$ Hz), 4.06 (2H, t, $J = 6.5$ Hz), 6.96 (2H, dm, $J = 9.0$ Hz), 6.98 (2H, dm, $J = 9.0$ Hz), 6.80–7.30 (2H, br), 7.30 (2H, d, $J = 12.0$ Hz), 8.10 (2H, dm, $J = 9.0$ Hz), and 8.13 (2H, d, $J = 9.0$ Hz). ^{13}C NMR δ 13.8, 19.2, 31.10, 31.13, 68.0, 68.1, 114.3 (2C), 114.5 (2C), 120.2, 120.7, 132.5 (2C), 132.7 (2C), 154.0, 163.7, 163.8, 164.1, and 164.4. IR ν 1725, 1600, 1250, and 1140 cm^{-1}, elemental analysis: found, C, 71.07; H, 6.27%. Calculated for $C_{29}H_{30}O_7$: C, 71.01; H, 6.16%.

Other compounds **1** with the same length of the alkoxy groups at the terminals were similarly synthesised. **1a**: 100%, elemental analysis: found, C, 67.92; H, 4.49%. Calculated for $C_{23}H_{18}O_7$: C, 67.98; H, 4.46%. **1h**: 68%, elemental analysis: found, C, 72.26; H, 7.10%. Calculated for $C_{33}H_{38}O_7$: C, 72.51; H, 7.01%. **1n**: 72%, elemental analysis: found, C, 73.94; H, 7.63%. Calculated for $C_{37}H_{46}O_7$: C, 73.73; H, 7.69%. **1t**: 46%, elemental analysis: found, C, 74.61; H, 8.45%. Calculated for $C_{41}H_{54}O_7$: C, 74.74; H, 8.26%. **1x**: 78%, elemental analysis: found, C, 75.51; H, 8.72%. Calculated for $C_{45}H_{62}O_7$: C, 75.60; H, 8.74%.

4.2 Synthesis of 2-(4-dodecyloxybenzoyloxy)-5-(4-butoxybenzoyloxy)tropone (1e)

A thionyl chloride solution (1 ml) of 4-decyloxybenzoic acid (66.8 mg, 0.24 mmol) and a drop of DMF were refluxed for 5 h. After excess thionyl chloride was removed under reduced pressure at 40–50°C, 5 ml of pyridine, 62.2 mg (0.2 mmol) of 5-(4-butoxybenzoyloxy)tropolone, and a catalytic amount of DMAP were added to the above residue. After the reaction mixture was similarly treated with the above workup, the residue was chromatographed on a silica-gel column to give **1e** (74.9 mg, 50%), elemental analysis: found, C, 73.44; H, 7.29%. Calculated for $C_{35}H_{42}O_7$: C, 73.15; H, 7.37%.

Other compounds **1** with the different length of the alkoxy groups at the terminals were similarly synthesised. **1c**: 74%, elemental analysis: found C, 72.03; H, 6.62%. Calculated for $C_{31}H_{34}O_7$: C, 71.80; H, 6.61%. **1d**: 76%, elemental analysis: found, C, 72.42; H, 7.08%. Calculated for $C_{33}H_{38}O_7$: C, 72.51; H, 7.01%. **1f**: 75%, elemental analysis: found, C, 73.85; H, 7.83%. Calculated for $C_{37}H_{46}O_7$: C, 73.73; H, 7.69%. **1g**: 40%, elemental analysis: found, C, 71.73; H, 6.54%. Calculated for $C_{31}H_{34}O_7$: C, 71.80; H, 6.61%. **1i**: 78.5%, elemental analysis: found, C, 73.82; H, 7.56%. Calculated for $C_{37}H_{46}O_7$: C, 73.73; H, 7.69%. **1j**: 62%, elemental analysis: found, C, 74.47; H, 8.01%. Calculated for $C_{39}H_{50}O_7$: C, 74.25; H, 8.00%. **1k**: 38%, elemental analysis: found, C, 72.53; H, 6.94%. Calculated for $C_{33}H_{38}O_7$: C, 72.51; H, 7.01%. **1l**: 87%, elemental analysis: found, C, 72.95; H, 7.02%. Calculated for $C_{34}H_{40}O_7$: C, 72.83; H, 7.19%. **1m**: 63%, elemental analysis: found, C, 73.47; H, 7.28%. Calculated for $C_{35}H_{42}O_7$: C, 73.14; H, 7.37%. **1o**: 67%, elemental analysis: found, 74.51; H, 7.84%. Calculated for $C_{39}H_{50}O_7$: C, 74.25; H, 8.00%. **1p**: 91%, elemental analysis: found, C, 75.02; H, 8.16%. Calculated for $C_{41}H_{54}O_7$: C, 74.74; H, 8.26%. **1q**: 78.5%, elemental analysis: found, C, 73.19; H, 7.33%. Calculated for $C_{35}H_{42}O_7$: C, 73.15; H, 7.37%. **1r**: 63%, elemental analysis: found, C, 73.42; H, 7.40%. Calculated for $C_{37}H_{46}O_7$: C, 73.73; H, 7.69%. **1s**: 70%, elemental analysis: found, C, 74.18; H, 7.85%. Calculated for $C_{39}H_{50}O_7$: C, 74.25; H, 8.00%. **1u**: 75%, elemental analysis: found, C, 75.41; H, 8.44%. Calculated for $C_{43}H_{58}O_7$: C, 75.19; H, 8.51%. **1v**: 32%, elemental analysis: found, C, 74.16; H, 7.72%. Calculated for $C_{39}H_{50}O_7$: C, 74.26; H, 7.99%. **1w**: 66%, elemental analysis: found, C, 75.06; H, 8.31%. Calculated for $C_{43}H_{58}O_7$: C, 75.19; H, 8.51%.

4.3 Synthesis of 2,5-di(3,4-butoxybenzoyloxy)-tropone (2a)

A thionyl chloride solution (2 ml) of 3,4-dibutoxybenzoic acid (160 mg, 0.6 mmol) was refluxed for 3 h. After excess thionyl chloride was removed under reduced pressure at 40–50°C, 3 ml of pyridine, 34 mg (0.25 mmol) of 5-hydroxytropolone and a catalytic amount of DMAP were added to the above residue. After the reaction mixture was stirred at room temperature overnight, the mixture was poured into sat. $KHSO_4$ solution and extracted with $CHCl_3$. The organic layer was washed with water, dried on $NaSO_4$, and evaporated under reduced pressure. The residue was chromatographed on a silica-gel column to give **2a** ($n = 4$) (151 mg, 95%), mp 119°C. ^{1}H NMR δ 0.98–1.02 (12H, m), 1.48–1.55 (8H, m), 1.83 (4H, quint, $J = 6.4$ Hz), 1.87 (4H, quint, $J = 6.4$ Hz), 4.07–4.11 (8H, m), 6.92 (1H, d, $J = 8.3$ Hz), 6.94 (1H, d, $J = 8.3$ Hz), 6.9 (1H, br s), 7.1 (1H, br s), 7.31 (2H, d, $J = 12.0$ Hz), 7.61 (1H, d, $J = 2.0$ Hz), 7.65 (1H, d, $J = 2.0$ Hz), 7.78 (1H, dd, $J = 8.3$ and 2.0 Hz), and 7.81 (1H, dd, $J = 8.3$ and 2.0 Hz), elemental analysis: found, C, 69.95; H, 7.26%. Calculated for $C_{37}H_{46}O_9$: C, 70.01; H, 7.30%.

Other compounds **2** were similarly synthesised. **2b** ($n = 6$): 78%, mp 105°C, elemental analysis: found, C, 72.31; H, 8.29%. Calculated for $C_{45}H_{62}O_9$: C, 72.36; H, 8.37%. **2c** ($n = 8$): 55%, mp 109°C, elemental analysis: found, C, 74.00; H, 9.08%. Calculated for $C_{53}H_{78}O_9$: C, 74.09; H, 9.15%. **2d** ($n = 10$): 59%, mp 112°C, elemental analysis: found, C, 75.30; H, 9.67%. Calculated for $C_{61}H_{94}O_9$: C, 75.42; H, 9.75%. **2e** ($n = 12$): 37%, mp 114°C, elemental analysis: found, C, 76.20; H, 10.14%. Calculated for $C_{69}H_{110}O_9$: C, 76.48; H, 10.23%. **2f** ($n = 14$): 27%, mp 115°C, elemental analysis: found, C, 77.10; H, 10.53%. Calculated for $C_{77}H_{126}O_9$: C, 77.34; H, 10.62%. **2g** ($n = 16$): 73%, mp 116°C, elemental analysis: found, C, 77.83; H, 10.86%. Calculated for $C_{85}H_{142}O_9$: C, 78.05; H, 10.94%.

4.4 Synthesis of 2,5-di(3,4,5-tributoxybenzoyloxy)-tropone (3a)

A thionyl chloride solution (2 ml) of 3,4,5-dibutoxybenzoic acid (258 mg, 0.6 mmol) was refluxed for 3 h. Excess thionyl chloride was removed under reduced pressure at 40–50°C, 3 ml of pyridine, then 34 mg (0.25 mmol) of 5-hydroxytropolone and a catalytic amount of DMAP were added to the above residue. After the reaction mixture was similarly treated with the above workup of compound **2**, the residue was chromatographed on a silica-gel column to give **3a** (129 mg, 67%), ^{1}H NMR δ 0.96 (18H, m), 1.46–1.52 (12H, m), 1.71–1.87 (12H, m), 4.03–4.09 (12H, m), 6.93 (1H, br s), 7.09 (1H, br s), 7.32 (2H, d, $J = 12.0$ Hz), 7.36 (2H, s), and 7.40 (2H, s), elemental analysis: found, C, 69.15; H, 7.93%. Calculated for $C_{45}H_{62}O_{11}$: C, 69.38; H, 8.02%.

Other compounds **3** were similarly synthesised. **3b**: 62%, elemental analysis: found, C, 72.07; H, 9.19%. Calculated for $C_{57}H_{86}O_{11}$: C, 72.27; H, 9.15%. **3c**: 27%, elemental analysis: found, C, 74.00; H, 9.82%. Calculated for $C_{69}H_{110}O_{11}$: C, 74.29; H, 9.94%. **3d**: 94%, ^{1}H NMR (at 18.4°C) δ 0.86–0.90 (18H, m), 1.27–1.51 (84H, m), 1.73–1.86 (12H, m), 4.01–4.07 (12H, m), 6.90 (1H, br s), 7.20 (1H, br s), 7.32 (2H, d, $J = 12.3$ Hz), 7.36 (2H, s), and 7.39 (2H, s). ^{1}H NMR (at –59.9°C) δ 0.87–0.89 (18H, m), 1.25–1.47 (84H, m), 1.76–1.85 (12H, m), 4.05–4.07 (12H, m), 7.01 (1H, dd, $J = 10.3, 2.6$ Hz), 7.26 (1H, dd, $J = 12.8, 2.6$ Hz), 7.37 (2H, s), 7.41 (2H, s), 7.41 (1H, d, $J = 12.8$ Hz), and 7.48 (1H, d, $J = 10.3$ Hz), elemental analysis: found, C, 75.68; H, 10.42%. Calculated for $C_{81}H_{134}O_{11}$: C, 75.77; H, 10.52%. **3e**: 62%, elemental analysis: found, C, 76.80; H, 10.92%. Calculated for $C_{93}H_{158}O_{11}$: C, 76.92; H, 10.97%. **3f**: 30%, elemental analysis: found, C, 77.53; H, 11.24%. Calculated for $C_{105}H_{182}O_{11}$: C, 77.82; H, 11.32%. **3g**: 24%, elemental analysis: found, C, 78.48; H, 11.63%. Calculated for $C_{117}H_{206}O_{11}$: C, 78.55; H, 11.61%.

4.5 Synthesis of 5-(4-butoxybenzoylamino)-2-(4-butoxybenzoyloxy)tropone (4b)

A thionyl chloride solution (2 ml) of 4-butoxybenzoic acid (194 mg, 1.2 mmol) and a drop of DMF was refluxed for 5 h. After excess thionyl chloride was removed under reduced pressure at 40–50°C, 5 ml of pyridine, 70 mg (0.5 mmol) of 5-aminotropolone, and a catalytic amount of DMAP were added to the above residue. After the reaction mixture was similarly treated with the above workup of compound **2**, the residue was chromatographed on a silica-gel column to give **4b** (162 mg, 67%), ^{1}H NMR δ 0.99 (3H, t, $J = 7.6$ Hz), 1.00 (3H, t, $J = 7.6$ Hz), 1.51 (2H, quint, $J = 7.6$ Hz), 1.52 (2H, quint, $J = 7.6$ Hz), 1.74–1.83 (4H, m), 3.96 (2H, t, $J = 6.6$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 6.84 (2H, d, $J = 9.0$ Hz), 6.95 (2H, d, $J = 9.0$ Hz), 7.23 (2H, br s), 7.79 (2H, br s), 7.84 (2H, d, $J = 9.0$ Hz), 8.07 (2H, d, $J = 9.0$ Hz), and 8.38 (1H, s), elemental analysis: found, C, 70.98; H, 6.73; N, 2.85%. Calculated for $C_{29}H_{31}NO_6$: C, 71.15; H, 6.38; N, 2.86%.

Other compounds **4** were similarly synthesised. **4a**: 38%, ^{1}H NMR (DMF-d$_7$, 400 MHz): δ 3.86 (3H, s), 3.88 (3H, s), 6.84 (2H, d, $J = 9.0$ Hz), 6.95 (2H, d, $J = 9.0$ Hz), 7.23 (2H, br), 7.79 (2H, br), 7.84 (2H, d, $J = 9.0$ Hz), 8.07 (2H, d, $J = 9.0$ Hz), and 8.38 (1H, s), elemental analysis: found, C, 67.95; H, 4.77; N, 3.45%. Calculated for $C_{23}H_{19}NO_6$: C, 68.14; H, 4.72; N, 3.46%. **4c**: 84%, elemental analysis: found, C, 72.41; H, 7.15; N, 2.55%. Calculated for $C_{33}H_{39}NO_6$: C, 72.64; H, 7.20; N, 2.57%. **4d**: 12%, elemental analysis: found, C, 73.68; H, 7.83; N, 2.30%. Calculated for $C_{37}H_{47}NO_6$: C, 73.85; H, 7.87; N, 2.33%. **4e**: 71%, elemental analysis: found, C, 74.80; H, 8.38; N, 2.12%. Calculated for $C_{41}H_{55}NO_6$: C, 74.85; H, 8.43; N, 2.13%. **4f**: 50%, elemental analysis: found, C, 75.44; H, 8.80; N, 1.92%. Calculated for $C_{45}H_{63}NO_6$: C, 75.70; H, 8.89; N, 1.96%. **4g**: 25%, elemental analysis: found, C, 76.20; H, 9.20; N, 1.78%. Calculated for $C_{49}H_{71}NO_6$: C, 76.42; H, 9.29; N, 1.82%.

4.6 *Synthesis of 5-(3,4-dibutoxybenzoylamino)-2-(3,4-dibutoxybenzoyloxy)tropone (5a)*

A thionyl chloride solution (2 ml) of 3,4-dibutoxybenzoic acid (320 mg, 1.2 mmol) and a drop of DMF were refluxed for 5 h. After excess thionyl chloride was removed under reduced pressure at 40–50°C, 5 ml of pyridine, 70 mg (0.5 mmol) of 5-aminotropolone, and a catalytic amount of DMAP were added to the above residue. After the reaction mixture was similarly treated with the above workup of compound **2**, the residue was chromatographed on a silica-gel column to give **5a** (271 mg, 86%), ^{1}H NMR δ 0.93–1.00 (12H, m), 1.40–1.58 (8H, m), 1.70–1.87 (8H, m), 3.94 (2H, t, $J = 6.6$ Hz), 3.95 (2H, t, $J = 6.6$ Hz), 3.98 (2H, t, $J = 6.6$ Hz), 4.06 (2H, t, $J = 6.6$ Hz), 6.64 (1H, d, $J = 8.6$ Hz), 6.85 (1H, d, $J = 8.6$ Hz), 7.16 (2H, br s), 7.47 (1H, d, $J = 8.6$ Hz), 7.48 (1H, s), 7.53 (1H, d, $J = 1.7$ Hz), 7.58 (2H, br s), 7.69 (1H, dd, $J = 8.6, 1.7$ Hz), and 9.11 (1H, s), elemental analysis: found, C, 69.97; H, 7.46; N, 2.19%. Calculated for $C_{37}H_{47}NO_8$: C, 70.12; H, 7.47; N, 2.21%.

Other compounds **5** were similarly synthesised. **5b**: 76%, elemental analysis: found, C, 72.39; H, 8.49; N, 1.88%. Calculated for $C_{45}H_{63}NO_8$: C, 72.45; H, 8.51; N, 1.88%. **5c**: 39%, elemental analysis: found, C, 74.07; H, 9.25; N, 1.61%. Calculated for $C_{53}H_{79}NO_8$: C, 74.18; H, 9.28; N, 1.63%. **5d**: 82%, elemental analysis: found, C, 75.52; H, 9.83; N, 1.42%. Calculated for $C_{29}H_{31}NO_6$: $C_{61}H_{95}NO_8$: C, 75.50; H, 9.87; N, 1.44%. **5e**: 92%, elemental analysis: found, C, 76.50; H, 10.28; N, 1.27%. Calculated for $C_{69}H_{111}NO_8$: C, 76.55; H, 10.33; N, 1.29%. **5f**: 78%, elemental analysis: found, C, 77.32; H, 10.66; N, 1.17%. Calculated for $C_{77}H_{127}NO_8$: C, 77.40; H, 10.71; N, 1.17%. **5g**: 61%, elemental analysis: found, C, 77.86; H, 11.09; N, 1.08%. Calculated for $C_{85}H_{143}NO_8$: C, 78.11; H, 11.03; N, 1.07%.

4.7 *Synthesis of 5-(3,4,5-tributoxybenzoylamino)-2-(3,4,5-tributoxybenzoyloxy)tropone (6a)*

A thionyl chloride solution (2 ml) of 3,4,5-tributoxybenzoic acid (57 mg, 1.2 mmol) and a drop of DMF were refluxed for 5 h. After excess thionyl chloride was removed under reduced pressure at 40–50°C, 5 ml of pyridine, 70 mg (0.5 mmol) of 5-aminotropolone, and a catalytic amount of DMAP were added to the above residue. After the reaction mixture was similarly treated with the above workup of compound **2**, the residue was chromatographed on a silica-gel column to give **6a** (78 mg, 20%), ^{1}H NMR δ 0.97 (6H, t, $J = 7.6$ Hz), 0.98 (12H, t, $J = 7.2$ Hz), 1.48–1.55 (12H, m), 1.72–1.82 (12H, m), 4.00–4.08 (12H, m), 7.05 (2H, s), 7.38 (2H, s), 7.3–7.7 (4H, br s), and 7.90 (1H, s), elemental analysis: found, C, 69.53; H, 8.22; N, 1.85%. Calculated for $C_{45}H_{63}NO_{10}$: C, 69.47; H, 8.16; N, 1.80%.

Other compounds **6** were similarly synthesised. **6b**: 38%, elemental analysis: found, C, 72.26; H, 9.24; N, 1.54%. Calculated for $C_{57}H_{87}NO_{10}$: C, 72.35; H, 9.27; N, 1.48%. **6c**: 56%, elemental analysis: found, C, 74.31; H, 10.01; N, 1.29%. Calculated for $C_{69}H_{111}NO_{10}$: C, 74.35; H, 10.04; N, 1.26%. **6d**: 25%, elemental analysis: found, C, 75.67; H, 10.55; N, 1.14%. Calculated for $C_{81}H_{135}NO_{10}$: C, 75.83; H, 10.61; N, 1.09%. **6e**: 43%, elemental analysis: found, C, 76.94; H, 11.01; N, 0.99%. Calculated for $C_{93}H_{159}NO_{10}$: C, 76.97; H, 11.04; N, 0.97%. **6g**: 78%, elemental analysis: found, C, 78.52; H, 11.64; N, 0.83%. Calculated for $C_{117}H_{207}NO_{10}$: C, 78.60; H, 11.67; N, 0.78%.

4.8 Synthesis of 2,5-di(4-butoxybenzoylamino)-tropone (7b)

A thionyl chloride solution (2 ml) of 4-butoxybenzoic acid (194 mg, 1.2 mmol) and a drop of DMF were refluxed for 5 h. After excess thionyl chloride was removed under reduced pressure at 40–50 °C, 5 ml of pyridine, 68 mg (0.5 mmol) of 2,5-diaminotropone, and a catalytic amount of DMAP were added to the above residue. After the reaction mixture was stirred at room temperature for 12 h, the mixture was poured into 2 M HCl solution at 0°C and extracted with AcOEt. The organic layer was washed with water, dried on $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on a silica-gel column to give **7b** (60 mg, 25%), ^{1}H NMR δ 1.00 (6H, t, $J = 7.0$ Hz), 1.49–1.55 (4H, m), 1.81 (4H, quint, $J = 7.0$ Hz), 4.04 (4H, t, $J = 7.0$ Hz), 6.98 (2H, d, $J = 8.8$ Hz), 6.98 (2H, d, $J = 8.8$ Hz), 7.43 (1H, d, $J = 12.9$ Hz), 7.53 (1H, dd, $J = 11.2$, 2.4 Hz), 7.83 (2H, d, $J = 8.8$ Hz), 7.84 (1H, s), 7.85 (1H, dd, $J = 12.9$, 2.4 Hz), 7.95 (2H, d, $J = 8.8$ Hz), 9.22 (1H, d, $J = 11.2$ Hz), and 10.2 (1H, s), elemental analysis: found, C, 71.16; H, 6.54; N, 5.73%. Calculated for $C_{29}H_{32}N_2O_5$: C, 71.29; H, 6.60; N, 5.73%.

Other compounds **7** were similarly synthesised. **7a**: 34%, elemental analysis: found, C, 68.12; H, 4.93; N, 6.86%. Calculated for $C_{23}H_{20}N_2O_5$: C, 68.31; H, 4.98; N, 6.93%. **7c**: 65%, elemental analysis: found, C, 72.71; H, 7.36; N, 5.13%. Calculated for $C_{33}H_{40}N_2O_5$: C, 72.77; H, 7.40; N, 5.14%. **7d**: 71%, elemental analysis: found, C, 74.01; H, 8.06; N, 4.64%. Calculated for $C_{37}H_{48}N_2O_5$: C, 73.97; H, 8.05; N, 4.66%. **7e**: 65%, elemental analysis: found, C, 74.92; H, 8.41; N, 4.30%. Calculated for $C_{41}H_{56}N_2O_5$: C, 74.96; H, 8.59; N, 4.26%. **7f**: 60%, elemental analysis: found, C, 75.76; H, 8.99; N, 3.91%. Calculated for $C_{45}H_{64}N_2O_5$: C, 75.80; H, 9.05; N, 3.93%. **7g**: 58%, elemental analysis: found, C, 76.45; H, 9.36; N, 3.59%. Calculated for $C_{49}H_{72}N_2O_5$: C, 76.52; H, 9.44; N, 3.64%.

4.9 Synthesis of 2,5-di(3,4-dibutoxybenzoylamino)-tropone (8a)

A thionyl chloride solution (2 ml) of 3,4-dibutoxybenzoic acid (320 mg, 1.2 mmol) and a drop of DMF were refluxed for 5 h. After excess thionyl chloride was removed under reduced pressure at 40–50°C, 5 ml of pyridine, 68 mg (0.5 mmol) of 2,5-diaminotropone, and a catalytic amount of DMAP were added to the above residue. After the reaction mixture was similarly treated with the above workup of compound **2**, the residue was chromatographed on a silica-gel column to give **8a** (212 mg 67%), ^{1}H NMR δ 1.00 (12H, t, $J = 7.6$ Hz), 1.48–1.55 (8H, m), 1.82–1.89 (8H, m), 4.06–4.12 (8H, m), 6.92 (1H, d, $J = 8.5$ Hz), 6.94 (1H, d, $J = 9.0$ Hz), 7.38 (1H, dd, $J = 8.5$, 2.2 Hz), 7.43 (1H, d, $J = 12.9$ Hz), 7.46 (1H, d, $J = 2.2$ Hz), 7.52–7.58 (2H, m), 7.54 (1H, s), 7.83 (1H, s), 7.84 (1H, dd, $J = 12.9$, 2.7 Hz), 9.22 (1H, d, $J = 11.2$ Hz), and 10.2 (1H, s), elemental analysis: found, C, 70.25; H, 7.55; N, 4.47%. Calculated for $C_{37}H_{48}N_2O_7$: C, 70.23; H, 7.65; N, 4.43%.

Other compounds **8** were similarly synthesised. **8b**: 63%, elemental analysis: found, C, 72.63; H, 8.66; N, 3.79%. Calculated for $C_{45}H_{64}N_2O_7$: C, 72.55; H, 8.66; N, 3.76%. **8c**: 70%, elemental analysis: found, C, 74.30; H, 9.40; N, 3.28%. Calculated for $C_{53}H_{80}N_2O_7$: C, 74.26; H, 9.41; N, 3.27%. **8d**: 74%, elemental analysis: found, C, 75.69; H, 10.01; N, 2.90%. Calculated for $C_{61}H_{96}N_2O_7$: C, 75.58; H, 9.98; N, 2.89%. **8e**: 75%, elemental analysis: found, C, 76.59; H, 10.43; N, 2.60%. Calculated for $C_{69}H_{112}N_2O_7$: C, 76.62; H, 10.44; N, 2.59%. **8f**: 73%, elemental analysis: found, C, 77.43; H, 10.82; N, 2.35%. Calculated for $C_{77}H_{128}N_2O_7$: C, 77.47; H, 10.81; N, 2.35%. **8g**: 41%, elemental analysis: found, C, 78.03; H, 11.10; N, 2.03%. Calculated for $C_{85}H_{144}N_2O_7$: C, 78.17; H, 11.11; N, 2.14%.

4.10 Synthesis of 2,5-di(3,4,5-trihexyloxybenzoylamino)tropone (9b)

A thionyl chloride solution (2 ml) of 3,4,5-trihexyloxybenzoic acid (507 mg, 1.2 mmol) and a drop of DMF were refluxed for 5 h. After excess thionyl chloride was removed under reduced pressure at 40–50°C, 5 ml of pyridine, 68 mg (0.5 mmol) of 2,5-diaminotropone, and a catalytic amount of DMAP were added to the above residue. After the reaction mixture was similarly treated with the above workup of compound **2**, the residue was chromatographed on a silica-gel column to give **9b** (263 mg, 53%), ^{1}H NMR δ 0.91 (18H, t, $J = 6.6$ Hz), 1.34–1.39 (24H, m), 1.46–1.52 (12H, m), 1.76 (4H, quint, $J = 6.6$ Hz), 1.84 (8H, quint, $J = 6.6$ Hz), 4.02–4.08 (12H, m), 7.05 (2H, s), 7.16 (2H, s), 7.43 (1H, d, $J = 12.7$ Hz), 7.56 (1H, d, $J = 11.0$ Hz), 7.80 (1H, s), 7.82 (1H, d, $J = 12.7$ Hz), 9.20 (1H, d, $J = 11.0$ Hz), and 10.16 (1H, s), elemental analysis: found, C, 72.16; H, 9.36; N, 2.93%. Calculated for $C_{57}H_{88}N_2O_9$: C, 72.42; H, 9.38; N, 2.96%.

Other compounds **9** were similarly synthesised. **9c**: 91%, elemental analysis: found, C, 74.18; H, 10.04; N, 2.46%. Calculated for $C_{69}H_{112}N_2O_9$: C, 74.42; H, 10.14; N, 2.52%. **9d**: 94%, elemental analysis: found, C, 75.59; H, 10.66; N, 2.13%. Calculated for $C_{81}H_{136}N_2O_9$: C, 75.89; H, 10.69; N, 2.19%. **9e**: 99%, elemental analysis: found, C, 76.72; H, 11.04; N, 1.92%. Calculated for $C_{93}H_{160}N_2O_9$: C, 77.02; H, 11.12; N, 1.93%. **9f**: 84%, elemental analysis: found, C, 77.39; H, 11.31; N, 1.74%. Calculated for $C_{105}H_{184}N_2O_9\bullet 1/2H_2O$: C, 77.54; H, 11.38; N, 1.72%. **9g**: 78%, elemental analysis: found, C, 78.39; H, 11.77; N, 1.61%. Calculated for $C_{117}H_{208}N_2O_9$: C, 78.64; H, 11.73; N, 1.57%.

4.11 *Synthesis of benzenoids 11–18*

The corresponding benzenoids **11**–**18** were similarly synthesised by the reactions of the corresponding benzoyl chlorides and 1,4-disubstituted benzenes. **11a** ($n = 4$): 73%, mp 129°C. ^{1}H NMR δ 1.00 (12H, t, $J = 7.6$ Hz), 1.49–1.58 (8H, m), 1.84 (4H, quint, $J = 6.6$ Hz), 1.86 (4H, quint, $J = 6.6$ Hz), 4.09 (4H, t, $J = 6.6$ Hz), 4.10 (4H, t, $J = 6.6$ Hz), 6.94 (2H, d, $J = 8.8$ Hz), 7.26 (4H, s), 7.67 (2H, d, $J = 2.2$ Hz), and 7.82 (2H, dd, $J = 8.8$, 2.2 Hz), elemental analysis: found, C, 71.14; H, 7.63%. Calculated for $C_{36}H_{46}O_8$: C, 71.26; H, 7.64%. **11b** ($n = 6$): 28%, mp 124°C, elemental analysis: found, C, 73.39; H, 8.46%. Calculated for $C_{44}H_{62}O_8$: C, 73.51; H, 8.69%. **11c** ($n = 8$): 43%, mp 107°C, elemental analysis: found, C, 75.05; H, 9.43%. Calculated for $C_{52}H_{78}O_8$: C, 75.14; H, 9.46%. **11d** ($n = 10$): 73%, mp 114°C, elemental analysis: found, C, 76.41; H, 9.89%. Calculated for $C_{60}H_{94}O_8$: C, 76.39; H, 10.04%. **11e** ($n = 12$): 81%, mp 109°C, elemental analysis: found, C, 77.19; H, 10.45%. Calculated for $C_{68}H_{110}O_8$: C, 77.37; H, 10.50%. **11f** ($n = 14$): 41%, mp 110°C, elemental analysis: found, C, 78.07; H, 10.83%. Calculated for $C_{76}H_{126}O_8$: C, 78.16; H, 10.88%. **11g** ($n = 16$): 16%, mp 112°C, elemental analysis: found, C, 78.67; H, 11.19%. Calculated for $C_{84}H_{142}O_8$: C, 78.82; H, 11.18%. **12a** ($n = 4$): 76%, mp 119°C. ^{1}H NMR δ 0.97 (6H, t, $J = 7.3$ Hz), 0.99 (12H, t, $J = 7.3$ Hz), 1.48–1.56 (24H, m), 1.76 (4H, quint, $J = 6.4$ Hz), 1.84 (8H, quint, $J = 6.4$ Hz), 4.06 (8H, t, $J = 6.4$ Hz), 4.07 (4H, t, $J = 6.4$ Hz), 7.26 (4H, s), and 7.42 (4H, s), elemental analysis: found, C, 70.19; H, 8.25%. Calculated for $C_{44}H_{62}O_{10}$: C, 70.37; H, 8.32%. **12b** ($n = 6$): 94%, mp 66°C, elemental analysis: found, C, 73.09; H, 9.46%. Calculated for $C_{56}H_{86}O_{10}$: C, 73.17; H, 9.43%. **12c** ($n = 8$): 67%, mp 73°C, elemental analysis: found, C, 74.99; H, 10.04%. Calculated for $C_{68}H_{110}O_{10}$: C, 75.09; H, 10.19%. **12d** ($n = 10$): 66%, mp 69°C, elemental analysis: found, C, 76.43; H, 10.72%. Calculated for $C_{80}H_{134}O_{10}$: C, 76.51; H, 10.75%. **12e** ($n = 12$): 49%, mp 67°C, elemental analysis: found, C, 77.47; H, 11.07%. Calculated for $C_{92}H_{158}O_{10}$: C, 77.58; H, 11.18%. **12f** ($n = 14$): 36%, mp 68°C, elemental analysis: found, C, 78.25; H, 11.54%. Calculated for $C_{104}H_{182}O_{10}$: C, 78.43; H, 11.52%. **12g** ($n = 16$): 60%, mp 79°C, elemental analysis: found, C, 79.11; H, 11.92%. Calculated for $C_{116}H_{206}O_{10}$: C, 79.12; H, 11.79%. **13c**: 39%, ^{1}H NMR δ 0.92 (6H, t, $J = 7.3$ Hz), 1.35–1.50 (12H, m), 1.80–1.84 (4H, m), 4.03 (2H, t, $J = 6.6$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 6.97 (4H, d, $J = 8.8$ Hz), 7.21 (2H, d, $J = 8.8$ Hz), 7.68 (2H, d, $J = 9.0$ Hz), 7.76 (s), 7.84 (2H, d, $J = 9.0$ Hz), and 8.14 (2H, d, $J = 8.8$ Hz), elemental analysis: found, C, 74.09; H, 7.58; N, 2.69%. Calculated for $C_{32}H_{39}NO_5$: C, 74.25; H, 7.59; N, 2.71%. **13d**: 57%, elemental analysis: found, C, 75.28; H, 8.22; N, 2.41%. Calculated for $C_{36}H_{47}NO_5$: C, 75.36; H, 8.26; N, 2.44%. **13e**: 44%, elemental analysis: found, C, 76.11; H, 8.78; N, 2.19%. Calculated for $C_{40}H_{55}NO_5$: C, 76.27; H, 8.80; N, 2.22%. **13f**: 37%, elemental analysis: found, C, 76.89; H, 9.26; N, 2.01%. Calculated for $C_{44}H_{63}NO_5$: C, 77.04; H, 9.26; N, 2.04%. **13g**: 19%, elemental analysis: found, C, 77.52; H, 9.60; N, 1.87%. Calculated for $C_{48}H_{71}NO_5$: C, 77.69; H, 9.64; N, 1.89%. **14a** ($n = 4$): 86%, mp 180°C. ^{1}H NMR δ 0.95–1.02 (12H, m), 1.50–1.56 (8H, m), 1.82–1.87 (8H, m), 4.06–4.16 (8H, m), 6.92 (1H, d, $J = 8.3$ Hz), 6.94 (1H, d, $J = 8.0$ Hz), 7.21 (2H, d, $J = 9.0$ Hz), 7.37 (1H, d, $J = 8.3$, 2.2 Hz), 7.49 (1H, d, $J = 2.2$ Hz), 7.67 (1H, d, $J = 2.0$ Hz), 7.69 (2H, d, $J = 9.0$ Hz), 7.77 (1H, s), and 7.82 (1H, dd, $J = 8.0$, 2.0 Hz), elemental analysis: found, C, 71.18; H, 7.81; N, 2.27%. Calculated for $C_{36}H_{47}NO_7$: C, 71.38; H, 7.82; N, 2.31%. **14b** ($n = 6$): 82%, mp 162°C, elemental analysis: found, C, 73.65; H, 8.79; N, 1.91%. Calculated for $C_{44}H_{63}NO_7$: C, 73.61; H, 8.84; N, 1.95%. **14c** ($n = 8$): 92%, mp 155°C, elemental analysis: found, C, 75.22; H, 9.56; N, 1.65%. Calculated for $C_{52}H_{79}NO_7$: C, 75.23; H, 9.59; N, 1.69%. **14d** ($n = 10$): 81%, mp 147°C, elemental analysis: found, C, 76.44; H, 10.10; N, 1.46%. Calculated for $C_{60}H_{95}NO_7$: C, 76.47; H, 10.16; N, 1.49%. **14e** ($n = 12$): 72%, mp 137°C, elemental analysis: found, C, 77.38; H, 10.59; N, 1.29%. Calculated for $C_{68}H_{111}NO_7$: C, 77.44; H, 10.61; N, 1.33%. **14f** ($n = 14$): 33%, mp 133°C, elemental analysis: found, C, 78.04; H, 10.95; N, 1.16%. Calculated for $C_{76}H_{127}NO_7$: C, 78.23; H, 10.97; N, 1.20%. **14g** ($n = 16$): 57%, mp 132°C, elemental analysis: found, C, 78.77; H, 11.22; N, 1.05%. Calculated for $C_{84}H_{143}NO_7$: C, 78.88; H, 11.27; N, 1.10%. **15a**: 73%, ^{1}H NMR δ 0.97 (6H, t, $J = 6.8$ Hz), 0.99 (12H, t, $J = 7.3$ Hz), 1.51–1.57 (12H, m), 1.73–1.84 (12H, m), 4.03–4.07 (12H, m), 7.06 (2H, s), 7.20 (2H, d, $J = 8.8$ Hz), 7.41 (2H, s), 7.69 (2H, d, $J = 8.8$ Hz), and 7.75 (2H, s), elemental analysis: found, C, 70.58; H, 8.53; N, 1.93%. Calculated for $C_{44}H_{63}NO_9$: C, 70.47; H, 8.47; N, 1.87%. **15b**: 71%, elemental analysis: found, C, 73.31; H, 9.52; N, 1.55%. Calculated for $C_{56}H_{87}NO_9$: C, 73.24; H, 9.55; N, 1.53%. **15c**: 42%, elemental analysis: found, C, 75.27; H, 10.30; N, 1.32%. Calculated for $C_{68}H_{111}NO_9$: C, 75.16; H, 10.30; N, 1.29%. **15d**: 98%, elemental analysis: found, C, 76.63; H, 10.87; N, 1.15%. Calculated for $C_{80}H_{135}NO_9$: C, 76.57; H, 10.84; N, 1.12%. **15e**: 95%, elemental analysis: found, C, 77.46; H, 11.22; N, 1.00%. Calculated for $C_{92}H_{159}NO_9$: C, 77.64; H, 11.26; N, 0.98%. **15f**: 67%, elemental analysis: found, C, 78.53; H, 11.56; N, 0.93%. Calculated for $C_{104}H_{183}NO_9$: C, 78.48; H, 11.59; N, 0.88%. **15g**: 82%, elemental analysis: found, C, 79.08; H, 11.90; N, 0.81%. Calculated for $C_{116}H_{207}NO_9$: C, 79.17; H, 11.86; N, 0.80%. **16a**: 76%, ^{1}H NMR (DMSO-d_6) δ 3.84 (6H, s), 7.06 (4H, d, $J = 8.8$ Hz), 7.65 (4H, s), 7.91 (4H, d, $J = 8.8$ Hz), and 10.07 (2H, s), elemental analysis: found, C, 70.05; H, 5.40; N, 7.45%. Calculated for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44%. **16b**: 82%, elemental analysis: found, C, 72.92; H, 6.98; N, 6.07%. Calculated for $C_{28}H_{32}N_2O_4$: C, 73.02; H, 7.00; N, 6.08%. **16c**: 75%, elemental analysis: found, C, 74.26; H, 7.78; N, 5.44%. Calculated for $C_{32}H_{40}N_2O_4$: C, 74.39; H, 7.80; N, 5.42%. **16d**: 37%, elemental analysis: found, C, 75.51; H, 8.43; N, 4.88%. Calculated for $C_{36}H_{48}N_2O_4$: C, 75.49; H, 8.45; N, 4.89%. **16e**: 95%, elemental analysis: found, C, 76.20; H, 8.95; N, 4.47%. Calculated for $C_{40}H_{56}N_2O_4$: C, 76.39; H, 8.98; N, 4.45%. **16f**: 82%, elemental analysis: found, C, 76.99; H, 9.37; N, 4.06%. Calculated for $C_{44}H_{64}N_2O_4$: C, 77.15; H, 9.42; N, 4.09%. **16g**: 90%, elemental analysis: found, C, 77.69; H, 9.73; N, 3.77%. Calculated for $C_{48}H_{72}N_2O_4$: C, 77.79; H, 9.79; N, 3.78%. **17a** ($n = 4$): 96%, mp 286°C. ^{1}H NMR (DMSO-d_6) δ 0.95 (6H, t, $J = 7.6$ Hz), 0.96 (6H, t, $J = 7.6$ Hz), 1.43–1.50 (8H, m), 1.72 (8H, quint, $J = 6.6$ Hz), 4.05 (8H, t, $J = 6.6$ Hz), 7.08 (2H, d, $J = 8.8$ Hz), 7.54 (2H, s), 7.58 (2H, dd, $J = 8.8$ and 2.2 Hz), 7.70 (4H, s), and 10.03 (2H, s), elemental analysis: found, C, 71.31; H, 7.94; N, 4.60%. Calculated for $C_{36}H_{48}N_2O_6$: C, 71.50; H, 8.00; N, 4.63%. **17b** ($n = 6$): 93%, mp 244°C, elemental analysis: found, C, 73.62; H, 8.95; N, 3.87%. Calculated for $C_{44}H_{64}N_2O_6$: C, 73.71; H, 9.00; N, 3.91%. **17c** ($n = 8$): 89%, mp 225°C, elemental analysis: found, C, 75.28; H, 9.66; N, 3.36%. Calculated for $C_{52}H_{80}N_2O_6$: C, 75.32; H, 9.72; N, 3.38%. **17d** ($n = 10$): 94%, mp 216°C, elemental analysis: found, C, 76.40; H, 10.19; N, 2.93%. Calculated for $C_{60}H_{96}N_2O_6$: C, 76.55; H, 10.28; N, 2.98%. **17e** ($n = 12$): 89%, mp 205°C, elemental analysis: found, C, 77.46; H, 10.67; N, 2.64%. Calculated for $C_{68}H_{112}N_2O_6$: C, 77.52; H, 10.71; N, 2.66%. **17f** ($n = 14$): 97%, mp 197°C, elemental analysis: found, C, 78.23; H, 11.00; N, 2.39%. Calculated for $C_{76}H_{128}N_2O_6$: C, 78.30; H, 11.07; N, 2.40%. **17g** ($n = 16$): 86%, mp 189°C, elemental analysis: found, C, 78.80; H, 11.31; N, 2.08%. Calculated for $C_{84}H_{144}N_2O_6$: C, 78.94; H, 11.36; N, 2.19%. **18a**: 65%, ^{1}H NMR δ 0.96 (6H, t, $J = 7.3$ Hz), 0.97 (12H, t, $J = 7.3$ Hz), 1.48–1.56 (12H, m), 1.74 (4H, quint, $J = 6.4$ Hz), 1.82 (8H, quint, $J = 6.4$ Hz), 4.03 (4H, t, $J = 6.4$ Hz), 4.05 (8H, t, $J = 6.4$ Hz), 7.06 (4H, s), 7.64 (4H, s), and 7.74 (2H, s), elemental analysis: found, C, 70.49; H, 8.56; N, 3.70%. Calculated for $C_{44}H_{64}N_2O_8$: C, 70.56; H, 8.61; N, 3.74%. **18b**: 80%, elemental analysis: found, C, 73.24; H, 9.61; N, 3.04%. Calculated for $C_{56}H_{88}N_2O_8$: C, 73.32; H, 9.67; N, 3.05%. **18c**: 68%, elemental analysis: found, C, 75.04; H, 10.34; N, 2.56%. Calculated for $C_{68}H_{112}N_2O_8$: C, 75.23; H, 10.40; N, 2.58%. **18d**: 43%, elemental analysis: found, C, 76.39; H, 10.84; N, 2.17%. Calculated for $C_{80}H_{136}N_2O_8$: C, 76.63; H, 10.93; N, 2.23%. **18e**: 67%, elemental analysis: found, C, 77.46; H, 11.23; N, 1.92%. Calculated for $C_{92}H_{160}N_2O_8$: C, 77.69; H, 11.34; N, 1.97%. **18f**: 67%, elemental analysis: found, C, 78.36; H, 11.61; N, 1.59%. Calculated for $C_{104}H_{184}N_2O_8$: C, 78.53; H, 11.66; N, 1.76%. **18g**: 31%, elemental analysis: found, C, 78.98; H, 11.83; N, 1.54%. Calculated for $C_{116}H_{208}N_2O_8$: C, 79.21; H, 11.92; N, 1.59%.

Note

1. The number (n) of molecules is estimated according to the equation $[n = (a^2/2)\sqrt{3}h(N_A/M)r]$, where a is the columnar lattice parameter, h the thickness of a hypothetical disk, N_A the Avogadro constant, and M the molecular weight and the density r is assumed to be 1 g/cm^3. See Borisch *et al.* [18].

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